CHLORPYRIFOS-METHYL (090)

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EXPLANATION

Chlorpyrifos-methyl is an organophosphorous insecticide effective against a wide range of insect pests in crops of commercial importance. The compound was evaluated by previous Joint Meetings many times since 1975, and was listed at the 40th session of the CCPR (2008) for periodic review by the 2009 JMPR for both residue and toxicological aspects. An ADI of 0–0.01 mg/kg bw and a ARfD of 0.1 mg/kg bw were established by the Meeting. The manufacturer submitted data on metabolism of chlorpyrifos-methyl in farm animals and plants, environmental fate, methods of analysis, GAP information, supervised residue trials on citrus, pome fruit, stone fruits, cherries, grapes, strawberries, kiwi fruit, onion, tomato, peppers, sugar beet, potato, carrot, artichoke, green beans, oilseed rape, cotton and cereals, and processing studies on various crops. Additionally, metabolism studies on chlorpyrifos in plants were submitted.

IDENTITY

ISO common name: Chlorpyrifos-methyl

IUPAC name: *O,O*-dimethyl O-3,5,6-trichloro-2-pyridyl phosphorothioate.

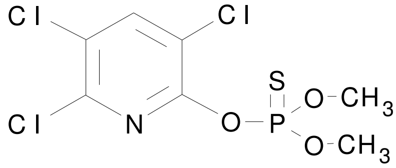
Chemical Abstract name: O,O-dimethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate

CAS No.: 5598-13-0

CIPAC No.: 486

Molecular Formula: $C_7H_7Cl_3NO_3PS$

Structural Formula:



Molecular Weight: 322.5 g/mol

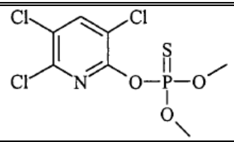
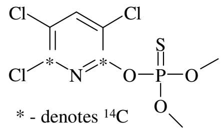
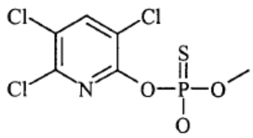
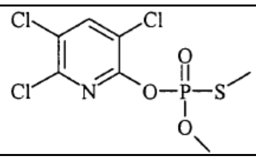
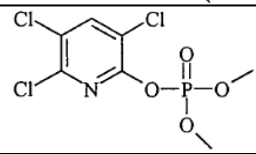
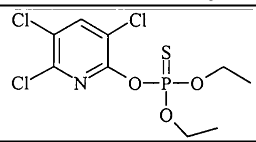
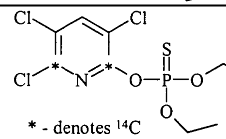
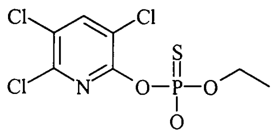
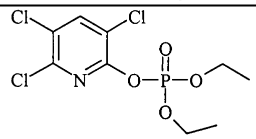
Physical and chemical properties

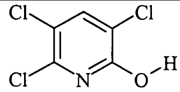
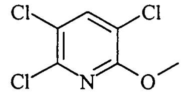
Property	Result	Reference
Melting point:	46.0 °C	Boothroyd, 1993a
Relative density:	1.642 at 23 °C	Boothroyd, 1994a
Vapour pressure:	3×10^{-3} Pa at 25 °C, (2.0×10^{-3} Pa at 20 °C, by calculation)	Boothroyd, 1993b
Henry's law constant:	0.235 Pa m^3 mol^{-1}, (by calculation at 20 °C)	Watson, 2002
Spectra for active substance		Boothroyd *et al.*, 1994b

Property	Result	Reference
UV-VIS Molecular extinction coefficients (ε, $molL^{-1}$ cm^{-1}):	2.21×10^4, 204.1 nm	
	1.17×10^4, 229.1 nm	
	6.07×10^3, 288.9 nm	
IR Bands and assignments:	3063 cm^{-1} C-H (Ar) stretching, consistent with aromatic ring	
	3012 cm^{-1} C-H (Ar) stretching, consistent with aromatic ring	
	2954 cm^{-1} C-H stretching, consistent with RCH_3	
	1548 cm^{-1} consistent with substituted pyridine	
	1408 cm^{-1} consistent with substituted pyridine	
	1240 cm^{-1} P-O stretching	
	1165 cm^{-1} P-O stretching, consistent with POAr	
	967 cm^{-1} P-O stretching, consistent with POAr	
NMR Proton and ^{13}C assignments:	1H: 7.88 (1H, s) aromatic	
	4.04 (6H, d) CH_3	
	^{13}C: 150.7 (s) quaternary	
	144.1 (s) quaternary	
	141.3 (d) aromatic	
	127.0 (s) quaternary	
	120.5 (s) quaternary	
	55.9 (dq) CH_3	
	$^2J_{CP}$ = 5.35 Hz	
MS m/z ions and assignments:	m/z 327 ($3 \times {}^{37}Cl$)	
	m/z 325 (^{35}Cl, $2 \times {}^{37}Cl$)	
	m/z 323 ($2 \times {}^{35}Cl$, ^{37}Cl)	
	m/z 321 ($3 \times {}^{35}Cl$)	
	m/z 288 (loss of one Cl from parent)	
	m/z 199 ($2 \times {}^{35}Cl$, ^{37}Cl)	
	m/z 125; m/z 79	
Solubility		
	Water at 20 °C	Boothroyd, 1993b
	distilled water: 2.74 mg/L	
	pH 5 buffer: 2.36 mg/L	
	pH 7 buffer: 2.74 mg/L	
	pH 9 buffer: 2.22 mg/L	
Organic solvents		Knowles, 1993
	Hexane: 12.0 g/100 mL	
	Toluene: 574 g/100 mL	
	Methanol: 18.9 g/100 mL	
	N-octanol: 11.0 g/100 mL	
	Dichloromethane > 400 g/100 mL	
	Acetone miscible: > 400 g/100 mL	
	Ethyl acetate miscible: > 400 g/100 mL	
	Acetonitrile: > 400 g/100 mL	
Partition coefficient:	Log Kow = 4.0	Sydney, 1997
Hydrolysis rate constants, 25 °C	pH 4: 26.6 days	Yon and Muller, 1994a
	pH 7: 20.9 days	
	pH 9: 13.1 days	
Direct photo-transformation	Observed at 290 nm with *ca* 50% degradation after 8 hr irradiation in the preliminary test. No significant quantities of degradation products (≥ 10% active substance added) were observed.	Yon and Muller, 1994b:

Property	Result	Reference
Other properties		
Quantum yield:	2.6×10^{-3}	Yon and Muller, 1994b
Stability in air:	Half-life of 2.112 hours (reaction with hydroxyl radicals)	Day and Rudel, 1993
Flammability:	Non-flammable (melted but did not ignite)	Knowles, 1991a
Auto-flammability:	Auto-ignition temperature = 272 ± 5 °C	Richardson, 1995
Explosive properties:	Non-explosive	Knowles, 1991b
Surface tension:	70.5 mN/m (90% saturated solution)	Sydney, 1997
Oxidizing properties:	Non-oxidizing	Knowles, 1991c

METABOLISM AND ENVIRONMENTAL FATE

Abbreviation	Name	Structure
CPM	Chlorpyrifos-methyl	
^{14}C-chlorpyrifos-methyl	^{14}C-labelled chlorpyrifos-methyl at 2- and 6-positions of the pyridinyl ring	
DEM	Des-methyl chlorpyrifos-methyl, (O-methyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothoic acid).	
S-methyl isomer	S-methyl chlorpyriphos-methyl, ,S-dimethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate	
OXM	Chlorpyrifos-methyl oxon, (O,O-dimethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphate).	
CHP	Chlorpyrifos	
^{14}C-chlorpyrifos	^{14}C-labelled chlorpyrifos at 2- and 6-positions of the pyridinyl ring	
DES	Des-ethyl chlorpyrifos, (O-ethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothoic acid).	
OXON	Chlorpyrifos-oxon, (O,O-diethyl-O-(3,5,6-trichloro-2-pyridinyl) phosphate).	

Abbreviation	Name	Structure
TCP	3,5,6-trichloro-2-pyridinol	
TMP	2-methoxy-3,5,6-trichloropyridine	

Metabolism in animals

Goat

[^{14}C]chlorpyrifos-methyl (unspecified label position, > 99% radiochemical purity) was fed to two lactating goats in a dosing rate *ca*. 32 mg/kg feed, administered in gelatin capsules twice a day for 7 days (McConnel *et al*., 1982; Study 33688). Milk, blood, urine and faeces were collected throughout the dosing period. Tissues and gut contents were collected at sacrifice, 14 hours after the final dose.

Whole milk samples were radioassayed by liquid scintillation counting (LSC) prior to separation into milk fat and skim milk by centrifugation. Liquid samples were radioassayed by direct LSC and solids (faeces and milk fat) were combusted prior to determination of radioactivity. One goat was monitored for CO_2 and volatiles were collected using Chromosorb absorption tubes, which were extracted with methanol and radioassayed using LSC.

Liver, kidney, fat and milk fat were extracted with acetonitrile (ACN) and the extract partitioned three times with hexane. The acetonitrile layer was dried and the residue reconstituted in methanol prior to radio TLC and HPLC analysis. The non-extracted residue was subject to base hydrolysis (0.1 N NaOH in 80% methanol under reflux for 2 hours). The extract was evaporated to remove the methanol, and the resulting aqueous solution was adjusted to pH 1 with sulphuric acid. This solution was partitioned three times with diethyl ether, the ether extract dried, resuspended in methanol and analysed by radio TLC and HPLC. All extracts were analysed by LSC and the final remaining residue was combusted prior to LSC determination. Recovery was > 91% of administered dose and approximately 95% of recovered radioactivity was in the urine (approximately 22 mg/kg chlorpyrifos-methyl eq.). Total radioactive residues (TRR) in tissues never exceeded 0.62 mg/kg, level that was found in kidney; in milk, residues were concentrated in fat (Table 1). Most of the radioactivity was found in the ACN extract (Table 2).

Table 1 Total radioactive residues (TRR) in tissues (mg/kg parent equivalents) following feeding of [^{14}C] chlorpyrifos-methyl to goats at ca. 32 mg/kg feed

Sample	Goat 1	Goat 2
Liver	0.32	0.40
Kidney	0.60	0.62
Fat (visceral and subcutaneous)	0.065	0.14
Heart	0.092	0.16
Skeletal muscle	0.029	0.047
Whole milk	0.021	0.027
Skin milk	0.016	0.015
Milk fat	0.061	0.115

Table 2 Percentage TRR of residues following dosing with [^{14}C]chlorpyrifos-methyl (mean of 2 goats)

Matrix	Acetonitrile extraction	Acetonitrile unextracted	Base extraction of acetonitrile unextracted	Base insoluble	Total[a]
Liver	ACN—73.6 hexane—2.8	18.6	aq—1.4 ether—10.0	6.4	95.0
Kidney	ACN—78.8 hexane—2.4	13.1	aq—0.6 ether—7.4	4.1	94.3
Fat	ACN—73.8 hexane—10.2	4.8	–	–	88.8
Milk fat	ACN—77.6 hexane—13.8	1.7	–	–	93.1

[a] ACN extraction + ACN unextracted

Table 3 shows the TLC metabolite profiles of tissue and milk ACN extracts. In liver and kidney, most of the residues were found as TCP, while in fat and milk fat, the parent compound was predominant. Similar results were found by HPLC analysis.

Table 3 TLC metabolite identification of residues in the acetonitrile extract fat following dosing of goats with [^{14}C]chlorpyrifos-methyl at ca. 32 mg/kg feed %TRR and mg/kg

	Chlorpyrifos-methyl		S-methyl isomer		TCP		DEM		Total	
Matrix	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Liver	0.3	0.001	0.4	0.001	66.7	0.24	4.5	0.02	82.0	0.30
Kidney	0.4	0.002	0.5	0.003	74.2	0.45	7.0	0.04	88.9	0.54
Fat	55.3	0.06	0.7	0.001	16.5	0.02	2.6	0.003	75.1	0.08
Milk fat	61.8	0.06	0.0	0.0	12.8	0.01	1.9	0.002	82.5	0.07

Base extracts of liver and kidney showed no parent compound and only TCP as metabolite (10.5%TRR in liver and 6.8%TRR in kidney). Base extracts of tissue insolubles showed traces of chlorpyriphos-methyl (up to 0.2% TRR), TCP plus S-methyl isomer (up to 9%TRR) and up to 1%TRR of DEM in kidney.

Urine samples were analysed directly by LSC and also incubated with glusulase for 24 hours at 38 °C (contains beta-glucuronidase and sulfatase). Metabolites identified by TLC in urine before and after glusulase extraction are showing on Table 4, and agreed well with the HPLC results.

Table 4 TLC results of glusulase extraction in urine (mean % of total residue)

Compound	Goat 1		Goat 2	
	Before glusulase	After glusulase	Before glusulase	After glusulase
Chlorpyrifos-methyl	0.1	0.5	0.1	0.0
S-methyl isomer	0.2	0.1	0.4	0.0
TCP	54.4	70.7	73.0	77.6
DEM	24.5	22.2	18.6	17.0
Origin of TLC	19.1	5.6	6.0	4.2
Total	96.3	99.1	98.1	98.8

Poultry

Four laying hens (White Leghorn) received a daily dose of [^{14}C] chlorpyrifos-methyl (specific activity 12.4 mCi/mmol, radiopurity > 99%) at a dietary intake of *ca* 25 mg/kg feed, for 10 days (Wilkes *et al*., 1982; Study 33689). Eggs were collected from each hen, once daily prior to dosing, separated into yolk and white fractions and frozen for analysis. Excreta was also collected for each 24-hour period from the floor and frozen for extraction with methanol. Tissue and fat (visceral and subcutaneous) samples were collected at sacrifice, approximately 16 hours after the tenth daily dose (apart from one bird that was terminated on Day 7 due to ill health) and frozen for analysis.

Radioactivity levels were determined by combustion analysis/LSC. Tissue and egg samples were extracted with ACN, the extracts partitioned with hexane and analysed by TLC and HPLC. The unextracted residues in egg yolk and kidney were subjected to base hydrolysis (0.1 N NaOH in 80% methanol) and the extracts analysed by LSC. Excreta methanol extract was evaporated, the pH of aqueous phase reduced to 1 with sulphuric acid, partitioned with diethyl ether, evaporated, resuspended into methanol and analysed by LSC.

The majority of the radioactivity (*ca* 70% applied radioactivity; 4.7–20 mg/kg) was present in the excreta. Radioactivity was low in tissues, exceeding 0.1 mg/kg only in fat, kidney and egg yolk (Table 5).

Table 5 Total radioactive residues (mg/kg) in tissues following dosing of hens with [^{14}C] chlorpyrifos-methyl at 10N rate

Sample	TRR , mg/kg chlorpyrifos-methyl eq.
Liver	0.02–0.04
Kidney	0.09–0.15
Dark muscle	< 0.01–0.02
Light muscle	< 0.01
Fat	0.07–0.35
Heart	0.01–0.02
Skin	0.02–0.09
Egg white	< 0.01–0.03
Egg yolk	< 0.01–0.10

The radioactivity found in the kidney, fat and egg yolk solvent extract are given in Table 6. Over 75% TRR was found in the ACN fractions. Pooled tissue samples and eggs were characterized for metabolite composition by TLC/HPLC (Table 7). The majority of the residue present in kidney was the TCP and DEM metabolites. Fat contained mainly the parent and egg yolk contained roughly equal quantities of all three components. Excreta contained mainly TCP, which appeared to be more tightly bound with storage, and low levels of parent and DEM. The metabolite profiles were similar for HPLC and TLC.

Table 6 The characterization of residues in kidney, fat and egg yolk following dosing of hens with [^{14}C]chlorpyrifos-methyl at 10N rate (%TRR)

Tissue	ACN extraction	ACN unextracted	Base extraction of ACN unextracted	Base insoluble	Total [a]
Kidney	ACN—78.7 hexane—0.0	17.0	aq—4.3 ether—12.6	8.5	95
Fat	ACN—82.0 hexane—14.2	0.2	–	–	96.4
Egg yolk	ACN—75.7 hexane—6.8	20.5	aq—2.0 ether—18.2	3.6	103

[a] ACN extraction + ACN unextracted

Table 7 TLC metabolite identification of residues in kidney, fat and egg yolk following dosing of hens with [^{14}C]chlorpyrifos-methyl at 10N rate, in %TRR

Matrix	Chlorpyrifos-methyl	S-methyl isomer	TCP	DEM	Total
Kidney	0.0	0.0	ACN: 56.2 Base:10.9	ACN:22 Base: 0	89.7

Matrix	Chlorpyrifos-methyl	S-methyl isomer	TCP	DEM	Total
Fat [a]	74.8	0.4	1.1	2.3	78.6
Egg yolk [a]	16.1	0.0	19.9	23.2	59.2

[a] ACN extract

Plant Metabolism

Two studies were conducted in plants using chlorpyrifos methyl (tomato and cereal grains) and four with chlorpyrifos (citrus, cabbage, peas and radish).

Tomato

Tomato plants were grown in plastic pots (0.30 m diameter) containing a silt loam soil and kept in the greenhouse for germination and during early growth (Graper, 2002a; Study GH-C 5483). The plants were transferred outdoors and maintained for at least eight weeks prior to one spray application of [^{14}C]chlorpyrifos methyl at a rate equivalent to 0.99 kg ai/ha, within the seasonal label rate range of 0.5 to 3.0 kg ai/ha. Fruit, leaf or vine samples were collected at 0, 5, 13, 26 and 42 days after application (DAT). Fruit and leaf samples were further processed by rinsing first with DCM and then with ACN, cut up, frozen, and milled with dry ice and/or liquid nitrogen until analysed.

Rinsed or unrinsed tomato fruit tissue was extracted three times with 80/20 ACN/water, filtered and partitioned three times with DCM. The organic phase was concentrated to low volume, partitioned with hexane, the hexane phase was partitioned twice with ACN and this phase concentrated for HPLC analysis. The extracted tissue and spent filter paper were allowed to air dry and assayed by combustion. TRR in all tissues were determined by oxidative combustion and LSC. TRR levels in all liquid samples were determined by direct LSC.

The stability of DEM during extraction was evaluated by adding [^{14}C]DEM to a 5 DAT rinsed control tomato fruit sample. The synthesis of DEM was extremely difficult due to its instability and a purity of 76.0% was the best that could be achieved. The main contaminant appeared to be TCP, which comprised 18.1% of the radioactivity eluting from HPLC. Other minor contaminants did not exceed 6%. A concentrate of the 26-DAT fruit extracted aqueous phase was subjected to treatment using ß-glucosidase, the sample partitioned with DCM, the extract concentrated and prepared for HPLC. In order to assess the stability of DEM to the enzyme procedure, an aliquot of a [^{14}C]DEM solution was subjected to the same procedure. Elution of non-radiolabelled reference standards was monitored at 280 nm.

TRR values declined over the time for both fruit and leaves (Table 8). The TRR in fruit that had not been present when the ^{14}C test substance was applied (42NP) was 0.211 mg/kg. In fruit at 0 and 5 DAT, the majority of the radioactivity was found in the DCM rinses, and increased in fruit tissue over time

Table 8 TRR in tomato fruit and leaves and distribution of radioactivity in rinses and rinsed tissue presented as mg chlorpyrifos-methyl equivalents per kg and as % of TRR

	DCM Rinse		ACN Rinse		Rinsed or Unrinsed Tissue		Total
DAT	%TRR	mg/kg[a]	%TRR	mg/kg[a]	%TRR	mg/kg[a]	mg/kg[a]
Fruit							
0	86.7	0.475	1.4	0.008	11.9	0.065	0.548
5	50.0	0.237	2.0	0.009	48.0	0.228	0.475
5U	NA	NA[e]	NA	NA	100.0	0.825	0.825
13	24.0	0.116	1.0	0.005	75.0	0.364	0.485
26	0.8	0.004	0.1	0.000	99.1	0.439	0.443
42U	NA	NA	NA	NA	100.0	0.309	0.309
42NP	NA	NA	NA	NA	100.0	0.211	0.211

	DCM Rinse		ACN Rinse		Rinsed or Unrinsed Tissue		Total
DAT	%TRR	mg/kg[a]	%TRR	mg/kg[a]	%TRR	mg/kg[a]	mg/kg[a]
Leaves							
5	6.2	0.771	7.6	0.947	86.2	10.727	12.45
13	3.2	0.284	7.2	0.641	89.6	7.956	8.88

[a] Minimum detectable amount (MDA) and minimum quantifiable amount (MQA) were 0.002 and 0.007 mg/kg, respectively;

U = unrinsed tissue;

NP = fruit that was not present at ^{14}C-test substance application. This fruit was not rinsed;

NA = not applicable.

By 13 DAT, half of the TRR was found in the ACN and aqueous extracts and about 15% remained in the tissues (Table 9). About 100% of the [^{14}C]DEM radioactivity was recovered during the procedure.

Table 9 Distribution of radioactivity in extracts of rinsed and unrinsed tomato fruit presented

	Hexane Phase		ACN Phase		Extracted Aqueous		Tissue[a]	
DAT	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
0	< 0.1	< 0.001	11.8%	0.065	0.2%	0.001	0.2%	0.001
5	< 0.1	< 0.001	33.2%	0.158	8.5%	0.040	3.9%	0.019
5U	0.3%	0.002	87.3%	0.720	4.8%	0.040	2.7%	0.022
13	0.1%	0.001	30.1%	0.146	20.0%	0.097	15.0%	0.073
26	1.0%	0.004	33.9%	0.150	40.9%	0.181	18.6%	0.082
42U	1.4%	0.004	32.1%	0.099	54.8%	0.169	16.1%	0.050
^{14}C-DEM stability	< 0.1	< 0.001	95.3%	0.036	5.2%	0.002	0.6%	< 0.001

[a] after combustion

The results of HPLC analysis of tomato fruit extracts are summarized in Table 10. Only a small % of TRR in the fruit surface rinses was found as residues other than chlorpyrifos-methyl. Chlorpyrifos-methyl was metabolized in fruit tissue rinses primarily to TCP and polar residues. For all fruit samples, no greater than 2.5% of TRR was found in the region where DEM was expected to elute; the region of TCP contained up to 23.8% of TRR. The MQL was not exceeded for TMP, S-methyl isomer, and OXN at any sample times.

When an extracted aqueous phase from 26-DAT fruit containing a relatively large amount of polar radioactivity (26, Enz) was subjected to treatment with β-g1ucosidase, 6.5%TRR that was liberated eluted in the TCP region; little or no radioactivity was released that chromatographed in the DEM region. When an aliquot of a [^{14}C]DEM solution was subjected to the same procedure, 61.7 and 24.2% of the sample radioactivity eluted in the DEM and TCP regions, respectively. Knowing that the purity of the solution was 74.8%, about 17% of the radioactivity was lost during the procedure. The authors concluded that if DEM were formed in tomato samples, it would be only partially degraded by the methods used, and would be found in the ACN phases and extracted aqueous fractions.

Table 10 Distribution of radioactivity in regions of chromatograms from the HPLC analysis of fruit rinses and extracts presented as % of TRR and mg/kg chlorpyrifos methyl

	Polar residues (6–7 min)		DEM		TCP		Chlorpyrifos-methyl	
DAT, Description	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
0, DCM[a] Rinse	< MQL	< 0.007	< MQL	< 0.007	–	–	78.7	0.432
0, ACN[a] Phase	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007	11.6	0.063
Total	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007	90.3	0.495
5, DCM Rinse	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007	47.2	0.224

	Polar residues (6–7 min)		DEM		TCP		Chlorpyrifos-methyl	
DAT, Description	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
5, ACN Phase	< MQL	< 0.007	1.3	0.006	7.2	0.034	23.2	0.110
5, Aqueous	7.9	0.038	< 0.007	< 0.007	< MQL	< 0.007	< MQL	< 0.007
Total	7.9	0.038	1.3	0.006	7.2	0.034	70.4	0.334
5U, ACN Phase	< MQL	< 0.007	< 0.007	< 0.007	4.8	0.039	82.2	0.678
5U, Aqueous	4.3	0.036	0.5	0.004	< MQL	< 0.007	< MQL	< 0.007
Total	4.3	0.036	0.5	0.004	4.8	0.039	82.2	0.678
13, DCM Rinse	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007	20.4	0.099
13, ACN Phase	< MQL	< 0.007	2.5	0.012	11.3	0.055	13.8	0.067
13, Aqueous	19.6	0.095	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007
Total	19.6	0.095	2.5	0.012	11.3	0.055	34.3	0.166
26, ACN Phase	1.5	0.007	< MQL	< 0.007	23.8	0.106	3.0	0.013
26, Aqueous	39.8	0.176	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007
Total	41.3	0.183	< MQL	< 0.007	23.8	0.106	3.0	0.013
26, Enz DCM	0.3	0.001	< MQL	< 0.007	6.5	0.029	< MQL	< 0.007
26, Enz AQ	23.2	0.103	< MQL	< 0.007	< 0.007	< 0.007	< MQL	< 0.007
Total	23.5	0.104	< MQL	< 0.007	6.5	0.029	< MQL	< 0.007
42U,ACN Phase	2.2	0.007	< MQL	< 0.007	21.2	0.065	1.7	0.005
42U, Aqueous	30.4	0.094	< MQL	< 0.007	< MQL	< 0.007	< MQL	< 0.007
Total	32.6	0.101	< MQL	< 0.007	21.2	0.065	1.7	0.005
^{14}C-DEM[a] ACN Phase	< MQL	< 0.007	40.3	0.015	33.1	0.012	< MQL	< 0.007
^{14}C-DEM[a] Aqueous	0.6		4.4	0.002	< MQL	< 0.007	< MQL	< 0.007
Total	0.6		44.7	0.017	33.1	0.012	< MQL	< 0.007
Enz ^{14}C-DEM[b] DCM	< MQL	< 0.007	< MQL	< 0.007	22.5		< MQL	
Enz ^{14}C-DEM[b] AQ	1.2		61.7		1.6		< MQL	
Total	1.2		61.7		24.2		< MQL	

MQL = less than 0.1% to 2.4% TRR

U = unrinsed tissue

[a] 76% purity

[b] 74.8 % purity

The results of HPLC analysis of tomato leaf extracts are summarized in Table 11. Like what was found for fruit extracts, chlorpyrifos-methyl was metabolized in leaf rinses primarily to TCP and to polar residues.

Table 11 Distribution of radioactivity in regions of chromatograms from the HPLC analysis of leaf rinses and extracts presented as % of TRR and mg/kg chlorpyrifos methyl

Sample Type -	Polar residues (6–7 min)		TCP		Chlorpyrifos-methyl	
DAT, Description	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
5, DCM Rinse	0.3	0.038	1.6	0.204	2.9	0.366
5, ACN Rinse	4.3	0.535	1.0	0.126	0.5	0.066
Total	4.6	0.572	2.6	0.329	3.5	0.432
13, DCM Rinse	0.1	0.013	1.2	0.105	1.1	0.095
13, ACN Rinse	2.8	0.250	0.3	0.024	< 0.1	0.004
Total	3.0	0.263	1.5	0.129	1.1	0.099

Stored Grain

The [^{14}C]chlorpyrifos-methyl was formulated, together with unlabelled material, as an emulsifiable concentrate (McConnell *et al*., 1982; Study GH-C 1578). The formulation was applied to samples of wheat grain or maize grain at a rate equivalent to 32.4 mg ai/kg grain. Treated grain was stored in sealed glass bottles maintained at 25 ± 1 °C for up to 180 days. Samples were taken prior to storage, 30, 90 and 180 days, extracted and characterized by TLC and HPLC. Residues after 180 days of storage are shown in Table 12. Parent compound represent about 1/3 of the radioactivity in maize and 45% in wheat.

Table 12 Levels of parent and metabolite/degradation products arising after 180 days of storage (expressed as % AR)

	% of total ^{14}C residues	
Residue	Maize	Wheat
Chlorpyrifos-methyl	30	45
TCP	39	19
DEM	24	19
Alkali-liberated pyridinol	6	15
Alkali insolubles	1	2

Metabolism of chlorpyrifos

Citrus fruits

The metabolism of [^{14}C]chlorpyrifos (98.8% and specific activity of 1.4 mCi/mmol) was investigated in oranges (Magnussen, 2002; Study GH-C 5484). One Washington Navel orange tree received a single spray application at a rate of 3.97 kg ai/ha, and samples of whole fruit were collected at 0, 6 and 21 days after treatment (DAT). The oranges were subjected to one or two organic solvent rinses using DCM/ACN (2:1) followed by ACN (6 and 21 DAT samples only). Rinsed oranges were separated into the peel, pith and pulp fractions. The peel and pith fractions were frozen in liquid nitrogen and ground, while the pulp samples were blended unfrozen. Portions of each sample were assayed for total radioactivity by combustion.

Rinsed peel fractions were extracted with ACN and the 6 and 21 DAT samples further extracted in ACN/water and ACN/DCM (1:1). Stability of the DES metabolite to the procedure was determined using the [^{14}C]DES standard. Due to the much lower TRR levels in the pith and pulp fractions (Table 13), no additional work was done with these samples.

Citrus leaves were initially analysed by rinsing with DCM/ACN (2:1) followed by ACN. The rinsed leaves were further extracted with ACN and/or ACN/water (70:30) following partitioning with DCM/ACN (1:1). To evaluate the nature of the polar residues in the aqueous fractions, the residues in the spent aqueous fractions from 21-DAT leaves were characterized following enzyme (β-glucosidase) and base hydrolysis (1.0 N in NaOH). Following acidification of the hydrolysate solutions, radioactive residues released were partitioned using ACN/DCM and analysed by HPLC. The stability of the DES metabolite to these hydrolysis procedures was determined using control samples spiked with [^{14}C]DES.

To evaluate the nature of the unextracted residues (NER), extracted 21-DAT leaves were subjected to enzyme (cellulase or driselase), acid (50:50 1.0 N HCl: ACN) and base (1.0 N NaOH) hydrolysis. Any remaining spent tissue was assayed for total radioactivity by combustion. Aliquots of the hydrolysate solutions were assayed for total radioactivity by direct LSC. The base hydrolysate solution was subsequently acidified and partitioned using ACN/DCM and this extract analysed by HPLC. The stability of the DES metabolite to these hydrolysis procedures was determined using [^{14}C]DES. The acid detergent fibre (ADF) fraction of the extracted 21-DAT leaf tissue was isolated to determine the radioactivity associated with the lignin and cellulose fractions.

TRR levels in both leaves and fruit declined by approximately 50% or more in the three-week interval between application and harvest (Table 13). Over 99% of the whole fruit TRR remained associated with the peel.

Table 13 Total radioactive residue levels in whole oranges and in orange leaves plus the percent distribution of whole orange residues among the peel, pith and pulp fractions

	Whole Fruit Residues (mg/kg)	Percent Distribution of Residues (mg/kg chlorpyrifos eq.)		
		Peel	Pith	Pulp
Oranges: 0 Time	3.44	99.5 (26.1)	0.3 (0.10)	0.2 (0.009)
6 DAT	3.01	99.5 (27.9)	0.4 (0.10)	0.1 (0.002)
21 DAT	1.5	99.3 (15.4)	0.6 (0.05)	0.1 (0.003)
Leaves: 6 DAT	86.5			
21 DAT	44.4			

Table 14 shows the percent distribution of the whole fruit TRR among the solvent rinses and the fractions generated following the extraction of rinsed peel. At all sampling times, most of the radioactivity was removed with the solvent rinse. For the 0 Time sample, virtually all the radioactivity remaining in the rinsed peel was readily extractable using ACN. By 21 DAT, only about 40% of the non-rinsed residue (13% of the TRR) could be accounted for in the extract and reflux fractions. Less than 1.5% of the TRR was associated with the polar, aqueous soluble fraction that is usually assumed to represent conjugated residues. The remainder of the residue was associated with the spent peel.

Table 14 Distribution of residues in whole oranges treated with [14C]chlorpyrifos among fractions generated by the rinse and extraction of peels

	Percent of Whole Fruit Residue (mg/kg chlorpyrifos eq.)			
	Solvent Rinses	ACN Ext	ACN/H2O Reflux	Spent Peel
0 Time	94.5 (3.25)	4.4 (0.151)	–	0.6 (0.021)
6 DAT	80.5 (2.42)	10.3 (0.310)	2.0 (0.060)	6.7 (0.202)
21 DAT	69.0 (1.04)	9.1 (0.137)	3.9 (0.059)	17.3 (0.261)

Table 15 summarizes the percent distribution and the mg/kg of parent equivalents of the whole fruit residues in the peel extracts and rinses determined by HPLC. At 0 Time, chlorpyrifos represented most of the residue. For the rinse, none of the metabolites investigated were observed at levels exceeding the MQL. For the peel extract, low levels of radioactivity were observed eluting in the region of the OXON (the identity of this material was not confirmed by LC/MS). For the 6-DAT fruit, both fractions also contained low levels of an unidentified component (Metabolite A) that was only slightly less polar than chlorpyrifos. The peel extract also contained low levels of radioactivity eluting in the region of the OXON. Analyses of the 21-DAT fractions showed a similar residue profile to that seen at 6 DAT.

Table 15 Percent distribution of the TRR in the rinses and extracts of treated orange peel among chlorpyrifos and its metabolites as determined by HPLC

	Percent of Whole Fruit Residue [a]								
	CHP	Met A	TMP	OXON	TCP	DES	Polar Unkns [b]	Nonpolar Unkns [c]	NER [d]
0 Time:									
Solvent Rinse	93.0	< 0.007	–	–	–	–	–	0.8	–
Organic Ext	4.0	–	< 0.007	0.2	< 0.007		< 0.007	< 0.007	–
Total	97.0	< 0.007	< 0.007	0.2	< 0.007		< 0.007	0.8	0.6
(mg/kg)	(3.336)			(0.007)				(0.028)	(0.021)
6 DAT:									
Solvent Rinses	76.7	2.6	–	–	–	–	–	1.2	–
Organic Ext	8.6	0.4	–	0.3	< 0.007	–	0.6	< 0.007	–
Total	85.3	3.0		0.3	< 0.007		0.6	1.2	6.7
(mg/kg)	(2.566)	(0.090)		(0.009)			(0.018)	(0.036)	(0.202)

	Percent of Whole Fruit Residue [a]								
	CHP	Met A	TMP	OXON	TCP	DES	Polar Unkns [b]	Nonpolar Unkns [c]	NER [d]
21 DAT:									
Solvent Rinses	61.8	5.3	–	< 0.007	–	–	–	1.5	–
Organic Exts	8.2	0.7	–	–	< 0.007	–	1.9	< 0.007	–
Total	70.0	6.0		< 0.007	< 0.007		1.9	1.5	17.3
(mg/kg)	(1.056)	(0.090)					(0.029)	(0.023)	(0.261)

[a] MQL were in the range of 0.1–0.3% TRR

[b] unidentified, polar components that eluted before the DES reference standard. Depending on the sample, this group was comprised of 3–6 peaks of which no single fraction represented more than 1.3% of the TRR

[c] unidentified components that eluted either just before or immediately after chlorpyrifos. Depending on the sample, this group was comprised of 3–5 components, all of which appeared to be contaminants that were present in the ^{14}C-test material

[d] Non-extractable Residues (NER)

As with fruit, a significant portion of the leaf TRR was accounted for as surface residues that could be readily removed by the solvent rinses. Most of the residues remaining in the rinsed leaves were extracted and found to contain higher levels of the polar, aqueous soluble residues than were seen in fruit. These residues were assumed to represent conjugates. HPLC analyses of the leaf rinses and extracts showed a similar residue profile to that seen in fruit (Table 16).

Table 16 Percent distribution of the TRR in the rinses and extracts of treated orange leaves as determined by HPLC

	Percent of Total Leaf Residue [a]								
	CHP	Met A	CHP-Me Oxon	TCP	DES	Polar Unkns [b]	Nonpolar Unkns [c]	Aqueous Soluble [d]	NER [e]
6 DAT:									
Solvent Rinse	72.3	0.8	< 0.007	< 0.007	–	–	3.7	–	–
Organic Ext	13.2	0.6	< 0.007	< 0.007	–	2.9	< 0.007	–	–
Total	85.4	1.4	< 0.007	< 0.007		2.9	3.7	4.3	5.7
(mg/kg)	(73.8)	(1.21)				(2.51)	(3.20)	(3.72)	(4.93)
21 DAT:									
Solvent Rinses	42.2	1.6	0.2	< 0.007	–	–	3.1	-	–
Organic Ext	16.4	0.9	0.3	0.3	0.3	7.9	0.8	–	–
Total	58.8	2.5	0.5	0.3	0.3	7.9	3.9	10.8	14.6
(mg/kg)	(26.1)	(1.11)	(0.222)	(0.133)	(0.13)	(3.50)	(1.73)	(4.79)	(6.48)

[a] MQL of 0.1–0.3%

[b] unidentified, polar components that eluted before the DES reference standard. For both samples, this group was comprised of three peaks of which no single fraction represented more than 4.6% of the TRR

[c] unidentified components that eluted either just before or immediately after chlorpyrifos. Depending on the sample, this group was comprised of 4–7 components, most of which appeared to be contaminants that were present in the ^{14}C test material

[d] This fraction represents those residues in the ACN/water refluxes that could not be partitioned into organic solvent

[e] Non-extractable Residues (NER)

Following enzyme hydrolysis of an aliquot of 21 DAT leaf aqueous soluble fraction, approximately 60% of the sample radioactivity was extracted into organic solvent. HPLC analysis of these organosoluble residues showed 32.0% of the sample radioactivity to elute in the region of TCP, 2.3% in the region of DES and 49.7% to elute as an unknown fraction more polar than DES. When [^{14}C]DES was subjected to these same hydrolysis conditions, approximately 40% was found to degrade to TCP. Correcting for any degradation that might have occurred the maximum level of DES in the aqueous soluble fraction was only 3.8% of the total sample residue (0.4% of the TRR). A second aliquot of this same aqueous soluble fraction was subjected to base hydrolysis. Approximately 90% of the sample radioactivity was extracted, with nearly 80% of these residues eluting in the same region as TCP. Under these same conditions, over 90% of a [^{14}C]DES sample was converted to TCP. Results of this work confirmed that most of the aqueous soluble residues still contained the intact TCP moiety.

About 90% of the leaf NER was solubilised by base hydrolysis and about 85% of the bound radioactivity remained associated with the ADF (Table 17). Subsequent partitioning of the aqueous phase from this step resulted in the extraction of 82.9% of the solubilised radioactivity into organic solvent. HPLC analysis of this residue showed the presence of seven or more components, with TCP representing 36.7% of the recovered radioactivity. Since chlorpyrifos and the DES metabolite both convert to TCP under the base hydrolysis conditions, the presence of peaks other than TCP in this chromatogram would seem to suggest the presence of metabolites in the NER fraction that have undergone changes to the central ring structure of the chlorpyrifos molecule. It was suggested that it may involve the loss or replacement of one or more of the chlorine atoms.

Table 17 Percent distribution of the non-extracted residues in 21-dat leaves following enzyme, acid or base hydrolysis or isolation of the acid detergent fibre fraction

Characterization Procedure	Percent of Non-extractable Residue [a]	
	Aqueous Phase	Spent Tissue
Enzyme Hydrolysis: Cellulase	4.2	95.8
Driselase	6.6	93.4
Acid Hydrolysis	16.3	83.7
ADF Isolation	15.4	84.6
Base Hydrolysis	89.4	10.6

[a] The non-extractable residues in the extracted 21-DAT leaves represented 14.6% of the TRR.

Cabbage

Cabbage plants received one foliar spray application of [^{14}C]chlorpyrifos (radiopurity of 96.9% and specific activity of 13,062 dpm/µg) at a rate equivalent to 1.43 kg ai/ha (Graper, 2002b; GH-C 5482). Plants were collected at 0, 7, 14, 21 and 42 days after application (DAT), with the 21-DAT sample representing the label recommended pre-harvest interval (PHI). The plants were separated into head and wrapper and flat leaves. Some samples were rinsed with DCM and ACN; rinsed and unrinsed samples were cut up, frozen, and milled with dry ice and/or liquid nitrogen. Samples were extracted with 80/20 ACN/water: some samples were partitioned with DCM and further with hexane to provide further clean up. The extracted tissue and spent filter paper were allowed to air dry and assayed by combustion.

The stability of DES was evaluated by adding [^{14}C]DES (64.8% purity) to a 7 DAT rinsed control cabbage head sample that was extracted by the method described previously. A concentrate of the 80/20 extract from the 21-DAT rinsed wrapper leaf tissue was subjected to treatment using ß-glucosidase. [^{14}C]DES solution was subjected to the same enzyme procedure. Elution of radioactivity was monitored either by an in-line flow detector or by collection of one-minute fractions followed by LSC analysis. Elution of non-radiolabelled reference standards was monitored at 280 nm.

Table 18 shows the TRR values for cabbage heads and leaves. The majority of the radioactivity was found in the DCM and ACN rinses. TRR values declined over the 42 days in all cases, probably due to volatilization from the plant surfaces, since they were close to maturity when treated. The increase from 0 to 7 DAT in the tissue of rinsed heads and of rinsed wrappers indicated that the applied radioactivity was penetrating into plant tissue. The flat leaves did not show an increase from 0 to 7 DAT for mg/kg in rinsed tissue, but the percentage distribution at all sample times was comparable for the head, wrapper, and flat leaves.

Table 18 TRR in cabbage heads and leaves and distribution of radioactivity in rinses and rinsed tissue presented as mg chlorpyrifos equivalents per kg and as % of TRR

	DCM Rinse		ACN Rinse		Rinsed or Unrinsed Tissue[a]		Total
DAT	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	mg/kg
Heads							
0	74.5	1.430	11.1	0.214	14.4	0.276	1.920
7	17.8	0.305	4.4	0.075	77.8	1.334	1.713
14	3.0	0.021	2.7	0.019	94.3	0.650	0.690
21	1.8	0.013	2.7	0.020	95.5	0.705	0.738
21U[b]	NA	NA[d]	NA	NA	100.0	0.654	0.654
42	0.8	0.005	2.2	0.015	97.0	0.677	0.698
Wrapper Leaves							
0	79.4	69.04	1.9	1.673	18.7	16.294	87.006
7	26.0	17.04	2.4	1.589	71.6	47.011	65.637
14	8.1	2.484	2.5	0.751	89.4	27.282	30.517
21	4.2	1.111	1.9	0.515	93.8	24.776	26.401
21U[c]	NA	NA	NA	NA	100.0	19.437	19.437
42	1.7	0.317	1.9	0.349	96.4	17.876	18.542
Flat Leaves							
0	64.0	62.181	3.5	3.360	32.5	31.599	97.140
7	23.8	10.568	3.5	1.560	72.7	32.335	44.464
14	9.7	3.848	2.7	1.064	87.6	34.865	39.778
21	5.7	1.995	2.2	0.769	92.2	32.463	35.228
21U[c]	NA	NA	NA	NA	100.0	28.298	28.298
42	3.0	0.893	1.6	0.469	95.5	28.703	30.066
Secondary Heads [c]							
42U[c]	NA	NA	NA	NA	100.0	4.191	4.191

[a] rinsed tissue with the exception of 21 DAT

[b] sprouted between the existing wrapper leaves and flat leaves

[c] U = unrinsed tissue

NA = not applicable.

Table 19 shows the distribution of radioactivity in the extracts and tissues. Up to 7 DAT, most of the radioactivity was found in the organic phase; at 21 DAT and after, 70% of the TRR or over in head samples was found in the extracted aqueous. By 42 DAT, 77.2% of TRR for wrapper leaves were accounted for in the extracted aqueous and extracted tissue. Over 93 % of the added [^{14}C]DES was recovery during the procedure, mostly in the organic phase.

Table 19 Distribution of radioactivity in extracts and tissue presented as mg chlorpyrifos equivalents per kg and as % of TRR

	Organic Phase		Extracted Aqueous		Tissue	
DAT	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Heads						
0	13.7	0.263	0.5	0.009	0.1	0.001
7	44.8	0.768	16.0	0.273	5.2	0.089
14	21.4	0.148	48.7	0.336	8.6	0.059
21	19.1[a]	0.141[a]	70.8	0.523	11.0	0.081
21U [b]	16.5	0.108	72.4	0.474	11.4	0.075
42	12.1	0.085	70.0	0.488	12.6	0.088
DES stability	77.5	0.047	15.8	0.010	0.2	0.000[c]
Wrapper Tissue						
0	18.1 [d]	15.787 [d]	– [d]	– [d]	0.7	0.615
7	63.3 [d]	41.573 [d]	– [d]	– [d]	11.5	7.546
14	74.1 [d]	22.620 [d]	– [d]	– [d]	24.3	7.423

	Organic Phase		Extracted Aqueous		Tissue	
DAT	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
21	52.3 [d]	13.808 [d]	– [d]	– [d]	36.5	9.642
21U [b]	18.9	3.680	39.7	7.717	45.5	8.845
42	17.0	3.146	35.2	6.529	42.0	7.785

[a] ACN phase, the hexane phase comprised 0.2% TRR

[b] U = unrinsed tissue; on the basis of the theoretical amount of ^{14}C-DES added

[c] Note that values of 0.000 or 0.0% indicate values less than 0.001 or 0.1%

[d] for the 80/20 ACN/water extract.

The results of HPLC analysis of the samples are summarized in Table 20. In the rinses, the radioactivity was primarily chlorpyrifos. At 7 DAT, organic extracts contained 42% of TRR, most of it as chlorpyrifos. From 21 DAT on, most of the radioactivity was composed primarily of polar radioactivity (regions H and J). At 21 DAT, chlorpyrifos accounted for 5.2%, DES for 2.4% and TCP for 6.1% of TRR radioactivity. The percent distribution in the HPLC regions is similar for heads and wrappers (data not shown). About 78% of the ^{14}C-DES (64.8% purity) that was added was recovered during the procedure.

Table 20 Distribution of radioactivity from the HPLC analysis of head rinses and extracts

Sample Type —	J (6–8 min.)		H (11–12 min.)		DES		TCP		Chlorpyrifos	
DAT, Description	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
0, DCM Rinse	< 0.1	–	< 0.1	–	< 0.1	–	< 0.1	–	73.0	1.402
0, ACN Rinse	< 0.1	–	< 0.1	–	< 0.1	–	< 0.1	–	10.4	0.200
0, 80/20 Extract	< 0.1	–	< 0.1	–	< 0.1	–	< 0.007	< 0.007	12.9	0.248
Total	< 0.1	–	< 0.1	–	< 0.1	–	< 0.007	< 0.007	96.4	1.850
7, DCM Rinse	< 0.1	–	< 0.1	–	< 0.1	–	< 0.1	–	17.6	0.301
7, ACN Rinse	0.3	0.004	0.8	0.014	< 0.1	–	< 0.007	< 0.007	3.1	0.053
7, Organic	< 0.1	–	0.9	0.016	< 0.1	–	2.0	0.035	38.7	0.664
7, Aqueous	4.2	0.073	11.0	0.188	< 0.1	–	< 0.007	< 0.007	< 0.1	–
Total	4.5	0.077	12.8	0.219	< 0.1	–	2.0	0.035	59.4	1.018
14, DCM Rinse	< 0.1	–	< 0.1	–	< 0.1	–	< 0.007	< 0.007	2.8	0.019
14, ACN Rinse	0.5	0.004	1.0	0.007	< 0.1	–	< 0.007	< 0.007	0.6	0.004
14, Organic	1.5	0.010	3.5	0.024	< 0.1	–	4.5	0.031	9.2	0.064
14, Aqueous	15.6	0.108	21.2	0.146	5.3	0.037	< 0.1	–	–	–
Total	17.6	0.121	25.7	0.177	5.3	0.037	4.5	0.031	12.6	0.087
21, DCM Rinse	< 0.1	–	< 0.007	< 0.007	< 0.1	–	< 0.007	< 0.007	1.4	0.010
21, ACN Rinse	0.7	0.005	< 0.1	–	0.2	0.002	< 0.007	< 0.007	0.4	0.003
21, Organic	1.3	0.009	3.4	0.025	2.4	0.017	6.1	0.045	5.2	0.038
21, Aqueous.	38.7	0.285	27.1	0.200	< 0.1	–	< 0.1	–	–	–
Total	40.6	0.300	30.5	0.225	2.6	0.019	6.1	0.045	7.0	0.052
21U, Organic	2.6	0.017	< 0.1	–	3.4	0.022	3.9	0.026	6.0	0.039
21U, Aqueous	40.8	0.267	29.2	0.191	< 0.1	–	< 0.1	–	–	–
Total	43.4	0.284	29.2	0.191	3.4	0.022	3.9	0.026	6.0	0.039
42, DCM Rinse	< 0.007	< 0.007	< 0.1	–	< 0.1	–	< 0.1	–	0.5	0.004
42, ACN Rinse	0.9	0.006	1.0	0.007	< 0.1	–	0.1	–	0.1	0.001
42, Organic	2.2	0.015	5.5	0.038	< 0.1	–	3.5	0.024	2.6	0.018
42, Aqueous	47.0	0.328	21.2	0.148	< 0.1	–	< 0.1	–	–	–
Total	50.0	0.349	27.6	0.193	< 0.1	–	3.6	0.025	3.3	0.023
DES, Organic[a]	< 0.007	< 0.007	< 0.1	–	38.3	0.023	29.4	0.018	< 0.007	< 0.007
DES, Aqueous[a]	0.9	0.001	< 0.1	–	12.3	0.008	0.8	0.000	–	–
Total	0.9	0.001	< 0.1	–	50.6	0.031	30.2	0.018	< 0.007	< 0.007

Sample Type —	J (6–8 min.)		H (11–12 min.)		DES		TCP		Chlorpyrifos	
DAT, Description	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
^{14}C-desethyl[b]	< 0.007	< 0.007	< 0.1	–	64.8	0.040	22.2	0.014	< 0.007	< 0.007

DCM = DCM; ACN = ACN; U = unrinsed tissue

[a] from adding ^{14}C-DES to a 7 DAT control rinsed head sample

[b] ^{14}C-DES solution used for addition to control tissue.

The distribution of radioactivity in 21-DAT wrapper leaf samples after enzyme treatment shows that radioactivity in the extract was divided almost equally between the organic and extracted aqueous phases (approximately 28%TRR). For the [^{14}C]DES, most of the radioactivity was present in the aqueous phases (62% TRR).

An additional portion of the 21 DAT rinsed wrapper leaf sample was extracted with ACN:water (80:20 v/v), the extract subjected to extensive purification and the highly purified isolates analysed by HPLC-MS to investigate the structures of the metabolites and a metabolic pathway (Balcer *et al.,* 2003; Study 020135). Chlorpyrifos appears to be metabolized to TCP, which is extensively conjugated with glucose and malonic acid. The locations and orientations of the linkages between TCP and glucose and malonic acid were not determined.

Peas

EC formulated [^{14}C]chlorpyrifos was applied to fifteen pots of pea plants as a single foliar spray application at a rate equivalent to 1.9 kg ai/ha, 3.2 times greater than GAP rate for legumes (Magnussen and Balcer, 2006; Study 50021). Treated samples were collected at 0, 7, 14, 21and 28 days after application (DAT), with the 21 DAT sample representing the label recommended pre-harvest interval (PHI). Pods with peas were removed from the plants (pod samples) and the remainder of the plants were collected (whole plant samples). Samples were frozen, cryogenically milled and stored at –20 ºC until analysed, within 18–20 days of collection.

Samples were extracted with ACN/water (80:20) and the extracts partitioned with 1:1 ACN/DCM (neutral). The aqueous phase was acidified and again partitioned with ACN/DCM. No additional work was done to characterize non-extracted residues. TRR in all tissue samples both before and after extraction were determined by oxidative combustion and entrapment of the evolved $^{14}CO_2$ in an alkaline scintillation cocktail. TRR levels in all liquid samples were determined by direct counting. Some HPLC column eluant that was collected in 96-well plates was analysed using a TopCount-NXT microplate scintillation and luminescence counter.

Radioactivity declined rapidly in the pod and whole plant during the first 7 days following application (Table 21). By 28 DAT, it was equally distributed between the acidic extracts and the spent aqueous fractions. For all samples, the accountability of radioactivity during the extraction and partitioning steps ranged of 89.7–116.4% of theory.

Table 21 TRR in the pods and whole plants of peas treated with [^{14}C]chlorpyrifos

	TRR a (mg/kg)	% Distribution of TRR Following Extraction			
		Neutral Organic	Acidic Organic	Spent Aqueous	NER [b]
Whole Plants:					
0 Time	18.043	99.5	–	0.2	0.3
7 DAT	3.256	64.7	13.8	15.2	6.3
14 DAT	2.419	38.0	16.6	35.1	10.2
21 DAT	3.412	34.5	15.1	39.6	10.7
28 DAT	2.796	27.0	16.2	41.8	15.0

	TRR a (mg/kg)	% Distribution of TRR Following Extraction			
		Neutral Organic	Acidic Organic	Spent Aqueous	NER [b]
Pea Pods:					
0 Time	1.327	98.1	–	0.3	1.6
7 DAT	0.594	69.3	10.8	11.1	8.8
14 DAT	0.332	44.3	15.9	28.0	11.8
21 DAT	0.377	33.1	19.4	34.8	12.7
28 DAT	0.247	26.7	17.0	42.8	13.5

[a] Expressed as mg/kg of chlorpyrifos equivalents;

[b] Non-extracted Residues

The distribution of radioactivity in the organic extracts and the spent aqueous phase, as determined by HPLC, showed a steady decrease over time in the levels of chlorpyrifos and an increase in TCP conjugates (Table 22). TCP levels were below 10% TRR during the whole period. From the 5 conjugates observed, only 2 were at levels higher than 10% TRR. As much as 10–30% of the radioactivity in the 7–28 DAT corresponded to at least twenty components more polar than the conjugates. LC/MS analysis confirmed the identity of chlorpyrifos, TCP and sugar related conjugate of TCP. No conjugates of metabolites that still contained the intact phosphate ester were observed in any of the isolated fractions.

Table 22 Summary of the Distribution of the Residues in the Pods and Whole Plants of Peas among Chlorpyrifos and Its Metabolites

	0 Time		7 DAT		14 DAT		21 DAT		28 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Whole Plants										
Chlorpyrifos	95.3	17.195	33.0	1.074	11.7	0.283	6.9	0.235	3.9	0.109
TCP	0.8	0.144	7.3	0.238	7.9	0.191	5.1	0.174	3.3	0.092
TCP Conjs.[a]	NDR	–	23.6	0.768	42.4	1.026	53.2	1.815	46.9	1.311
Pods										
Chlorpyrifos	89.6	1.189	33.4	0.198	9.7	0.032	5.8	0.022	3.8	0.009
TCP	0.9	0.012	9.8	0.058	6.8	0.023	8.6	0.032	8.7	0.021
TCP Conjs. [a]	NDR	–	16.8	0.100	33.4	0.111	40.9	0.154	42.5	0.105

[a] The TCP conjugates consisted of at least five different sugar or sugar plus malonic acid conjugates of TCP.

Radish

[^{14}C]chlorpyrifos was applied to the plants in one box as a single foliar spray application at a rate equivalent to 1.92 kg ai/ha, 3.3 times greater than the maximum label rate (GAP) for use on tuber crops (Graper *et al,* 2006; Study 50020). Treated samples were collected at 0, 7, 14, 21 and 35 days after application or treatment (DAT). The aerial portion of the plants (tops) was removed, a portion of each top sample rinsed with DCM followed by ACN and the rinsed and un-rinsed sample frozen for analysis. Aliquots of both rinses were assayed for total radioactivity by LSC and analysed by HPLC. Root samples were cut into smaller pieces and frozen for analysis. Frozen root and top samples were submitted to cryogenic milling and stored frozen at –20 ºC pending analysis. All samples were analysed within 100 days of collection

Samples were extracted with ACN/water (80:20). The 0, 7 and 14 DAT top samples were analysed directly by LSC and HPLC; the other two samples were also partitioned using 1:1 ACN/DCM before analysis. Spent tissue was submitted to combustion analysis. Sample portions of the extracted top tissues were stirred overnight in 0.01 N HCl; the remaining tissue removed by centrifugation and the pellet further extracted by refluxing in 1 N HCl. The extracted tissue was again removed by centrifugation and was subsequently submitted for combustion analysis. The two-hydrolysate solutions were partitioned with 1:1 ACN/DCM.

Additional portions of the tissues following extraction with ACN/water were also subjected to enzyme digestion using cellulose or driselase. The spent tissue was removed by centrifugation and the resulting supernatants partitioned with DCM after acidifying to pH 2–3. All fractions were analysed for total radioactivity, determined by oxidative combustion and entrapment of the evolved $^{14}CO_2$. TRR levels in all liquid samples were determined by direct counting (LSC). Some HPLC column eluant that was collected in 96-well plates was analysed using a TopCount-NXT microplate scintillation and luminescence counter.

Radioactive residues in the top samples decreased by 80–95% during the first 7 days following application (Table 23). The residue levels in roots were much smaller than in tops, with no pattern of decline over time. Based on the results from the 21 and 35 DAT top samples, there also appeared to be a decline over time in the portion of the residues that were organosoluble along with a corresponding increase in the level of aqueous soluble residues.

Residues in roots were readily extracted at 0 Time and remained so throughout the remainder of the study, as the NER levels never exceeded 10% TRR. Partitioning of the extracted residues at each time point showed virtually all the 0 Time residue to be organosoluble as only 0.6% TRR was accounted for in the spent aqueous phase. At 35 DAT, most of TRR was partitioned into organic solvent.

Table 23 TRR in the roots and tops of radishes treated with [^{14}C]chlorpyrifos and the percentage distribution of residues in the extraction

	TRR (mg/kg) [a]	% Distribution of TRR Following Extraction			
		Solvent Rinses	ACN/H2O or Organic extract	Spent Aqueous	NER [b]
Rinsed Tops:					
0 Time	147.6	67.1	31.9	–	1.0
7 DAT	14.2	21.2	65.5	–	13.3
14 DAT	11.2	25.4	61.6	–	12.9
21 DAT	6.8	13.9	43.3	22.9	19.8
35 DAT	1.3	6.5	25.6	40.7	27.3
Unrinsed Tops:					
0 Time	59.7	–	98.3	–	1.7
7 DAT	12.7	–	88.5	–	11.5
14 DAT	8.5	–	76.5	–	23.5
21 DAT	4.7	–	42.9	36.0	21.1
35 DAT	1.6	–	28.2	38.6	33.2
Roots:					
0 Time	1.9	–	97.3	0.6	2.1
7 DAT	1.0	–	84.8	10.4	4.8
14 DAT	2.7	–	81.2	8.8	10.0
21 DAT	1.1	–	72.1	20.2	7.7
35 DAT	2.2	–	53.5	38.5	8.0

[a] Expressed as mg/kg of chlorpyrifos equivalents

[b] Non-extracted residues

Table 24 shows the distribution of the extracted radioactivity from both roots and tops as determined by HPLC. Since there were no differences in the nature of the residues between the rinsed and unrinsed tops, only results of the unrinsed tops are shown. By 7 DAT, the level of chlorpyrifos that remained had declined to 60.6% TRR and this level continued to decline over the remainder of the study while TCP conjugates increased (mainly glucose and malonic acid conjugates). Besides chlorpyrifos, the only other non-conjugated components that represented more than 2–3% of the TRR were TCP and an unknown compound that was less polar than the parent. LC/MS analysis confirmed the identity of those residue components that co-chromatographed by HPLC with the reference standards for chlorpyrifos, TCP and glucose plus malonic acid TCP conjugates. Attempts to identify the unknown compound were not successful.

Table 24 Distribution of the residues in radish tops and roots among chlorpyrifos and its metabolites

	0 Time		7 DAT		14 DAT		21 DAT		35 DAT	
	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg
Radish Tops										
Chlorpyrifos	93.7	55.98	60.6	7.7	38.3	3.3	22.3	1.0	14.8	0.236
TCP	< LOQ	–	< LOQ	–	NDR	–	1.4	0.07	2.5	0.040
TCP Conjs.	0.9	0.52	23.4	2.61	33.9	2.887	36.6	1.7	43.0	0.686
Radish Roots										
Chlorpyrifos	93.8	1.77	80.1	0.824	76.3	2.046	61.4	0.690	41.5	0.906
TCP	1.3	0.025	2.3	0.023	3.1	0.084	1.5	0.017	1.2	0.026
TCP Conjs.	NDR	–	9.0	0.093	8.4	0.225	21.4	0.240	44.7	0.978

Residues remaining in the extracted top samples were subjected to acid and enzyme hydrolysis procedures. Following the two sequential acid extraction steps, only an additional 3.4–5.8% TRR was found to have been released. Partitioning work with these hydrolysate samples showed 45–75% of the radioactivity to be aqueous soluble in nature. No additional characterization work was done with any of these fractions. For those samples that were subjected to an enzyme digestion step using cellulose, 43–88% of the bound residue (11.9–18.5% of the TRR) was solubilised. Partitioning work with these fractions showed 55–80% of the released residues to be aqueous soluble. For those samples that were subjected to enzyme digestion using driselase, 30.9–94.2% of the NER (8.4–19.8% of the TRR) was released, with most of these residues (70–85%) being aqueous soluble in nature. No additional characterization work was done with any of these fractions.

Based on the results from the metabolism studies conducted in orange, cabbage, peas and radish, a single primary metabolic pathway was observed to be responsible for the breakdown of chlorpyrifos in plants. This pathway involved hydrolysis of the phosphate ester in chlorpyrifos to give TCP, which in turn was then conjugated with glucose and malonic acid. A large number of additional polar components that were also thought to represent TCP conjugates were also observed in the studies. The proposed pathway is shown in Figure 1.

Environmental Fate in Soil

Aerobic degradation

[^{14}C]Chlorpyrifos-methyl (radiochemical purity *ca* 98%; specific activity 1084 MBq/mmol) was incubated in Speyer 2.2 soil (loamy sand) and three UK agricultural soils (Marcham sandy loam, Marcham sandy clay loam and Derby silt loam) at a rate equivalent to 0.5 kg ai/ha at 40% MHC and 20 ºC (Reeves, 1994; GHE-P-3638). Sodium hydroxide solution and PUF bungs were used to trap evolved $^{14}CO_2$ and organic volatiles, respectively. Samples were taken at regular intervals up to 100 days after treatment (DAT), extracted with solvent and the extracts analysed by LSC and HPLC. The data were subject to Timme-Frehse analysis to calculate the DT_{50} (half life) and DT_{90} using best-fit kinetics.

Table 25 illustrates the distribution of radioactivity (as % AR) in the Speyer 2:2 loamy sand, which was considered representative of the four soils tested. The initial degradation product in all soils was TCP, accounting for up to 65% of applied radioactivity (AR) within 7 days, which was subsequently mineralised to $^{14}CO_2$. In addition, up to nine minor metabolites were observed (generally ≤ 10% AR each, but 15–16% AR on one occasion in two soils), one of which at ca 2% AR co-chromatographed with TMP. The other minor metabolites were unassigned. The majority of these minor metabolites were transient. Non-extracted residues (NER) reached 17-26% AR at 100 days, and little or no organic volatiles were observed. Degradation was most rapid in the two soils with greatest microbial activity. Half life of all soils ranged from 0.63 to 3.6 days (Table 26).

Table 25 Distribution of radioactivity (as % AR) in Speyer 2:2 Loamy Sand

	Days After Treatment							
Component	0	1	3	7	14	30	59	100
Chlorpyrifos-methyl	92.9	55.3	31.7	5.7	5.6	1.9	3.0	2.6
TCP	4.1	28.3	43.2	26.9	3.8	3.5	1.7	1.0
TMP	1.9	ND	0.4	0.7	0.1	ND	ND	ND
$^{14}CO_2$	NS	2.5	10.9	34.8	55.5	57.5	64.3	67.6
Unidentified a	ND	9.6	5.1	10.1	11.0	9.0	6.0	4.7
NER	1.1	2.8	7.0	18.3	20.1	18.7	19.8	19.4
Total	100.0	98.5	98.2	96.6	96.0	90.7	94.7	95.3

ND—not detected,

NS—no sample.

Table 26 Half life (DT_{50}) and DT_{90} for chlorpyrifos methyl in soils under aerobic conditions

Soil	DT_{50}, days	DT_{90}, days	Modified Likelihood	Order, function
Speyer 2.2	3.6	39.3	0.5633	Sqroot 1st
Marcham sandy loam	1.4	38.0	0.9382	Sqroot 1.5st
Marcham sandy clay loam	0.63	17.3	0.9266	Sqroot 1.5st
Derby silt loam	1.7	46.8	0.6872	Sqroot 1.5st

The route of aerobic degradation of [2,6-^{14}C]-TCP was investigated in four representative agricultural soils—Marcham sandy clay loam (UK), Charentilly silty clay loam (France), Cuckney sand (UK) and Thessaloniki loam (Greece)—under laboratory conditions (De Vette & Schoonmade, 2001; GH-C-5182). The soils were placed in conical flasks fitted with a glass column containing soda lime for trapping evolved CO_2, and quartz glass wool covered with paraffin oil for trapping organic volatiles. Soils were treated with [2,6-^{14}C]-TCP at a rate equivalent to 250 g/ha in a soil depth of 5 cm and a soil bulk density of 1.5 g/cm^3, adjusted to 40% WHC_{max} and incubated at 20 °C in the dark. Aerobic conditions were maintained by allowing passive entry of air. Further incubations were carried out using sterile Marcham soil at 40% WHC_{max} and 20 °C to elucidate the degradation route (biotic versus abiotic).

Samples were collected at regular intervals up to 120 days after treatment (152 days for sterile Marcham soil). The amount of $^{14}CO_2$ evolved from the soil was determined by LSC. The soil was extracted with acetone/0.1M HCl and taken for LSC analysis. The level of non-extracted radioactivity (NER) was determined by air drying the soil residue and combusting triplicate aliquots in oxygen using a sample oxidiser. The pooled soil extracts were evaporated, the remaining aqueous residue acidified, extracted with DCM, evaporated in a rotary evaporator at *ca* 40 °C and the radioactivity measured by LSC.

The amounts of TCP and its degradation products in the extracts were determined HPLC and confirmed by TLC. For the non-sterile soils, the overall recovery ranged between 83.1 and 103.7% of applied radioactivity. The levels of radioactivity in the soil extracts declined from 97.7 to 102.4% AR at 0 DAT to between 6.6 and 50.8% AR by 120 days. The level of NER and of evolved $^{14}CO_2$ increased throughout the incubation period (up to 58 % AR), whilst the levels of ^{14}C organic volatiles were very low throughout (< 0.5%AR).

TCP was the major component present in all the soil extracts, dropping to about 32% AR after 120 days in Marchand sandy clay loam soil. At this time, TMP level reached 13%AR, while an unknown compound was observed at 5.5%AR In sterile Marcham soil, only TCP was detected.

Further work to characterise the nature of the unknown by HPLC and LC/MS was not successful, however, it was characterised as a neutral organic or weak base.

^{14}C-ring-labeled TMP, label position not stated, was assayed in top soil taken from three USA sites at a TMP concentration of approximately 1.0 mg/kg soil at 100% or 35% 1/3 bar and 25 ºC (Laskowski *et al.*, 1977; GH-C 964). The soils were fractionated and partitioned before extraction with solvent prior to combustion analysis and TLC chromatography. Extensive mineralisation to carbon dioxide (*ca* 70%AR) was observed in the two silty soils but not in the sandy soil, a known poor degrader, where TMP accounted for *ca* 70% AR after 300 days. Low levels of TCP (*ca* 10%AR) were observed in all three soils.

Using the information from the aerobic soil degradation studies described and metabolite in soils, the degradation route of chlorpyrifos-methyl in soils shown in Figure 2 is proposed.

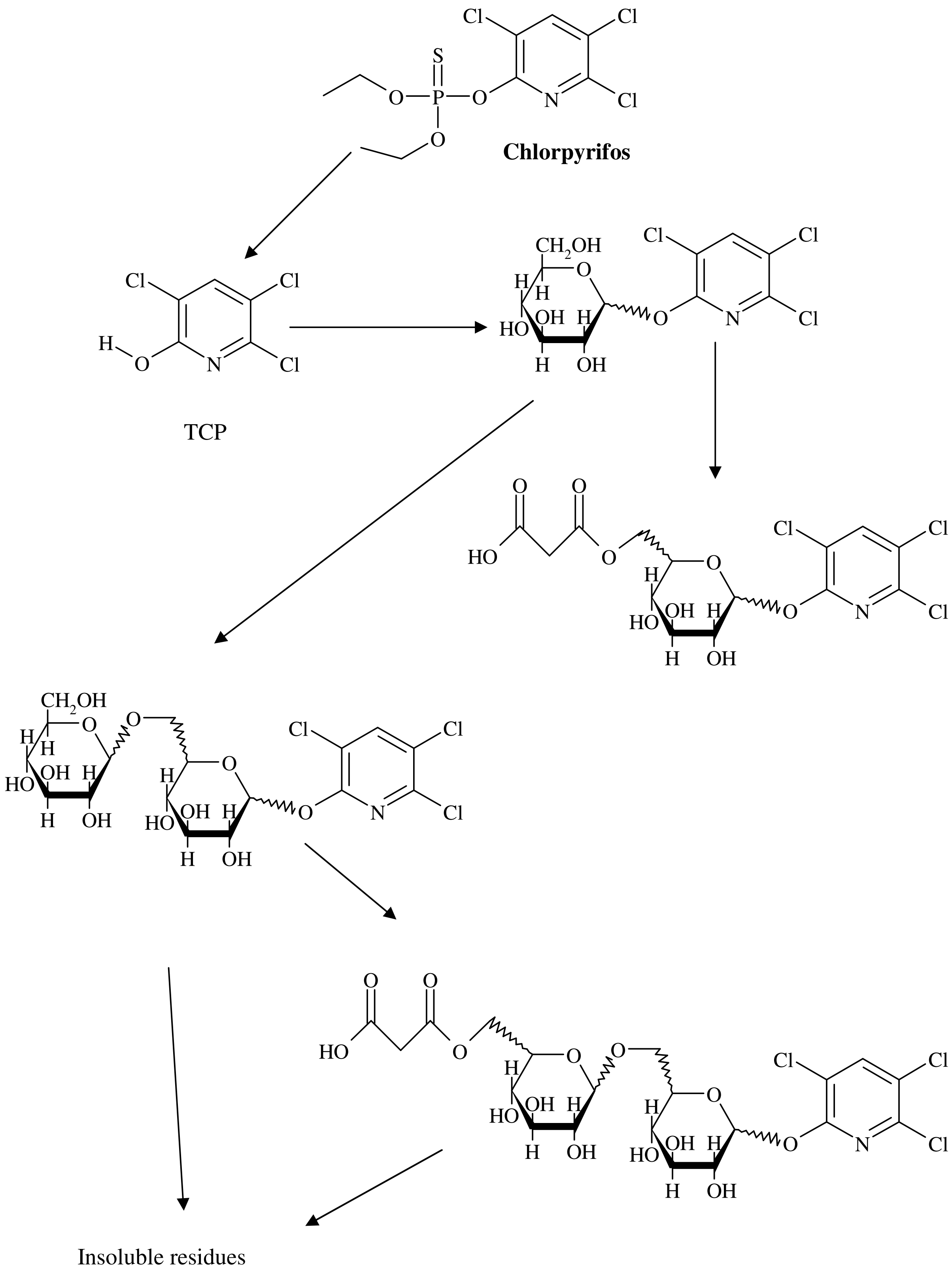


Figure 1 Proposed metabolic pathway for chlorpyrifos in plants

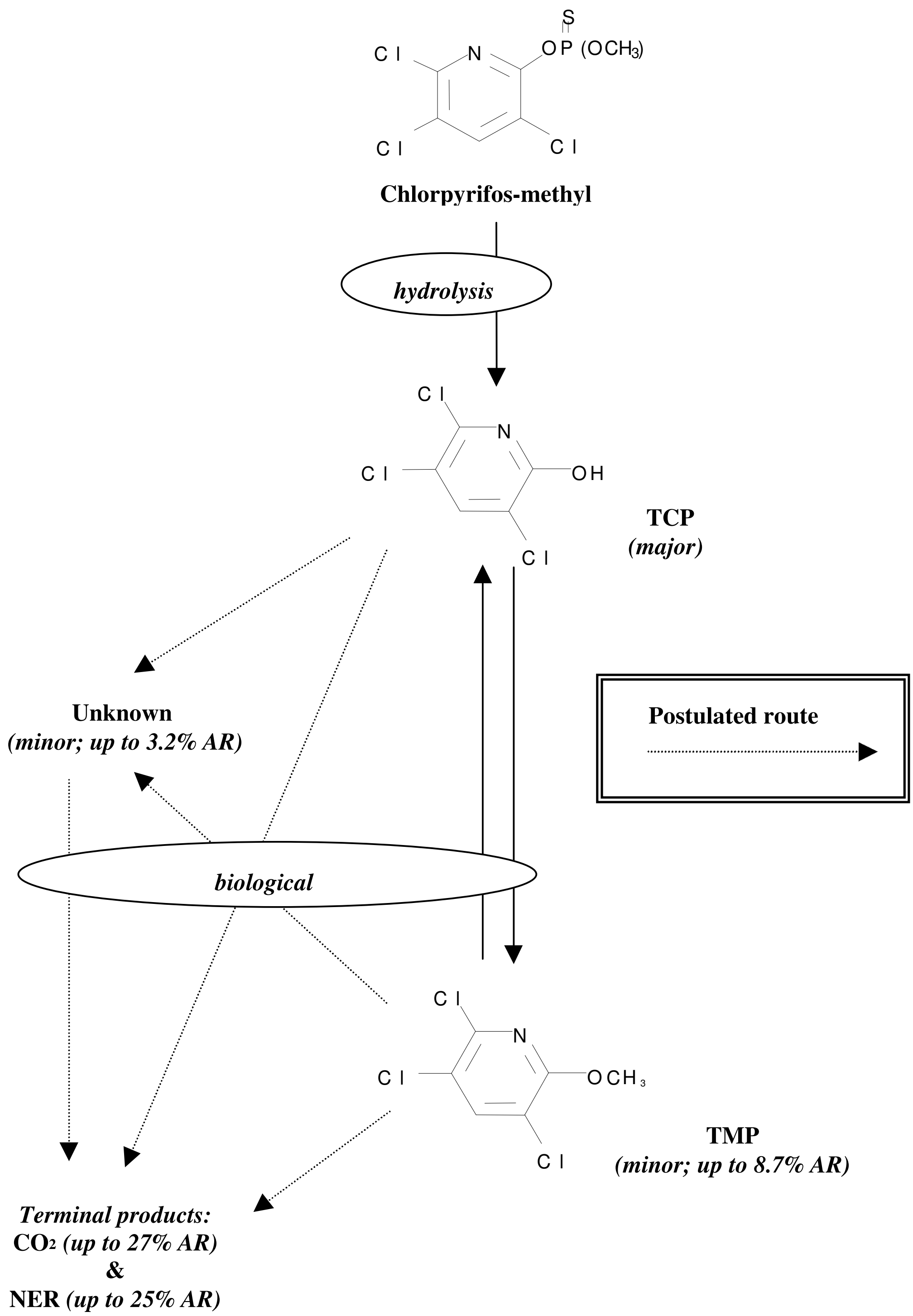


Figure 2 Aerobic degradation route of chlorpyrifos-methyl in soil

Aerobic degradation in water and sediment

In a study conducted with sandy loam and clay loam sediments with their associated surface water were treated with [^{14}C]Chlorpyrifos-methyl at a nominal rate equivalent to 0.5 kg ai/ha (Philips and Hall, 1994; GHE-P-3756). The samples were incubated under aerobic/anaerobic gradient in the dark at 17–20 °C and ^{14}C volatiles collected in ethanolamine traps and polyurethane foam plugs. Samples were taken at interval up to 100 days.

The mean radiochemical balance was about 93–94% for both systems, with lower recoveries at 60–100 days. $^{14}CO_2$ and other volatile organic compounds accounted for up to 11% AR. The radioactivity associated with surface water declined from about 80% at time zero to 21–38% AR at the end of the experiment. HPLC analysis indicated that parent compound was the main component at 0 time, with low levels of TMP. Degradation of chlorpyrifos-methyl was rapid in both systems with less than 2% AR after 100 days. DT_{50} values in the sandy loam and clay loam water/sediment systems were 2.6 and 25.4 days, respectively. In the water phase alone the dissipation was rapid, with DT_{50} values of 2 and 4 days, respectively. The principal degradation product was TCP, which was detected at maximum levels of 83 and 62% AR in 30 day sandy loam and clay loam samples, respectively.

Photochemical degradation

The aqueous photolytic degradation rate and quantum yield of [^{14}C]chlorpyrifos-methyl (specific activity 1084 MBq/mmol, radiochemical purity 99 + %) were determined by irradiation of chlorpyrifos-methyl solutions (8.8–13.7 mg/L) in water/ACN (9:1) at 20°C (Yon and Muller, 1994b; GHE-P-3981). The experiment was conducted under a 450 W Xenon high-pressure lamp at 290 nm for periods of up to eight hours. Chlorpyrifos-methyl degraded with a calculated quantum yield of 2.6 $\times 10^{-3}$. Degradation half-lives, based on this quantum yield were calculated using the ABIWAS model to be in the range 1.8–9.1 days (June) and 0.8–3.8 months (December).

METHODS OF RESIDUE ANALYSIS

Method ERC 93.1 (Khoshab and Laurie, 1993) is applicable to the quantitative determination of chlorpyrifos-methyl residues in citrus. The compound is extracted from the sample with an acetone/water solvent mixture, additional water is added, chlorpyrifos-methyl is partitioned into hexane and quantified by GC/FPD. The method was validated for residues of chlorpyrifos-methyl in lemons, mandarins and oranges (Table 27).

Table 27 Recovery rate of chlorpyrifos-methyl in citrus for method ERC 93.1

Matrix	Level (mg/kg)	Recovery (%)	RSD, %
Lemon peel	0.01	85.5, 75.5, 93.5	10.6
	0.10	77	–
	1.0	83.5	–
	10	84.5	–
Lemon pulp	0.01	91.5, 84.5, 85.5	4
	0.1	84.5	–
	1	87	–
Mandarin Peel	0.01	90, 85, 86.5	2.9
	0.10	84.7	–
	5	87	-
Mandarin Pulp	0.01	84.5, 84.5, 87.5	2.0
	0.10	85	–
	1.0	80	–
Orange peel	0.01	84.5, 85, 97.5	8.2
	0.10	94, 85.5	6.6
	5	92.5	–
Orange pulp	0.01	73, 85, 82.5	7.9
	0.10	78, 81	2.6
	1.0	75	–

Method GRM 05.07 was validated in various crops by Pinheiro *et al.* (2006). In this method, residues of chlorpyrifos-methyl are extracted with an 80% acetone/20% water solution. An aliquot of 0.5 mL is added into a 96-well plate, isotope standard is added prior to purifying by on-line SPE using a C_{18} cartridge. Residues are analysed by HPLC/MS/MS. Quantitation is achieved using a stable isotope internal standard, $^{13}C_2{}^{15}N$-chlorpyrifos-methyl (t_R = 2.21) with specific MS/MS transitions m/z Q1/Q3 321.8/125.1. Limit of quantification (LOQ) was 0.01 mg/kg. Table 28 shows the validation data

Table 28 Recovery rate of chlorpyrifos-methyl in various crops (n = 1 or 2) for method GRM 05.7

Matrix	Level (mg/kg	Recovery (%)	Matrix	Level (mg/kg	Recovery (%)
Pear	0.01	88–90	Orange	0.01	88–91
	5	77–82		5	89–90
Tomato	0.01	90–92	Orange Peel	0.01	96–98
	5	81–84		5	95–102
Grape	0.01	81–90	Orange Pulp	0.01	76–107
	5	75–87		5	88–92
Peach	0.01	71–82	Whole Apple	0.01	91–106
	5	83–84		5	90–97
Apricot	0.01	90–96	Maize Plant	0.01	92–102
	5	80–87		5	94–98
Pepper	0.01	91–93		20	NA
	5	76–81	Maize Stover	0.01	86–92
Mandarin	0.01	85–89		5	105–108
	5	79–102		20	NA
Mandarin Peel	0.01	96	Maize Cobs	0.01	83–99
	5	91–96		5	109–110
Mandarin Pulp	0.01	80–96		20	NA
	5	89–95			

Method GRM 00.10 was applied for the determination of chlorpyrifos-methyl in crops with a high water content (Teasdale, 2000). The compound is extracted from the sample with acetone/water, additional water is added and chlorpyrifos-methyl partitioned into hexane. Quantification is done by GC/FPD. The method was validated for 25 matrixes, including tomato, apple, grapes, maize, onion, pepper, potato and sugar beet and processing products (Table 29). Method GRM 00.10 was independently validated, with recoveries averaging 97% at 0.01–0.2 mg/kg for whole grapes (n = 10) and 97% at 0.01–0.5 mg/kg for whole apples (n = 10). The corresponding relative standard deviations (RSD) were 3 and 7%, respectively (Maliani, 2002b; GH-C 5429).

Table 29 Recovery rate of chlorpyrifos-methyl in crops (n = 48 at each level) for method GRM 00.10

Level, mg/kg	Recovery range, %	Recovery mean, %	RSD, %
0.01	73–109	91	8.4
0.1	81–96	89	4.3
1	71–97	88	6.0
5	81–96	89	4.3

The method GRM 02.4 was validated for orange, barley, wheat and their processing products (Olberding *et al.*, 2002). Residues are extracted with acetone:water (80:20) or acetone (orange oil) and clean-up is performed with C_{18} SPE, eluting with ACN:0.1HCL (90:10). Residues are then partitioned into isooctane. Quantification is done by GC with negative ion chemical ionization (GC/NCI-MS), using $^{13}C_2$ ^{15}N-chlorpyrifos-methyl as internal standard. A summary of the validation data is shown in Table 30. Method GRM 02.04 has undergone an independent laboratory validation studies (Clark, 2002; GH-C 5430). Recoveries averaged 89 ± 6% in whole oranges and 99 ± 8% for in wheat grain over the concentration range of 0.01 mg/kg to 0.50 ug/g for whole oranges and 0.01 mg/kg to 6.0 mg/kg for wheat grain. The individual percent recoveries were within the range of 70–120%. RSD of replicate recovery measurements did not exceed the level of ± 20%.

Table 30 Recovery rate of chlorpyrifos-methyl in various crops for method GRM 02.4

Crop	Level, mg/kg	Recovery range, %	Recovery mean, %	N	RSD, %
Orange and processed products (peel, pulp, juice and oil)	0.01	88–96	91	12	2.7
	0.05	88–93	90	6	1.9
	0.25	86–97	91	6	3.9
	0.5	88–93	90	6	2.9
Barley grain, forage and straw	0.01	91–102	94	12	3.4
	0.05	91–97	92	3	3.4
	0.25	93–99	95	3	3.7
	0.5	98	–	–	–
	5.0	95–100	97	4	2.6
Wheat grain, forage and straw	0.01	91–100	97	12	3.1
	0.05	93–102	97	3	4.6
	0.25	97	97	3	0
	0.5	98	–	–	–
	1.0	99–102	100	2	–
	5.0	100–102	100	4	0.6

Maliani (2002b; GH-C 5437) validated the Method GRM 02.01 for the analysis of chlorpyrifos-methyl in kidney, liver, milk, muscle and egg. Samples are extracted with acetone and cleaned-up in a C_{18} SPE. Residues were eluted with ACN:0.1 HCL (90:10) and then extracted with isooctane containing $^{13}C_2$ ^{15}N-chlorpyrifos-methyl as internal standard. Fat samples did not undergo the SPE step. Quantification is done by GC/NCI-MS. A total of 80 samples underwent the validation procedure, with fortification levels at 0.01, 0.05, 0.25 and 0.50 mg/kg. Individual recoveries ranged from 88 to 103%.

Stability of Pesticide Residues in Stored Analytical Samples

Control samples of agricultural commodities were fortified at 0.10 mg/kg with chlorpyrifos-methyl and stored frozen at approximately –20 °C in high density polyethylene (HDPE) containers (Thomas *et al.*, 2002a; GH-C 5410). Samples that had been stored frozen for 99 days and 0 days were analysed on the same date. Unfortified agricultural commodities were placed in similar containers and stored frozen with the fortified samples. In each analytical set, samples were analysed in triplicate along with freshly-fortified controls per matrix. Analyses were conducted according to method GRM 02.4 (LOQ of 0.01 mg/kg). The percent of chlorpyrifos-methyl remaining per matrix are summarized in Table 31.

Table 31 Stability of chlorpyrifos-methyl residues in crops after 90 days of storage

Days of	Chlorpyrifos-methyl (Average % Remaining[a])					
Storage	Oranges	Grapes	Grape wine	Tomatoes	Tomato juice	Wheat grain
0	88	91	89	87	86	99
99	83	80	85	84	83	106

[a] Average of three replicate analyses

Control samples of animal tissues were fortified at 0.10 mg/kg with chlorpyrifos-methyl and stored frozen at approximately –20 °C in HDPE containers (Thomas *et al.*, 2000b; GH-C 5409). Samples that had been stored frozen for 90 days and 0 days were analysed on the same date. Unfortified animal tissues were placed in similar containers and stored frozen with the fortified samples. In each analytical set, samples were analysed in triplicate along with freshly-fortified controls per matrix. Analyses were conducted according method GRM 02.01 (LOQ of 0.01 mg/kg). Results are shown in Table 32.

Table 32 Stability of chlorpyrifos-methyl residue levels in animal products after frozen storage

Days of Storage	Chlorpyrifos-methyl (Average % Remaining; n = 3)					
	Beef muscle	Beef liver	Beef fat	Beef kidney	Dairy milk	Eggs
0	84	91	95	90	95	88
90	78	77	75	78	85	54

A study on stability of chlorpyrifos-methyl on various crops under frozen conditions up to 18 months was submitted (Austin, 2009). Samples were fortified at a concentration of 0.1 mg/kg, stored at –18°C and analysed for chlorpyrifos-methyl. At each time point, the analysis include duplicate fortified samples and two procedural recoveries of chlorpyrifos-methyl fortified at 0.1 mg/kg immediately prior to extraction. Procedural recoveries ranged from 70–120 %. The results of the stability of chlorpyrifos-methyl are shown in Table 33.

Table 33 Stability of chlorpyrifos-methyl residues in crops after 18 months of storage

Matrix	Months	% remaining		Matrix	Months	% remaining	
Apple	0	87	88	Orange peel	0	79	91
	6	84	98		6	85	83
	9	91	84		9	73	77
	12	74	73		12	69	80
	15	113	99		15	82	100
	18	98	97		18	89	91
Peach	0	85	89	Orange pulp	0	87	86
	6	93	95		6	97	99
	9	76	81		9	81	79
	12	72	74		12	77	66
	15	99	103		15	85	76
	18	94	92		18	97	94
Cabbage	0	90	85	Potato	0	84	88
	6	94	94		6	92	98
	9	81	91		9	80	83
	12	81	86		12	81	84
	15	105	106		15	76	81
	18	99	92		18	87	90
Tomato	0	82	83	Wheat straw	0	101	82
	6	88	92		6	110	106
	9	78	79		9	99	94
	12	76	77		12	73	80
	15	94	94		15	80	80
	18	93	85		18	108	101
Grape	0	91	104	Wheat grain	0	95	105
	6	97	100		6	113	109
	9	-	82		9	73	77
	12	68	81		12	77	81
	15	96	104		15	111	105
	18	78	88		18	96	89
Oil seed rape	0	75	87				
	6	93	96				
	9	79	75				
	12	73	79				
	15	104	99				
	18	95	94				

USE PATTERN

Chlorpyrifos-methyl is formulated for use in agricultural crops as a range of different emulsifiable concentrates (EC), including mixtures with various pyrethroid insecticides. Table 34 and 35 list the Good Agricultural Practice (GAP) given on current registered labels that are relevant for this evaluation.

Table 34 Good Agricultural Practices for foliar application of chlorpyrifos-methyl using EC formulation

Crop	Country	Formulation kg ai /L	Application rate per treatment				PHI (days)
			No.	kg ai/hL	Water, L/ha	kg ai/ha	
Orange, lemon	Italy	0.200 [a]	–	0.028–0.04			30
Orange, lemon, clementine, mandarin	Italy	0.225	–	0.056			15
Orange, lemon, mandarin	Spain	0.225	–	0.068–0.09			15
Apple , pear	Italy	0.225	–	0.045–0.088			15
Pear	Italy	0.200 [a]	1–2	0.028–0.06			15
Pome fruit	Greece	0.225	1	0.056	2000–4000		21
Pome fruit	Hungary.	0.400			800–1000	0.76	14
Pome fruit	Poland	0.400	–		500–750	0.6	21
Pome fruit	Spain	0.225		0.068–0.09			15
Pome fruit	Switzerland	0.400		0.048		0.76	21
Stone fruit	Bulgaria	0.400	1–2	0.04–0.05	1000–1500	0.48	14
Stone fruit	Greece	0.225	1–2	0.056	1500–2500		21
Peaches, apricots	Hungary.	0.400			800–1000	0.60	30
Peach	Italy	0.225	–	0.045–0.088			15
Peach	Italy	0.200 [a]	1–2	0.025–0.040			15
Peach, nectarine	Spain	0.225		0.068–0.09			15
Cherries	Hungary	0.400		0.048–0.072	800–1000	0.60	30
Grapes	Chile	0.480	1	0.048–0.058			Po [b].
Grapes	France	0.225	2			0.338	21
Grapes	Hungary	0.400			600–1000	0.52–0.60	30
Grape rootstock	Hungary	0.400			600–1000	0.76	n/a
Grapes	Italy	0.225		0.023–0.045			15
Grapes	Italy	0.200 [a]		0.026–0.030			15
Grapes	Spain	0.225		0.068–0.09			15
Grapes	Spain	0.200 [a]		0.03–0.05			21
Grapes	Switzerland	0.400	1–2			0.76–0.96	–
Strawberries	Italy	0.225		0.068–0.09			15
Strawberries	Spain	0.225		0.068–0.09			5
Potatoes	Italy	0.225		0.33–0.45			15
Potatoes	Italy	0.225				0.34–0.45	15
Potatoes	Italy	0.200 [a]		0.028–0.04			15
Potatoes	Spain	0.225		0.068–0.09			15
Potatoes	Spain	0.200 [a]		0.03–0.05			15
Onions	Hungary	0.400			400–500	0.48	30
Onions	Poland	0.400			200–600	0.36	21
Peppers	Greece	0.225	1–3	0.056–0.06	500–1000		5
Peppers	Italy	0.200 [a]		0.032–0.04			15
Peppers/Egg plants	Italy	0.225				0.34–0.45	15
Peppers	Spain	0.225		0.068–0.09			5
Peppers	Spain	0.200 [a]		0.03–0.05			5
Tomatoes	Greece	0.225	1–3	0.056–0.06	500–1000		5
Tomatoes	Italy	0.200 [a]		0.028–0.04			15
Tomatoes	Italy	0.225				0.34–0.45	15

Crop	Country	Formulation kg ai /L	Application rate per treatment No.	kg ai/hL	Water, L/ha	kg ai/ha	PHI (days)
Tomatoes	Spain	0.225		0.068–0.09			5
Tomatoes	Spain	0.200 [a]		0.03–0.05			5
Cotton	Greece	0.225	1–2		500–800	0.45–0.67	21
Cotton	Spain	0.225		0.068–0.09			15
Cotton	Spain	0.200 [a]		0.03–0.05			21
Maize	Italy	0.225		0.068			15
Maize	Italy	0.200 [a]		0.028–0.04			15
Maize	Spain	0.225		0.068–0.09			15
Sugar beet	Spain	0.200 [a]		0.30–0.05			15
Sugar beet	Poland	0.400			200–600	0.36	30

[a] mixed formulation

[b] Post-harvest

Table 35 Good Agricultural Practices for post-harvest use of chlorpyrifos-methyl EC formulation

Crop	Country	Formulation kg ai L	Application rate g ai/tonne	kg ai/hL	PHI, days
Stored grain (except malting barley & rice)	Australia	0.500	5–10	500 (up to 3 months) 1000 (3–9 months)	–
Grains	Belgium	0.025	2.5	–	120
Cereals	Hungary	0.400	1.6–2.4	–	21
Wheat, barley and maize	Spain	0.224	2.24	224–300	–
Cereals	UK	0.225	4.5	600	90

RESIDUES RESULTING FROM SUPERVISED TRIALS

Four hundred and ninety-two supervised residue trials were conducted with chlorpyrifos-methyl in Europe and one in Chile using EC formulation of chlorpyrifos-methyl. Table 36 summarize the data submitted. Residues of chlorpyrifos-methyl were determined using different methods with LOQ of 0.01 mg/kg, including GRM 02.04 (LC/MS/MS), GRM 05.07 (GC/NCI-MS), GRM 00.10 (CG/FPD) and ERC 93.1 (GC/FPD). LOD were 0.002 or 0.003 mg/kg. Most of the studies were conducted according to GLP. In all trials, concurrent determinations of residues in untreated crops gave residues < LOQ.

Residues of chlorpyrifos-methyl within 25% GAP are underlined and were considered for estimation maximum residue level, HR and STMR. Residues on the crop edible portion (pulp or flesh) were doubled underlined and considered only for estimation of STMR. When residues in samples harvested at a latter stage were higher than what was found at the critical PHI, they will be selected for the estimations.

Table 36 Summary of supervised trials conducted with chlorpyrifos-methyl in Europe

Table	Crop	Number of trials
37	Citrus (orange, mandarin, lemon)	51
38	Pome fruit (apple, pear)	72
39	Stone fruit (apricot, peach, nectarine)	34
40	Cherry	11
41	Grape	63

Table	Crop	Number of trials
42	Strawberry	23
42	Kiwi fruit	4
44	Onion	6
45	Tomato	55
46	Pepper	24
47	Green beans	6
48	Carrot	4
49	Potato	21
50	Sugar beet	4
51	Artichoke	4
52	Barley	12
53	Corn/maize	8
54	Wheat	12
55	Cotton	12
56	Oil seed rape	16
57–60	Animal feed	51

Citrus

A total of 51 trials with lemon, mandarin, clementine and oranges conducted in Italy and Spain during 1991–2006 were submitted. The results of the supervised trials are shown in Table 37.

Table 37 Results of supervised trials conducted with chlorpyrifos-methyl in citrus.

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
Italy, Latina Lazio, 2004	Mandarin, Clementine Comune		2567 2402	2.7	2	W. fruit	21	0.46	GHE-P-11004, CEMS-303E, Rawle, 2005
Italy, Lazio, 2004	Mandarin, Clementine Comune	(0.12)	2427 2362	2.73 2.77	2	W. fruit	< 0 0 5 11 15 21	0.07 2.4 1.0 0.40 0.47 0.38	GHE-P-11004, CEMS-2303A, Rawle, 2005
Italy, Lazio, 2004	Orange, Tarocco	(0.12)	2463 2351	2.8	2	W. fruit Peel Pulp	< 0 0 5 11 15 21 21 21	0.05 1.8 0.37 0.48 0.31 0.20 0.67 0.04	GHE-P-11003, CEMS-2302A, Rawle, 2006

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
Italy, Lazio 2004	Orange, Tarocco		2418 2189	2.8 2.6	2	Peel Pulp W. fruit Individual fruit	21	0.53 < 0.01 0.15 0.03 0.06 0.08 0.08 0.09 0.10 0.11 0.16 0.16 0.18 0.19 0.20	GHE-P-1003, CEMS-2302E, Rawle, 2006
Italy, Lazio, 2004	Orange, Valencia	(0.12)	2266 2384	2.7 2.8	2	W. fruit Peel Pulp	< 0 0 4 10 16 21 21 21	0.18 2.1 0.69 0.44 0.49 0.21 0.66 < 0.002[a]	GHE-P-1003, CEMS-2302F, Rawle, 2006
Italy, Lazio, 2005	Orange, Tarocco		2672 2826	2.7 2.8	2	Peel Pulp W. fruit Individual fruit	22	0.45 < 0.01 0.21 0.04 0.06 0.11 0.12 0.13 0.18 0.19 0.21 0.25 0.27 0.31 0.47	GHE-P-1003, CEMS-2302G, Rawle, 2006
Italy, Sicily, 2005	Orange, Navelina	0.11	2617 2437	2.8 2.6	2	W. fruit	< 0 0 5 9 15 21	0.14 1.7 0.78 0.40 0.32 0.58	GHE-P-11219, 686969D, Old, 2007
Italy Sicily, 2005	Mandarin, Nova	0.11	3420 3430	3.6	2	Peel Pulp W. fruit	21	0.92 < 0.003[a] 0.19	GHE-P-11218, 686953B, Old, 2007
Italy Sicily, 2005	Clementine Monreal	0.11	2995 2983	2.7	2	W. fruit	< 0 0 5 9 15 21	0.06 2.2 0.82 0.58 0.52 0.31	GHE-P-11218, 686953D, Old, 2007
Italy Sicily, 2006	Orange, Tarocco	0.071	2007 2012	1.4	2	W. fruit	< 0 0 5 11	0.07 0.83 0.43 0.27	GHE-P-11544, 690341B, Livingstone,

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
							15 21	0.15 0.16	
Italy Sicily, 2006	Orange, Tarocco	0.071	1972 1985	1.4	2	W. fruit	0 15 21	0.75 0.26 0.21	GHE-P-11544, 690341D, Livingstone,
Italy Sicily, 2006	Mandarin, Monreal	0.071	1981 2006	1.4	2	W. fruit W. fruit W. fruit W. fruit W. fruit Peel Pulp W. fruit Peel Pulp	< 0 0 5 11 15 15 15 21 21 21	0.02 0.94 0.70 0.33 0.23 0.75 < 0.003[a] 0.21 0.62 < 0.003[a]	GHE-P-11545, 690357B, Livingstone, 2008
Italy Sicily, 2006	Mandarin, Nova	0.071	2034 2019	1.4	2	W. fruit W. fruit Peel Pulp W. fruit Peel Pulp	0 14 14 14 20 20 20	0.87 0.18 0.76 0.01 0.11 0.46 0.01	GHE-P-11545, 690357D, Livingstone, 2008
Italy, Sicily, 2006	Orange, Tarocco	0.096	2490 2539	2.4	2	W. fruit	< 0 0 5 9 15 21	0.10 0.96 0.72 0.72 0.89 0.56	GHE-P-11219, 686969F, Old, 2007
Italy, Sicily 2005	Orange, Tarocco	0.11	2893 2996	3.3	2	Peel Pulp W. fruit	21	0.95 < 0.003[a] 0.21	GHE-P-11219, 686969B, Old, 2007
Spain, Cabezotorres 1991	Lemon, Fino	0.090	2860	–	1	W. fruit Peel Pulp	0 7 21 28 0 7 21 28 0 7 21 28	1.6 0.35 0.06 0.04 5.8 1.3 0.24 0.12 < 0.01 < 0.01 < 0.01 < 0.01	GHE-P-2905, R91-74A, Khoshab and Chen, 1993
Spain, Canals, 1991	Mandarin, Clemenule	0.090	3000	–	1	W. fruit Peel Pulp	60 82 130 60 82 130 60 82 130	0.30 0.27 0.29 1.2 1.0 0.92 < 0.01 < 0.01 < 0.01	GHE-P-2906, R91-75A, Khoshab and Chen, 1993

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
Spain, Carcaixent, 1991	Oranges, Navelina	0.090	3750	–	1	W. fruit Peel Pulp	60 90 119 60 90 119 60 90 119	0.07 0.16 0.10 0.33 0.46 0.42 < 0.01 < 0.01 < 0.01	GHE-P-2907, R91-76A, Khoshab and Chen, 1993
Spain, Valencia 1992	Oranges, Navelina	0.09	4800	–	1	W. fruit Peel Pulp	1 25 56 85 112 112 112	0.74 0.16 0.1 0.06 0.11 0.40 < 0.01	GHE-P-3230, R92-21A, Khoshab and Laurie, 1993
Spain, Sevilla 1992	Oranges, Navelino	0.09	3400	–	1	W. fruit Peel Pulp	0 15 30 45 60 60 60	1.2 0.18 0.14 0.11 0.13 0.35 < 0.01	GHE-P-3230, R92-21B, Khoshab and Laurie, 1993
Spain, Sevilla, 1992	Oranges, Salustian	0.09	3400	–	1	W. fruit Peel Pulp	0 30 60 90 120 120 120	1.2 0.26 0.30 0.22 0.20 0.66 < 0.01	GHE-P-3230, R92-21C, Khoshab and Laurie, 1993
Spain, Alhama, 1992	Lemon, Fino	0.09	3000	2.7	1	W. Fruit Peel Pulp	0 25 53 77 100 100 100	0.86 0.04 0.04 0.02 0.02 0.06 < 0.01	GHE-P-3096, R92-19A, Khoshab and Laurie, 1993.
Spain, Picasent, 1992	Mandarin, Clemenules	0.09	3000	–	1	W. fruit Peel Pulp	1 27 56 89 117 117 117	1.2 0.58 0.34 0.22 0.15 0.48 < 0.01	GHE-P-3229, R92-20A, Khoshab and Laurie, 1993
Spain, Picasent, 1992	Mandarin, Hernandina	0.09	3000	–	1	W. fruit Peel Pulp	1 27 56 89 117 117 117	1.4 0.78 0.38 0.37 0.31 1.0 < 0.01	GHE-P-3229, R92-20B, Khoshab and Laurie, 1993
Spain, Librilla, 1993	Mandarin, Nova	0.09	3300	–	1	W. fruit	24	0.36	GHE-P-3630, R93-13A, Khoshab and Berryman, 1994

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
Spain, Picana, 1993	Mandarin, Hernandina	0.090	3000	–	1	W. fruit	22	0.39	GHE-P-3630, R93-13B, Khoshab and Berryman, 1994
Spain, Librilla, 1993	Lemons, Fino	0.090	2600	2.34	1	W. fruit	7	0.70	GHE-P-3631, R93-12A, Khoshab and Berryman, 1994.
Spain, Sevilla, 1993	Oranges, Navelina	0.090	1397	–	1	W. fruit	21	0.15	GHE-P-3632, R93-14A, Khoshab and Berryman, 1994
Spain, Sevilla, 1993	Oranges, Navelina	0.090	3000	–	1	W. fruit	21	0.12	GHE-P-3632, R93-14B, Khoshab and Berryman, 1994
Spain, Sevilla, 1994	Orange, Navelino	0.090	2449	–	1	W. fruit	21	0.06, 0.10, 0.12 (2)	GHE-P-4497, R94-129A, Khoshab, 1995.
Spain, Aznalcazar, 1994	Orange, Navelino	0.090	2361	–	1	W. fruit	21	0.08	GHE-P-4497, R94-129B, Khoshab, 1995
Spain, Librilla, 1994	Lemon, Eureka	0.090	3666	–	1	W. fruit	21	0.15	GHE-P-4495, R94-127A, Khoshab, 1994
Spain, Silla, 1994	Mandarin, Satsuma	0.090	3580	–	1	W. fruit	21	0.04	GHE-P-4496, R94-128A, Khoshab, 1995
Spain, Picasent, 1994	Mandarin, Satsuma	0.090	2667	–	1	W. fruit	21	0.07	GHE-P-4496, R94-128B, Khoshab, 1995
Spain, Alfarp, 1994	Mandarin, Clemenule	0.090	4722	–	1	W. fruit	21	0.17	GHE-P-4496, R94-128C, Khoshab, 1995
Spain, Sevilla, 2004	Orange, Navelina	(0.12)	2313 2283	2.7	2	W. fruit Peel Pulp	< 0 0 5 11 15 21 21 21	0.02 1.5 0.57 0.36 0.26 0.18 0.67 < 0.002[a]	GHE-P-1003, CEMS-2302B, Rawle, 2006
Spain, Almonte, 2004	Orange, Navelate		2320–2417	2.6–2.7	2 2 2 2	W. fruit W. fruit W. fruit W. fruit	56 42 28 70	0.08 0.17 0.25 0.18	GHE-P-11003, CEMS-2302C Rawle, 2006

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
Spain, Sevilla, 2004	Orange, Navelina		2286 2227	2.7 2.6	2	Peel Pulp W. fruit	21	0.50 < 0.01 0.13	GHE-P-1003, CEMS-302D, Rawle, 2006
Spain, Seville, 2004	Mandarin, Clemenule		2279	2.7	2	W. fruit	< 0 0 5 10 15 21	< 0.01 1.4 0.93 0.59 0.69 0.31	GHE-P-11004, CEMS-2303B, Rawle, 2005
Spain, Almonte, 2004	Mandarin, Clemenule	–	2146–2283	2.6	2 2 2 2	W. fruit W. fruit W. fruit W. fruit	70 56 42 28	0.40 0.44 0.25 0.26	GHE-P-11004, CEMS-2303C, Rawle, 2005
Spain, Seville, 2004	Mandarin, Clementina	–-	2251 2319	2.64 2.72	2	Peel Pulp W. fruit Individual Fruit	21	1.2 < 0.01 0.32 0.04 0.05 0.09 0.16 0.23 0.27 0.30 0.34 0.44 0.52 0.59 0.85	GHE-P-11004, CEMS-2303D, Rawle, 2005
Spain, Andalucia, 2005	Mandarin, Clemenule	0.10	3008 2999	3.1	2	W. fruit	21	0.17	GHE-P-11218, 686953A, Old, 2007
Spain, Andalucia, 2005	Mandarin, Loretina	0.10	3015 3007	3.1	2	W. fruit	< 0 0 5 10 15 21	< 0.01 1.5 0.51 0.38 0.26 0.33	GHE-P-11218, 686953C, Old, 2007
Spain Andalucia, 2006	Mandarin, Loretina	0.071	2010 2000	1.4	2	W. fruit W. fruit W. fruit W. fruit W. fruit Peel Pulp W. fruit Peel Pulp	< 0 0 5 10 15 15 15 21 21 21	0.01 1.6 0.28 0.36 0.09 0.44 < 0.003[a] 0.07 0.31 < 0.01	GHE-P-11545, 690357A, Livingstone, 2008
Spain Andalucia, 2006	Mandarin, Clemenule	0.071	1993 2008	1.4	2	W. fruit W. fruit Peel Pulp W. fruit Peel Pulp	0 15 15 15 21 21 21	1.6 0.21 0.84 0.01 0.20 0.79 0.01	GHE-P-11545, 690357C, Livingstone, 2008
Spain, Andalucia, 2005	Orange, Navelina	0.094	2995	2.8	2	W. fruit	21	0.07	GHE-P-11219, 686969A,

Country, Region, year	Crop, Variety	Application				Portion Analysed	PHI (days)	Residue (mg/kg)	Report No., Trial No.,
		kg ai/hL	L/ha	kg ai/ha	No.				
									Old, 2007
Spain, Sevilla, 2005	Orange, Navelina	0.094	3042 3006	3.0	2	W. fruit	< 0 0 5 10 15 21	0.01 0.65 0.35 0.13 0.06 0.11	GHE-P-11219, 686969C, Old, 2007
Spain, Andalucia, 2006	Orange, Lane Late	0.094	3004 3009	2.8	2	W. fruit Peel Pulp	21	0.24 0.94 < 0.01	GHE-P-11219, 686969E, Old, 2007
Spain Andalucia, 2006	Orange, Navelina	0.071	1998 1996	1.4	2	W. fruit	< 0 0 5 10 15 21	0.01 0.73 0.31 0.13 0.11 0.06	GHE-P-11544, 690341A, Livingstone, 2008
Spain Andalucia, 2006	Orange, Navelina	0.071	1988 2007	1.4	2	W. fruit	0 15 21	1.0 0.09 0.02	GHE-P-11544, 690341C, Livingstone, 2008

[a] limit of detection (LOD)

Pome Fruit

A total of 84 trials were conducted in Northern and Southern Europe during 2004–2007. The results of the supervised trials are shown in Table 38.

Table 38 Results of supervised trials conducted with chlorpyrifos methyl in apple and pears

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Austria Wien, 2006	Apples Early Smith	0.10	594 641	0.6	2	Fruit, whole	0 21 28	0.13 0.02 0.01	GHE-P-11526 690142D Livingstone, 2008
Austria Kirchberg-Thening, 2006	Pears Williams Christ	0.10	605 648	0.6	2	Fruit, whole	< 0 0 7 14 21 28	0.01 0.47 0.18 0.05 0.02 < 0.01	GHE-P-11526 690142E Livingstone, 2008
Belgium Nodebais 2004	Pear Conference		1002 1015	0.6	2	Fruit, whole	28	0.04	GHE-P-10998 CEMS-2297E Rawle, 2005
Belgium Molenbaix, Hainaut 2005	Pear Doyenne du Comice	0.12 0.21	521 303	0.6	2	Fruit, whole	28	0.02	GHE-P-11222 687009B Old, 2006
France-North St.Mesmin 1999	Apple Golden	(0.09)	1406 1111	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.01 0.36 0.21 0.1 0.08 0.07	GHE-P-8642 Doran and Craig, 2001

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
France-North Maine et Loire 1999	Apple Golden		609 609	1.0	2	Fruit, whole	21	0.04	GHE-P-8643 Doran and Craig, 2001
France-South Meauzac 1999	Apple Fuji	(0.11)	984 905	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.01 0.19 0.18 0.13 0.04 0.04	GHE-P-8646 Doran and Craig, 2001
France-South Fregimont 1999	Apple Fuji		854 1139	1.0	2	Fruit, whole	21	0.09	GHE-P-8647 Doran and Craig, 2001
France-North De Tourraine 2000	Apple Delbard		837 1141	1.0	2	Fruit, whole	21	0.03, 0.03	GHE-P-9434 000216A Doran and Clements, 2002
France-South Dieupentale 2000	Apple Granny Smith	(0.08)	1201 1364	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.002 0.10 0.05 0.03 0.02 0.01	GHE-P-9551 000218A Doran and Clements, 2002
France-South St.Vicent de Paul 2000	Apple Golden	(0.09)	971 1164	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.002 0.50 0.27 0.33 0.19 0.12	GHE-P-9551 000218B Doran and Clements, 2002
France-South Les Herbonnes 2004	Apple Gala	0.09	1034 1142	– –	2	Fruit, whole	< 0 0 4 10 14 21	< 0.002 0.20 0.18 0.16 0.10 0.10	GHE-P-10995 CEMS-2294B Rawle, 2005
France-South Finhan 2004	Apple Granny Smith	0.09	810–833	– –	2 2 2 2	Fruit, whole Fruit, whole Fruit, whole Fruit, whole	70 56 42 28	< 0.002 < 0.002 < 0.01 < 0.01	GHE-P-10995 CEMS-2294C Rawle, 2005
France-North St Hillaire 2004	Apples Canada		1182 1174	0.6	2	Fruit, whole	< 0 0 7 14 21 28	< 0.002 0.58 0.23 0.10 0.04 0.03	GHE-P-10994 CEMS-2293B Rawle, 2005
France-North Corze 2004	Apples Fuji No. 6		1326 1265	0.6	2 2 2 2	Fruit, whole Fruit, whole Fruit, whole Fruit, whole	70 55 42 36	< 0.002 < 0.002 < 0.01 < 0.01	GHE-P-10994 CEMS-2293C Rawle, 2005
France-North Mezieres les Clery, 2004	Apples Golden		1185 1167	0.6	2	Fruit, whole	28	0.07	GHE-P-10994 CEMS-2293D Rawle, 2005
France-North Martin de la Place 2004	Apples Golden Delicious		1269 1260	0.6	2	Fruit, whole Fruit, whole, individual	28 28	0.04 0.02 (4) 0.03 (3) 0.04 < 0.01 (4)	GHE-P-10994 CEMS-2293E Rawle, 2005

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
France-South Castelsarrasin 2007	Apple Granny Smith	0.09	821 868	– –	2	Fruit, whole	21	0.02	GHE-P-10995 CEMS-2294D Rawle, 2005
France-South Moissac 2004	Pears Guillot	0.09	893 883	(0.72)	2	Fruit, whole	< 0 0 5 10 14 22	< 0.01 1.2 0.16 0.06 0.03 < 0.01	GHE-P-10997 CEMS-2296B Rawle, 2005
France-South Castelsarrasin 2004	Pears Williams	0.09	951– 1049	– –	2 2 2 2	Fruit, whole Fruit, whole Fruit, whole Fruit, whole	70 56 42 28	< 0.002 < 0.002 < 0.002 < 0.002	GHE-P-10997 CEMS-2296C Rawle, 2005
France-South Meauzac 2004	Pears Cornice	0.09	1079 790	– –	2	Fruit, whole Fruit, whole, individual	21 21	0.03 0.01 0.02 (2) < 0.01 (3) 0.03 0.08 (2) 0.09 (2) 0.06	GHE-P-10997 CEMS-2296D Rawle, 2005
France-North Mezieres lez Clery 2004	Pear Passe Crassane		1162 1229	0.6	2	Fruit, whole	< 0 0 7 14 21 28	< 0.002 0.35 0.11 0.04 0.02 0.01	GHE-P-10998 CEMS-2297A Rawle, 2005
France-North Varennes Le Grand 2004	Pear Passe Crassane		1139 1156	0.6	2	Fruit, whole	< 0 0 7 14 21 28	< 0.002 0.69 0.33 0.06 0.07 0.02	GHE-P-10998 CEMS-2297B Rawle, 2005
France-North Montbellet 2004	Pear Conference		1130– 1293	0.6	2 2 2 2	Fruit, whole Fruit, whole Fruit, whole Fruit, whole	70 56 35 42	< 0.002 < 0.002 < 0.01 < 0.01	GHE-P-10998 CEMS-2297C Rawle, 2005
France-South Rhone-Alpes 2005	Apples Golden Delicious	0.09	1000	– –	2	Fruit, whole	21	0.15	GHE-P-11214 686911A Old, 2005
France-South Rhone-Alpes 2005	Apples Golden	0.09	987 997	(0.9)	2	Fruit, whole	< 0 0 5 10 14 21	< 0.003a 0.93 0.17 0.56 0.22 0.07	GHE-P-11214 686911D Old, 2006
France-North Pas De Calais, 2005	Apple Jona Gold	0.12	509 505	0.6	2	Fruit, whole	28	< 0.01	GHE-P-11215 686927A Old, 2006
France-North Pas de Calais, 2005	Apple Elstar	0.12 0.21	523 310	0.6	2	Fruit, whole	28	0.04	GHE-P-11215 686927B Old, 2006
France-North Pas de Calais, 2005	Apple Boskoop	0.12 0.21	486 302	0.6	2	Fruit, whole	< 0 0 8 14 21	< 0.003a 1.3 0.10 0.02 0.05	GHE-P-11215 626927D Old, 2006

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
							28	0.08	
France-South Rhone-Alpes 2005	Pear Williams	0.09	1027 1038	0.9	2	Fruit, whole	21	< 0.003[a]	GHE-P-11221 686995A Old, 2006
France-South Rhone-Alpes 2005	Pear Louise Bonne	0.09	991 992	0.9	2	Fruit, whole	< 0 0 5 10 14 21	< 0.01 0.89 0.34 0.08 0.16 0.01	GHE-P-11221 686995D Old, 2006
France-North Pas de Calais, 2005	Pear Conference	0.12 0.21	486 310	0.6	2	Fruit, whole	< 0 0 8 14 21 28	< 0.003a 2.0 0.23 0.26 0.08 < 0.01	GHE-P-11222 687009C Old, 2006
France-North Pas de Calais, 2005	Pear Doyenne du Comice	0.12 0.21	469 303	0.6	2	Fruit, whole	< 0 0 8 14 21 28	< 0.003a 1.3 0.36 0.05 0.05 0.02	GHE-P-11222 687009D Old, 2006
France-North Pas de Calais, 2006	Apples Jona Gold	0.10	575 601	0.6	2	Fruit, whole	< 0 0 7 13 21 27	< 0.01 0.33 0.09 0.07 0.04 0.02	GHE-P-11526 690142A Livingstone, 2008
France-South Rhone Alpes 2006	Apples Granny- Smith	0.07	1200 1226	0.86 0.88	2	Fruit, whole	< 0 0 5 10 15 21	< 0.003a 0.16 0.09 0.04 0.03 0.02	GHE-P-11527 690158A Livingstone, 2008
France-South Rhone-Alpes 2006	Apples Golden	0.07	1221 1219	0.87	2	Fruit, whole	0 14 21	0.36 0.20 0.06	GHE-P-11527 690158D Livingstone, 2008
France-South Languedoc- Roussillon 2007	Pears Williams	(0.06)	1009	0.6	1	Fruit, whole	0 7 14 21	0.37 0.03 < 0.003[a] < 0.003[a]	GHE-P-11796 CEMS-3490H Devine, 2008
France-South Languedoc- Roussillon 2007	Apples Fuji		1067	0.6	1	Fruit, whole	22	0.03	GHE-P-11796 CEMS-3490A Devine, 2008
France-South Languedoc- Roussillon 2007	Apples Golden	(0.06)	1010	0.6	1	Fruit, whole	0 7 14 21	0.3 0.12 0.07 0.05	GHE-P-11796 CEMS-3490D Devine, 2008
France Rhone-Alpes 2007	Pears Conference		1063	0.6	1	Fruit, whole	21	< 0.01	GHE-P-11796 CEMS-3490E Devine, 2008
Germany Baden- Wurttemberg 1999	Apple Idared	(0.1)	997 1025	1.0	2	Fruit, whole	< 0 0 3 6 14	< 0.01 0.38 0.12 0.08 0.05	GHE-P-8644 Doran and Craig, 2001

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
							21	0.03	
Germany Rheinland-Pfalz 1999	Apples Pinova		1017 1089	1.0	2	Fruit, whole	20	0.03	GHE-P-8645 Doran and Craig, 2001
Germany Saxonia 2000	Apples Boskop	(0.07)	510 1546	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.01 0.93 1.0 0.71 0.56 0.24	GHE-P-9552 000217A Doran. and Clements, 2002
Germany Gotzdorf 2004	Apples Glostar	(0.06)	997 1012	0.6	2	Fruit, whole	< 0 0 7 14 21 29	< 0.002[a] 0.12 0.04 0.02 < 0.01 < 0.01	GHE-P-10994 CEMS-2293A Rawle, 2005
Germany Saxony 2004	Pear Condo		976 1008	0.6	2	Fruit, whole Fruit, whole, individual	29 29	0.02 0.02 0.01 (2) 0.03 < 0.01 (7) 0.07	GHE-P-10998 CEMS-2297D Rawle, 2005
Germany Baden-Wurttemberg, 2005	Apple Jona Gold	0.13 0.06	516 1013	0.6	2	Fruit, whole	< 0 0 6 13 20 28	< 0.003[a] 0.19 0.07 0.02 0.01 < 0.01	GHE-P-11215 686927C Old, 2006
Germany Baden-Wurttemberg 2005	Pear Alexander Lukas	0.22	300	0.6	2	Fruit, whole	28	< 0.01	GHE-P-11222 687009A Old, 2006
Greece Korifi, Imathia 2004	Apple Granny Smith	0.09	1200	0.6	2	Fruit, whole	< 0 0 5 10 14 21	< 0.002[a] 0.64 0.14 0.14 0.19 0.13	GHE-P-10995 CEMS-2294A Rawle, 2005
Greece Imathia 2004	Pears Highland	0.09	1200 1200	– –	2	Fruit, whole	< 0 0 5 10 14 21	< 0.01 1.0 0.69 0.1 0.04 < 0.01	GHE-P-10997 CEMS-2296A Rawle, 2005
Greece Imathia 2005	Apples Mondial Gala	0.09	1200	– –	2	Fruit, whole	< 0 0 5 10 14 21	< 0.003[a] 0.53 0.15 0.09 0.15 0.10	GHE-P-11214 686911C Old, 2005
Greece Imathia, 2005	Pear Williams	0.09	1200	0.9	2	Fruit, whole	< 0 0 5 10 14 21	< 0.003[a] 0.79 0.16 0.02 0.02 < 0.01	GHE-P-11221 686995C Old, 2006

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Italy Emilia-Romagna 1999	Apple Granny Smith	(0.09)	668 716	1.0	2	Fruit, whole	< 0 0 3 7 14 21	< 0.01 0.42 0.08 0.14 0.03 0.03	GHE-P-8648 R99-093 Doran and Craig, 2001
Italy Bologna, 2000	Apples Golden Mutsu		1025 1146	1.0	2	Fruit, whole	21	0.03, 0.04	GHE-P-9436 000051A Doran and Clements, 2001
Italy Verona. 2000	Apples Golden Delicious		780 1179	1.0	2	Fruit, whole	21	0.07, 0.09	GHE-P-9436 000051B Doran and Clements, 2002
Italy Piemonte 2006	Apples Golden	0.07	1168 1279	0.83 0.91	2	Fruit, whole	< 0 0 5 10 14 21	< 0.003[a] 0.58 0.14 0.15 0.08 0.03	GHE-P-11527 690158B Livingstone, 2008
Italy Piemonte 2006	Pears Santa Maria	0.07	1193 1278	0.85 0.91	2	Fruit, whole	< 0 0 5 9 15 22	< 0.003[a] 0.37 0.11 0.06 0.02 < 0.01	GHE-P-11527 690158E Livingstone, 2008
Italy Emilia Romagna 2007	Apples Imperatore	(0.06)	983	0.6	1	Fruit, whole	0 7 14 21	0.17 0.06 0.06 0.02	GHE-P-11796 CEMS-3490C Devine, 2008
Italy Emila Romagna 2007	Pears Abate Fetel	(0.06)	994	0.6	1	Fruit, whole	0 7 14 21	0.31 0.07 0.02 0.01	GHE-P-11796 CEMS-3490G Devine, 2008
Poland Central Poland 2006	Apples Golden Delicious	0.10	598 602	0.6	2	Fruit, whole	< 0 0 7 13 20 26	< 0.003[a] 0.14 0.05 0.03 0.01 0.02	GHE-P-11526 690142B Livingstone, 2008
Poland Gora Kalwaria 2006	Apples Jersey Mac	0.10	597 656	0.6	2	Fruit, whole	0 22 29	0.06 < 0.003[a] < 0.003[a]	GHE-P-11526 690142C Livingstone, 2008
Poland Central Poland 2006	Pears Klaps	0.10	599 638	0.6	2	Fruit, whole	0 20 27	0.39 0.02 < 0.01	GHE-P-11526 690142F Livingstone, 2008
Spain San Pere Pescador 1999	Apples Golden		702 917	1.0	2	Fruit, whole	21	0.07	GHE-P-8649 R99-094A Doran and Craig, 2001
Spain Zaragoza 2004	Apple Reineta	0.09	1178 1190	– –	2	Fruit, whole Fruit, whole, individual	21 21	0.08 0.04	GHE-P-10995 CEMS-2294E Rawle, 2005
Spain Zaragoza 2004	Pears Limonera	0.09	1215 1265	– –	2	Fruit, whole	20	0.01	GHE-P-10997 CEMS-2296E Rawle, 2005

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Spain Catalunya, 2005	Apples Mondial Gala	0.09	997 1001	– –	2	Fruit, whole	20	0.07	GHE-P-11214 686911B Old, 2005
Spain Catalunya 2005	Pear Conference	0.09	1003 1005	0.9	2	Fruit, whole	21	< 0.01	GHE-P-11221 686995B Old, 2006
Spain Arbeca 2006	Apples Golden	0.07	1206 1195	0.86 0.85	2	Fruit, whole	0 15 21	0.16 0.03 0.03	GHE-P-11527 690158C Livingstone, 2008
Spain Lleida 2006	Pears Conference	0.07	1213 1195	0.87 0.85	2	Fruit, whole	0 15 21	0.55 0.08 0.01	GHE-P-11527 690158F Livingstone, 2008
Spain Valencia 2007	Apples Royal Gala		1033	0.6	1	Fruit, whole	21	0.06	GHE-P-11796 CEMS-3490B Devine, 2008
Spain Valencia 2007	Pears Del Terreno		1045	0.6	1	Fruit, whole	21	< 0.003[a]	GHE-P-11796 CEMS-3490F Devine, 2008
United Kingdom Oxon 2000	Apple Golden Delicious		520 570	1.0	2	Fruit, whole	21	0.67, 1.1	GHE-P-9434 000216B Doran and Clements, 2002
United Kingdom Leckford, Hampshire 2000	Apples Cox		505 699	1.0	2	Fruit, whole	0 3 7 14 21	< 0.002[a] 0.57 0.48 0.35 0.18	GHE-P-9552 000217B Doran, A. and Clements, 2002.

[a] limit of detection (LOD)

Apricot and peach

A total of 34 trials were conducted in apricot**s** and peach**es** in Southern Europe during 1992**–**2007. The results of the supervised trials are shown in Table 39.

Table 39 Results of supervised trials conducted with chlorpyrifos methyl in stone fruit

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
France-South Garonne, 2004	Peaches Fidelia	(0.058)	1472 1456	0.82	2	Flesh Fruit, whole	< 0 0 5 10 14 21 < 0 0 5 10 14 21	< 0.002[a] 0.80 0.25 0.06 0.02 < 0.01 < 0.002[a] 0.66 0.22 0.05 0.01 < 0.01	GHE-P-10992 CEMS-2291B Rawle, 2005
France-South Meauzac, 2004	Peaches Fantasia		1481 1607	0.83 0.90	2	Flesh Fruit, whole	28 28	< 0.01 < 0.01	GHE-P-10992 CEMS-2291D Rawle, 2005

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
France, South Moissac 2004	Apricot Hargrand	0.06	1492 1496	0.84	2	Flesh	< 0	< 0.002[a]	GHE-P-10996 CEMS-2295B Rawle, 2005
							0	1.2	
							5	0.06	
							10	0.03	
							14	< 0.01	
							21	< 0.01	
						Fruit, whole	< 0	< 0.002[a]	
							0	1.02	
							5	0.05	
							10	0.03	
							14	< 0.01	
							21	< 0.01	
France, South Montauban 2004	Apricot Florilege	0.06	1499– 1597	0.85 0.84	2	Flesh	70	< 0.002[a]	GHE-P-10996 CEMS-2295C Rawle, 2005
						Fruit, whole	70	< 0.002[a]	
					2	Flesh	56	< 0.002[a]	
						Fruit, whole	56	< 0.002[a]	
					2	Flesh	41	< 0.002[a]	
						Fruit, whole	41	< 0.002[a]	
					2	Flesh	28	< 0.01	
						Fruit, whole	28	< 0.01	
France-South Rhone-Alpes 2005	Apricot Bergeron / FS 240	0.07	1258 1247	0.88	2	Flesh	< 0	< 0.01	GHE-P-11216 686932D Old, 2006
							0	2.4	
							5	0.17	
							10	0.03	
							14	0.02	
							21	< 0.01	
						Fruit, whole	< 0	< 0.01	
							0	2.0	
							5	0.13	
							10	0.02	
							14	0.02	
							21	< 0.01	
France-South Rhone Alpes, 2005	Peaches Rich Lady	0.07	1259 1232	0.88 0.86	2	Flesh	21	< 0.01	GHE-P-11220 686974A Old, 2006
						Fruit, whole	21	< 0.01	
France-South Rhone Alpes 2005	Peaches Sanguine Maguard	0.07	1263 1254	0.88	2	Flesh	< 0	< 0.003[a]	GHE-P-11220 686974D Old, 2006
							0	3.0	
							5	0.35	
							10	0.14	
							14	0.02	
							21	0.01	
						Fruit, whole	< 0	< 0.003[a]	
							0	3.8	
							5	0.42	
							10	0.16	
							14	0.02	
							21	0.01	
France-South Rhone Alpes, 69700 2006	Apricots Bergenow	0.07	1510 1504	1.1	2	Flesh	< 0	< 0.003[a]	GHE-P-11528 690163A Livingstone, 2008
							0	2.2	
							5	0.09	
							10	0.02	
							15	< 0.01	
						Fruit, whole	20	< 0.003[a]	
							< 0	< 0.003[a]	
							0	1.8	
							5	0.08	
							10	0.02	

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
							15 20	< 0.01 < 0.003[a]	
France-South Rhone-Alpes 2006	Peaches Sanguine Magnard	0.07	1501 1516	1.1	2	Flesh Fruit, whole	< 0 0 6 10 15 21 < 0 0 6 10 15 21	< 0.003[a] 0.96 0.24 0.02 < 0.01 < 0.01 < 0.003[a] 0.75 0.20 0.02 < 0.01 < 0.01	GHE-P-11528 690163C Livingstone, 2008
France-South Rhone-Alpes 2006	Peaches Lorrie	0.07	1503 1529	1.1	2	Flesh Fruit, whole	0 17 22 0 17 22	1.1 0.01 < 0.01 0.97 0.01 < 0.01	GHE-P-11528 690163F Livingstone, 2008
Greece Nikolopoulos 1992	Peach Red Gold	0.09	1500	1.35	1	Fruit, whole	0 9 19 29 39	2.0 0.42 0.17 0.02 < 0.01	GHE-P-3089 R92-24 Khoshab and Laurie 1993
Greece Halkidiki 2005	Apricot Bebeko	0.07	1250	0.84	2	Flesh Fruit, whole	< 0 0 5 10 14 21 < 0 0 5 10 14 21	< 0.003[a] 2.4 0.32 0.06 0.01 < 0.01 < 0.003[a] 2.0 0.28 0.06 0.01 < 0.01	GHE-P-11216 686932C Old, 2006
Greece Portaria, Halkidiki 2004	Apricot Bebeko	(0.07)	1250 1250	0.84	2	Flesh Fruit, whole	< 0 0 5 10 14 21 < 0 0 5 10 14 21	< 0.01 3.6 0.9 0.19 0.04 < 0.01 < 0.01 3.1 0.77 0.17 0.04 < 0.01	GHE-P-10996 CEMS-2295A Rawle, 2005
Greece Imathia 2007	Peaches Red Gold	0.068	1500	1.0	1	Flesh Fruit, whole	14 14	< 0.01 < 0.01	GHE-P-11797 CEMS-3491C Devine, 2008
Greece Halkidiki 2007	Apricots Bebeko	0.068	1500	1.0	1	Flesh Fruit, whole	15 15	< 0.003[a] < 0.003[a]	GHE-P-11797 CEMS-3491A Devine, 2008

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Italy Francolino 1992	Peaches Flavor Crest	0.09	1500	1.35	1	Flesh Fruit, whole	0 9 20 30 40 0 9 20 30 40	1.8 0.68 0.18 0.01 < 0.01 1.39 0.52 0.15 < 0.01 < 0.01	GHE-P-3120 R92-23A Khoshab and Laurie, 1993
Italy Buttapietra 1992	Peaches Red Haven	0.09	1500	1.35	1	Flesh Fruit, whole	0 10 20 30 42 0 10 20 30 42	2.0 0.55 0.18 0.03 < 0.01 1.5 0.42 0.14 0.02 < 0.01	GHE-P-3120 R92-23B Khoshab and Laurie, 1993
Italy Viterbo 1993	Peaches Spring Rest	0.09	1500	1.35	1	Flesh Fruit, whole	15 15	0.02 0.02	GHE-P-3722 R93-15A Khoshab and Berryman, 1994
Italy Ferrara. 1993	Peaches Flavor Crest	0.09	1467	1.32	1	Flesh Fruit, whole	15 15	0.04 (2), 0.06, 0.09 0.04 (2), 0.06, 0.08	GHE-P-3722 R93-15B Khoshab and Berryman, 1994
Italy Ferrara 1993	Peaches M3	0.09	1458	1.31	1	Flesh Fruit, whole	15 15	0.03, 0.05, 0.06, 0.07 0.03, 0.05, 0.06, 0.07	GHE-P-3722 R93-15C Khoshab and Berryman, 1994
Italy Ferrara 1993	Peaches Red Haven	0.09	1532	1.38	1	Flesh Fruit, whole	15 15	0.04 (2), 0.05, 0.06, 0.04 (2), 0.05, 0.06,	GHE-P-3722 R93-15D Khoshab and Berryman, 1994
Italy Bologna, 2004	Peaches Elegant Lady	(0.06)	1457 1402	0.82 0.79	2	Flesh Fruit, whole	< 0 0 5 10 14 21 < 0 0 5 10 14 21	< 0.002[a] 0.58 0.20 0.03 0.01 < 0.01 < 0.002[a] 0.49 0.17 0.03 0.01 < 0.01	GHE-P-10992 CEMS-2291A Rawle, 2005
Italy Emilia Romagna 2005	Peaches Royal Glory	0.07	1238 1301	0.87 0.91	2	Flesh	< 0 0 5 10 15 21	< 0.003[a] 1.2 0.25 0.14 0.01 0.01	GHE-P-11220 686974C Old, 2006

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
						Fruit, whole	< 0 0 5 10 15 21	< 0.003[a] 1.0 0.23 0.13 0.01 0.01	
Italy Piemonte 2006	Apricots Bulida	0.07	1534 1489	1.1	2	Flesh Fruit, whole	0 15 22 0 15 22	0.89 < 0.01 < 0.003[a] 0.79 < 0.01 < 0.003[a]	GHE-P-11528 690163B Livingstone, 2008
Italy Piemonte 2006	Peaches Duchessa d'Este	0.07	1453 1478	1.0	2	Flesh Fruit, whole	0 16 22 0 16 22	0.96 0.02 < 0.01 0.81 0.02 < 0.01	GHE-P-11528 690163D Livingstone, 2008
Italy Ferrara 2007	Peaches Cresthaven	0.068	1468	0.99	1	Flesh Fruit, whole	0 5 9 15 0 5 9 15	0.71 0.22 0.07 0.02 0.65 0.21 0.07 0.02	GHE-P-11797 CEMS-3491D Devine, 2008 Residues in controls < 0.01 to 0.2
Spain Sevilla 1992	Peaches Maycrest	0.09	1500	1.35	1	Flesh Fruit, whole	0 7 14 20 28 0 7 14 20 28	4.1 0.89 0.26 0.04 0.01 3.8 0.73 0.23 0.04 < 0.01	GHE-P-3088 R92-22 Khoshab and Laurie, 1992
Spain Calatorao, 2004	Peaches Catherine	(0.06)	1558 1558	0.88	2	Fruit, whole Fruit, whole, individual	20 20	0.03 < 0.002[a] (2), < 0.01 (4), 0.01 (4), 0.02, 0.04	GHE-P-10992 CEMS-2291E Rawle, 2005
Spain Calatorao 2004	Apricot Paviot	0.06	1438 1488	0.81 0.84	2	Flesh Fruit, whole	21 21	< 0.002[a] < 0.002[a]	GHE-P-10996 CEMS-2295E Rawle, 2005
Spain Calatorao 2004	Apricot Paviot	0.06	1529 1465 1488	0.82 0.84 0.86	3	Flesh Flesh, individual Fruit, whole Fruit, whole, individual	20 20 20 20 20	< 0.002[a] < 0.002[a] (12) < 0.002[a] < 0.002[a] (11), < 0.01	GHE-P-10996 CEMS-2295F Rawle, 2005
Spain Catalunya 2005	Apricot Cow / FS 240	0.07	1251 1249	0.88	2	Flesh Fruit, whole	20 20	< 0.01 < 0.01	GHE-P-11216 686932B Old, 2006

Country Region Year	Crop Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Spain Catalunya 2005	Peaches Escola	0.07	1253 1244	0.87	2	Flesh Fruit, whole	21 21	0.02 0.02	GHE-P-11220 686974B Old, 2006
Spain Andalucia, 2006	Peaches Maycrest	0.07	1502 1499	1.1	2	Flesh Fruit, whole	< 0 0 5 10 15 20 15 20	< 0.01 1.4 0.56 0.12 0.02 < 0.01 0.02 < 0.01	GHE-P-11528 690163E Livingstone, 2008
Spain Valencia 2007	Apricots Tadeo	0.068	1475	1.0	1	Flesh Fruit, whole	0 5 11 15 0 5 11 15	0.23 0.06 < 0.01 < 0.003[a] 0.19 0.06 < 0.01 < 0.003[a]	GHE-P-11797 CEMS-3491B Devine, 2008

[a] limit of detection (LOD)

Cherries

A total of 11 trials conducted in Northern and Central Europe during 2006–2007 were submitted. The results of the supervised trials are shown in Table 40.

Table 40 Results of supervised trials conducted with chlorpyrifos methyl in cherries

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		kg ai/hL	L/ha	kg ai/ha	No.				
Austria Oberosterreich 2007	Sweet Regina		642	0.64	1	Flesh Fruit, whole	21 21	< 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492D Marshall, 2008
Austria Oberosterreich 2007	Sour Gerema		656	0.66	1	Flesh Fruit, whole	21 21	< 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492H Marshall, 2008
Germany Brandenburg 2007	Sour Vowi		599	0.6	1	Flesh Fruit, whole	21 21	< 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492E Marshall, 2008
Germany Brandenburg 2007	Sweet Cherry Kordia		629	0.63	1	Flesh Fruit, whole	21 21	< 0.003a < 0.003[a]	GHE-P-11798 CEMS-3492A Marshall, 2008
Hungary Szekesfehervar- Csala, 2006	Sweet Katalin	0.10	587 572	0.62 0.61	2	Flesh Fruit, whole	< 0 0 7 14 21 28 < 0 0 7 14 21 28	< 0.01 1.0 0.04 0.01 < 0.003[a] < 0.003[a] < 0.01 0.45 0.03 < 0.01 < 0.003[a] < 0.003[a]	GHE-P-11529 690179A Livingstone, 2008

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		kg ai/hL	L/ha	kg ai/ha	No.				
Hungary Szekesfehervar-Csala, 2006	Sour Ciganymeggy	0.10	617 583	0.65 0.62	2	Flesh Fruit, whole	< 0 0 7 14 21 28 < 0 0 7 14 21 28	0.14 9.2 0.08 0.02 < 0.01 < 0.01 0.03 2.4 0.03 < 0.01 < 0.01 < 0.01	GHE-P-11529 690179C Livingstone, 2008
Hungary Fejer 2007	Sweet Valentine		576	0.58	1	Flesh Fruit, whole	0 5 10 15 21 0 5 10 15 21	3.09 0.03 < 0.01 < 0.003[a] < 0.003[a] 2.2 0.03 < 0.01 < 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492C Marshall, 2008
Poland (Central Poland) 2006	Sour Lutowka	0.10	610 611	0.65	2	Flesh Fruit, whole	0 22 29 0 22 29	0.74 < 0.003[a] < 0.003[a] 0.31 < 0.003[a] < 0.003[a]	GHE-P-11529 690179D Livingstone, 2008
Poland Wielkopolska 2007	Sweet Cherry Schneidera Pozna		302	0.18	1	Flesh Fruit, whole	0 5 10 15 21 0 5 10 15 21	0.96 0.09 < 0.01 < 0.003[a] < 0.003[a] 0.8 0.08 < 0.01 < 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492B Marshall, 2008
Poland Wielkopolska 2007	Sour Lutowka		475	0.44	1	Flesh Fruit, whole Juice Fruit, canned	0 5 10 14 21 0 5 10 14 21 21 21	1.0 0.03 < 0.003[a] < 0.003[a] < 0.003[a] 0.79 0.03 < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11798 CEMS-3492F Marshall, 2008
Poland Wielkopolska 2007	Sour Lutowka		425	0.29	1	Flesh Fruit, whole	0 5 10 14 21 0 5	0.75 0.03 < 0.003[a] < 0.003[a] < 0.01 0.57 0.02	GHE-P-11798 CEMS-3492I Marshall, 2008

Country Region Year	Variety	Application kg ai/hL	L/ha	kg ai/ha	No.	Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
							10 14 21	< 0.003[a] < 0.003[a] < 0.01	

[a] limit of detection (LOD)

Grapes

A total of 63 trials conducted in Northern and Southern Europe during 1998–2007 were submitted. The results of the supervised trials are shown in Table 41.

Table 41 Results of supervised trials conducted with chlorpyrifos methyl in grapes

Country Region, Year	Crop Variety	Application kg ai/hL	L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
Austria Gross 2006	Red table Nelly	0.068	955 1023	0.64 0.69	2	< 0 0 5 10 14 21	< 0.003a 0.34 0.04 0.03 0.03 0.03	GHE-P-11538 690273D Livingstone, 2008
Austria Gemeinlebarn, 2006	White wine Gruner Veltliner	0.07	1034 933	0.7 0.63	2	< 0 0 5 10 15 21	< 0.003a 0.89 0.25 0.06 0.07 0.02	GHE-P-11538 690273A Livingstone, 2008
Austria Oberosterreich 2007	White wine Chardonnay		519 511	0.35	2	21	< 0.01	GHE-P-11803 CEMS-3497C Devine, 2008
Chile VI Region 1998	Red Table Red Globe	0.065	2000 2000	1.3	2	0 18 38 58 86	6.8 < 0.01 < 0.001 < 0.001 < 0.001	GHB-P-421 LARP G023 Amaral et al , 1999
France-North Amboise 1995	Wine, COT		190	0.45	1	0 7 14 22 28	0.90 0.25 0.04 0.04 0.04	GHE-P-4944 R95-003A Teasdale, 1996
France, Southern Fronton 1995	Wine, Negrete		182	0.45	1	0 7 14 21 27	0.22 0.07 0.01 < 0.01 < 0.01	GHE-P-4944 R95-003B
France-North Indre et Loire 1999	White Wine Chenin/504 Clone 624		200	0.68	2	< 0 0 7 14 21 28	< 0.01 0.69 0.12 0.06 0.05 0.02	GHE-P-8650 R99-095 Doran and Craig, 2001
France-North Indre et Loire, 1999	White Wine Riparia Gloire		216	0.68	2	28	0.02	GHE-P-8651 R99-096A Doran and Craig, 2001

Country Region, Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
France-South Tarn-et-Garonne 1999	White Table Chasselas	0.075	956 880	0.72 0.66	2	< 0 0 7 14 21 28	< 0.002a 4.6 0.20 < 0.01 < 0.01 < 0.002a	GHE-P-8654 R99-099 Doran and Craig, 2001
France-South Tarn-et-Garonne. 1999	Red Wine Grape Syrah		760 944	0.72 0.655	2	28	0.01	GHE-P-8655 R99-100 Doran and Craig, 2001
France Loire 2000	White Wine Chenin		800	0.7	2	21	0.06, 0.08	GHE-P-9437 000219A Doran and Clements, 2002
France Beaumont En Veron 2000	Red Wine Cabernet Franc		800	0.7	2	22	0.04, 0.06	GHE-P-9437 000219B Doran and Clements, 2002
France-South Vincent de Paul 2000	Red Wine Cabernet Sauvignon		507–530	0.7	2	21	< 0.01 (2)	GHE-P-9441 000221A Doran and Clements, 2002
France Moissac, 2004	White table Chasselas	0.068	828 811	(0.56)	2	21	< 0.01	GHE-P-10999 CEMS-2298C Rawle, 2005
France-South Labastide du Temple 2004	Muscat	0.068	806 833	(0.54)	2	21	0.11	GHE-P-11000 CEMS-2299C Rawle, 2005
France-North Montgueret 2004	White Wine Chenin		880 1074	0.66 0.69	2	< 0 0 3 7 14 21	< 0.002a 0.50 0.12 0.02 0.01 < 0.01	GHE-P-11001 CEMS-2300B Rawle, 2006
France-North Mauze-Thouarsais 2004	White Wine Chenin	(0.81)	836 830	0.67	2	21	0.01	GHE-P-11001 CEMS-2300C Rawle, 2006
France Bouloc 2004	Red Wine Gamay		803 810	0.54	2	21	< 0.01	GHE-P-11002 CEMS-2301C Rawle, 2006
France-South Champagne Ardenne 2005	White Wine Meunier	0.07	503 510	0.36	2	21	< 0.01	GHE-P-11227 687061 A Old, 2006
France-North Champagne-Ardenne 2005	White Wine Chardonnay	0.07	498 515	0.35 0.37	2	< 0 0 4 7 14 21	< 0.003a 0.21 0.02 0.01 < 0.01 < 0.003a	GHE-P-11227 687061 C Old, 2006
France-South Rhone Alpes 2005	Red Wine Gamay	0.07	1164 1219	0.82 0.86	2	21	< 0.01	GHE-P-11228 687077A Old, 2006
France-South Cote d'Azur 2005	Red Table Alphonse Lavallee	0.07	1252 1246	0.88	2	21	0.02	GHE-P-11224 687035A Old, 2006
France-South Cote d'Azur 2005	White table Italia	0.07	1243 1231	0.87 0.86	2	21	0.02	GHE-P-11224 687035C Old, 2006

Country Region, Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
France-South Cote d'Azur 2006	White table Danlas	0.07	1002 979	0.7	2	< 0 0 6 10 14 21	< 0.003a 1.3 0.1 0.08 0.07 0.01	GHE-P-11539 690289A Livingstone, 2008
France Alsace 2007	White wine Pinot Auxerrois		521 487	0.36 0.33	2	21	0.03	GHE-P-11803 CEMS-3497E Devine, 2008
France-North Alsace 2007	Red wine Pinot Noir		522 505	0.36 0.34	2	< 0 0 7 14 21	< 0.01 0.22 0.05 0.03 0.01	GHE-P-11803 CEMS-3497G Devine, 2008
France Languedoc-Rousillon 2007	White wine Maccabau		478 500	0.33 0.34	2	21	< 0.003a	GHE-P-11803 CEMS-3497J Devine, 2008
Germany Baden-Wurttemberg 1999	White Wine Reisling	(0.08)	623 768	0.68 0.63	2	< 0 0 7 15 21 29	< 0.002a 0.5 0.09 0.02 < 0.01 < 0.01	GHE-P-8652 R99-097 Doran and Craig, 2001
Germany Baden-Wurttemberg 1999	White Wine Muller-Thurgau		577 808	0.63 0.67	2	30	0.01	GHE-P-8653 R99-098 Doran and Craig, 2001
Germany Baden-Wurttemberg 2000	White Wine Riesling	(0.08)	601 733	0.68 0.62	2	< 0 0 3 7 14 21	< 0.002a 1.6 0.41 0.29 0.23 0.12	GHE-P-9430 000220A Doran and Clements, 2000
Germany Baden-Wurttemberg 2000	White Wine Riesling	(0.08)	550 869	0.62 0.73	2	< 0 0 3 6 13 20	< 0.002a 1.7 0.44 0.29 0.19 0.14	GHE-P-9430 000220B Doran and Clements, 2000
Germany Baden Wurtenberg 2004	White Wine Schwarz-Riesling	(0.056)	809 1192	0.68 0.67	2	< 0 0 3 7 14 21	< 0.002a 1.2 0.16 0.06 0.06 0.03	GHE-P-11001 CEMS-2300A Rawle, 2006
Germany Baden Wurttemberg 2004	White Wine RIESLING		841 1190	0.71 0.7	2	21	0.22	GHE-P-11001 CEMS-2300D Rawle, 2006
Germany Baden-Wurttemburg 2005	White Wine Riesling	0.04 0.02	911 1625	0.33 0.36	2	20	0.02	GHE-P-11227 687061B Old, 2006
Germany Baden-Wuttemberg 2005	White Wine Muller-Thurgau	0.04 0.02	796 1577	0.35	2	< 0 0 3 7 14 21	< 0.003a 0.24 0.06 0.02 < 0.01 < 0.01	GHE-P-11227 687061 D Old, 2006

Country Region, Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
Germany Brandenburg 2007	Red wine Dornfelder		545 535	0.37 0.36	2	< 0 0 7 14 20	< 0.003a 0.67 0.05 0.01 < 0.01	GHE-P-11803 CEMS-3497D Devine, 2008
Germany Baden-Wurtemberg 2007	Red wine Schwarzriesling		469 491	0.32 0.33	2	20	0.02	GHE-P-11803 CEMS-3497F Devine, 2008
Germany Baden-Wurttemberg 2007	White wine Muller-Thurgau		516 503	0.35 0.34	2	< 0 0 8 14 20	< 0.01 0.36 0.09 0.03 0.02	GHE-P-11803 CEMS-3497H Devine, 2008
Greece Nea Plagia, Halkidiki 2000	White Wine Grape Roditis		1000	0.68	2	< 0 0 3 7 14 21	< 0.002a 0.82 0.14 0.09 0.01 0.03	GHE-P-9446 000222A Doran and Clements, 2002.
Greece Thessaloniki. 2000	Red Wine Muscat de Hamburg	(0.07)	1000	0.68	2	< 0 0 3 7 14 21	< 0.002a 1.7 0.39 0.16 0.07 0.05	GHE-P-9446 000222B Doran and Clements, 2002
Greece Thessaloniki 2004	Red Wine Cabernet Sauvignon		1000	0.68	2	21	< 0.002a	GHE-P-11002 CEMS-2301D Rawle, 2006
Greece Thessaloniki 2005	Red Wine Merlot	0.07	1000	0.68	2	22	< 0.003a	GHE-P-11228 697077B Old, 2006
Greece Thessaloniki 2007	Red wine Cabernet Sauvignon		500 500	0.34	2	21	< 0.003a	GHE-P-11803 CEMS-3497I Devine, 2008
Hungary Csiribpuszta, 2006	White wine Zoldveltelini	0.07	930 1028	0.66 0.73	2	< 0 0 5 10 14 21	< 0.003a 0.73 0.21 0.07 0.11 0.09	GHE-P-11538 690273B Livingstone, 2008
Hungary Pazmand, 2006	Red wine grape Zweigelt	0.07	913 960	0.65 0.68	2	0 14	1.4 0.08	GHE-P-11538 690273C Livingstone, 2008
Hungary Fejer 2007	White wine Ezerfurtu		473 465	0.32	2	< 0 0 7 14 21	0.02 0.58 0.06 0.02 0.01	GHE-P-11803 CEMS-3497A Devine, 2008
Italy, North Emilia-Romagna 1999	Grape Trebbiano		885 1029	0.67 0.7	2	28	0.03	GHE-P-8657 R99-102A Doran and Craig, 2001
Italy Emilia Romagna 2003	White Wine Malvasia	0.028	1000	0.28	2	21	< 0.01 (2)	GHE-P-10487 682854A Wardman, 2004
Italy Castel san Pietro 2004	Red Wine Barbera	(0.069)	770 816	0.52 0.55	2	< 0 0 3	< 0.002a 0.1 0.06	GHE-P-11002 CEMS-2301B Rawle, 2006

Country Region, Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
						7 15 21	0.02 < 0.01 < 0.01	
Italy Lombardia 2005	Red Wine Barbora	0.07	1271 1198	0.89 0.84	2	< 0 0 3 7 15 21	< 0.003a 0.26 0.16 0.05 < 0.003a 0.12	GHE-P-11228 687077D Old, 2006
Italy, North Emilia Romagna, 2006	Red table Moscato D'Adda	0.07	1035 971	0.74 0.69	2	0 13 21	0.38 0.01 < 0.003a	GHE-P-11539 690289D Livingstone, 2008.
Italy Bologna 2007	Red wine Sangiovese	(0.07)	498 508	0.340 0.347	2	< 0 0 7 14 21	< 0.003a 0.01 < 0.01 < 0.003a < 0.003a	GHE-P-11803 CEMS-3497L Devine, 2008
Poland Wielkopolska 2007	Red wine Seil Cascade		513 519	0.35	2	21	0.04	GHE-P-11803 CEMS-3497B Devine, 2008
Spain Provincia de Gerona 1999	Red wine Carignan	(0.068)	830 989	0.68	2	< 0 0 7 14 21 28	< 0.002a 0.36 0.02 < 0.01 < 0.01 < 0.01	GHE-P-8656 R99-101A Doran and Craig, 2001
Spain Sanlucar de Barrameda 2000	White Wine Palomino		607- 815	0.7	2	21	< 0.01 (2)	GHE-P-9441 000221B Doran and Clements, 2002
Spain Los Palacios y Villafranca 2004	Michael de Palieri	0.068	761 752		2	< 0 0 5 10 14 21	< 0.002a 0.1 0.03 < 0.002a < 0.002a < 0.002a	GHE-P-11000 CEMS-2299A Rawle, 2005
Spain Los Palacios y Villafranca 2004	Autumn Black	0.068	778– 822		2 2 2 2	70 56 42 28	< 0.002a < 0.002a < 0.002a < 0.002a	GHE-P-11000 CEMS-2299B Rawle, 2005
Spain Calatorao 2004	Red Wine Garnacha	(0.07)	802 1230	0.54 0.83	2	< 0 0 3 7 14 21	< 0.002a 3.4 2.2 0.54 0.53 0.20	GHE-P-11002 CEMS-2301A Rawle, 2006
Spain Dos Hermanas 2004	White table Matilde	0.07	774 824		2	< 0 0 5 10 14 21	< 0.002a 1.1 < 0.01 < 0.01 < 0.01 < 0.002a	GHE-P-10999 CEMS-2298A Rawle, 2005
Spain Dos Hermanas 2004	White table Regina	0.07	752– 822		2 2 2 2	70 56 42 28	< 0.002a < 0.002a < 0.002a < 0.002a	GHE-P-10999 CEMS-2298B Rawle, 2005

Country Region, Year	Crop Variety	Application kg ai/hL	L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
Spain Andalucia 2005	Red Table Shelva	0.07	1251 1254	0.88	2	< 0 0 5 9 14 21	< 0.003a 1.2 0.01 < 0.01 < 0.003a < 0.003a	GHE-P-11224 687035B Old, 2006
Spain Andalucia 2005	White table Airen	0.07	1250 1241	0.88 0.87	2	< 0 0 5 10 14 21	< 0.003a 0.29 < 0.003a < 0.003a < 0.003a < 0.003a	GHE-P-11224 687035D Old, 2006
Spain Andalucia 2006	White table Matilde	0.07	993 996	0.71	2	< 0 0 4 10 14 21	< 0.003a 0.71 0.13 0.04 < 0.003a < 0.003a	GHE-P-11539 690289B Livingstone, 2008
Spain Andalucia 2006	Red table Shelm	0.07	997 912	0.71 0.65	2	0 14 20	0.69 < 0.01 0.05	GHE-P-11539 690289C Livingstone, 2008
Spain Valencia 2007	White wine Macabeo	(0.07)	496 521	0.34 0.36	2	< 0 0 7 15 22	< 0.003a 2.7 0.26 0.03 0.04	GHE-P-11803 CEMS-3497K Devine, 2008

[a] limit of detection (LOD)

Strawberries

A total of 23 trials conducted in Northern and Southern Europe during 1999–2007 were submitted. The results are shown in Table 42.

Table 42 Results of supervised trials conducted with chlorpyrifos methyl in strawberries

Country Region Year	Variety	Application kg ai/hL	L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
Austria Oberosterreich 2007	Elsanta	(0.07)	803	0.54	1	5	0.03	GHE-P-11804 CEMS-3498M Devine, 2008
France south Rhone-Alpes, 2006	Elsanta	(0.07)	752 834	0.54 0.6	2	< 0 0 1 3 5 7	< 0.01 0.5 0.16 0.01 0.02 < 0.003[a]	GHE-P-11540 690294A Livingstone, 2008
France north Pas de Calais 2006	Darselect	(0.07)	796 845	0.57 0.6	2	0 5 8	0.53 0.02 < 0.01	GHE-P-11541 690315B Livingstone, 2008
France south Montesquieu 2007	Mara de Bori	(0.07)	807	0.54	1	5	0.02	GHE-P-11804 CEMS-3498A Devine, 2008
France south Pyrenees 2007	Mara de Bois	(0.07)	807	0.54	1	0 1 3 5	0.27 0.05 0.03 < 0.01	GHE-P-11804 CEMS-3498E Devine, 2008

Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
France north Bretagne 2007	Charlotte	(0.07)	733	0.50	1	5	0.05	N238 GHE-P-11804 CEMS-3498I Devine, 2008
Germany Saxony 2006	Elsanta	(0.07)	861 828	0.6	2	< 0 0 1 3 5 7	< 0.01 0.46 0.17 0.07 0.03 0.01	GHE-P-11541 690315C Livingstone, 2008
Germany Baden- Wurttemberg 2007	Elsanta	(0.07)	831	0.56	1	0 1 3 5	0.07 0.08 0.04 0.02	GHE-P-11804 CEMS-3498L Devine, 2008
Germany Brandenburg 2007	Madeleine	(0.07)	803	0.54	1	5	< 0.01	GHE-P-11804 CEMS-3498N Devine, 2008
Hungary Fejer 2007	Elsanta/fertodi 5	(0.07)	793	0.54	1	0 1 3 5	0.41 0.15 0.02 0.01	GHE-P-11804 CEMS-3498O Devine, 2008.
Italy Ferrara 2007	Arosa	(0.07)	797	0.54	1	0 1 3 5	0.27 0.05 0.03 < 0.01	GHE-P-11804 CEMS-3498G Devine, 2008
Italy Matera 2007	Camarosa	(0.07)	830	0.52	1	0 1 3 5	0.42 0.12 0.07 0.02	GHE-P-11804 CEMS-3498F Devine, 2008
Italy Forli-Cesena 2007	Marmolada	(0.07)	820	0.56	1	5	< 0.01	GHE-P-11804 CEMS-3498B Devine, 2008
Italy Veneto 2006	Onda	(0.07)	813 828	0.58 0.59	2	0 5 7	0.97 0.04 0.03	GHE-P-11540 690294C Livingstone, 2008
Netherlands 2007	Elsanta	(0.07)	863	0.584	1	5	0.05	GHE-P-11804 CEMS-3498J Devine, 2008
Poland Zakroczym 2006	Honey	(0.07)	814 779	0.58 0.56	2	0 5 7	0.71 0.02 0.01	GHE-P-11541 690315D Livingstone, 2008
Poland Wielkopolska 2007	Elicat	(0.07)	848	0.57	1	0 1 3 5	0.21 0.05 0.02 < 0.003[a]	GHE-P-11804 CEMS-3498P Devine, 2008
Spain Andalucia 2006	Camarosa	(0.07)	806 800	0.57	2	< 0 0 1 3 5 7	< 0.01 0.83 0.20 0.03 0.01 < 0.01	GHE-P-11540 690294B Livingstone, 2008
Spain Valencia 2007	Pajaru	(0.07)	796	0.54	1	0 1 3 5	1.0 0.13 0.08 0.02	GHE-P-11804 CEMS-3498H Devine, 2008
Spain Valencia	Camarosa	(0.07)	796	0.54	1	5	< 0.003[a]	GHE-P-11804 CEMS-3498C

Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
2007								Devine, 2008
Spain Valencia 2007	Camarosa	(0.07)	828	0.56	1	5	0.01	GHE-P-11804 CEMS-3498D Devine, 2008
United Kingdom Colchester 2006	Elsanta	(0.07)	805 803	0.57	2	< 0 0 1 3 5 7	< 0.01 0.97 0.67 0.03 0.01 < 0.01	GHE-P-11541 690315A Livingstone, 2008
United Kingdom 2007	Elsanta	(0.07)	822	0.565	1	0 1 3 5	0.2 0.12 0.02 0.02	GHE-P-11804 CEMS-3498K Devine, 2008

[a] limit of detection (LOD)

Kiwi Fruit

A total of four trials conducted in Italy during 2007 are included in this submission (Table 43).

Table 43 Results of supervised trials conducted with chlorpyrifos methyl in kiwi (var Hayward) in Italy in 2007 (Report No. 20075010/I1-FPKI; Miserocchi, 2007)

Region,	Application				PHI (days)	Residue (mg/kg)	Trial No.,
	kg ai/hL	L/ha	kg ai/ha	No			
Emilia	0.049	997 1013	0.48 0.49	2	0 1 7 15 21	0.51 0.25 0.11 0.07 < 0.003[a]	I071032R
Emilia	0.049	983 995	0.48	2	0 1 7 15 21	0.72 0.50 0.22 0.13 < 0.003[a]	I071033R,
Bari	0.049	998 999	0.48 0.49	2	0 1 7 15 21	0.97 0.76 0.60 0.30 < 0.003[a]	I071034R
Puglia	0.049	1002 992	0.49 0.48	2	0 1 7 15 21	0.81 0.81 0.23 0.25 < 0.003[a]	I071035R

[a] limit of detection (LOD)

Onions

A total of 6 trials conducted in Northern and Southern Europe during 1999–2000 were submitted. The results are shown in Table 44.

Table 44 Results of supervised trials conducted with chlorpyrifos methyl in onion

Country Region, Year	Variety	Application kg ai/hl.	L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No. Trial No., Author(s)
France Lambesc 2000	Dore de Parme	– –	840 833	0.52	2	< 0 0 2 3	< 0.002[a] 0.23 0.02 0.03	GHE-P-10013 000200A Doran. and Clements, 2000
Greece Thessaloniki 2000	Aldobo	– –	600	0.50	2	3	0.05 (2), 0.02, 0.04 , 0.06	GHE-P-9447 000199A Doran and Clements, 2002
Greece Thessaloniki 2000	Sonic F1	– –	610 597	0.50	2	3	0.02, 0.04	GHE-P-9447 000199B Doran and Clements, 2002
Hungary Szolnokmegye 1999	Stuttgarti	– –	490 477	0.49 0.48	2	< 0 0 3 7 14 22	< 0.002[a] 0.12 < 0.01 < 0.01 < 0.002[a] < 0.002[a]	GHE-P-8670 R99-170A Doran and Craig, 2001
Hungary Szolnokmegye 1999	Stuttgarti	– –	508 503	0.50	2	22	< 0.002[a]	GHE-P-8671 R99-171A Doran and Craig, 2001
Spain Barriada El Gordillo 2000	Tardia de Lerida	– –	538 633	0.48	2	< 0 0 2 3	< 0.002[a] 0.57 0.08 0.05	GHE-P-10013 000200B Doran. and Clements, 2000

[a] limit of detection (LOD)

Tomatoes

A total of 61 trials conducted in Northern and Southern Europe during 1999–2007 in tomato**es** were submitted. The results are shown in Table 45.

Table 45 Results of supervised trials conducted with chlorpyrifos methyl in tomatoes

Country Region Year	Variety	Application kg ai/hL	L/ha	kg ai/ha	No.	Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
Czech Republic Tvrdonice 2006	Protected Boreal	0.07	810 815	0.55	2	Tomato	0 5 7	0.28 0.16 0.13	GHE-P-11543 690336B Livingstone, 2008
France, South Noves 2000	Stampa	(0.15)	293 584 786	1.2	3	Tomato	< 0 0 2 3 5	< 0.002[a] 0.18 0.09 0.09 0.02	GHE-P-9557 000202A Doran and Craig, 2002
France, South Montauban 2004	Brenda	0.07	1202 1198		2	Tomato	< 0 0 1 3 4 7	< 0.002[a] 0.71 0.47 0.30 0.20 0.42	GHE-P-10988 CEMS-2287B Rawle, 2005
France, South Orgueil 2004	Brenda	0.07	1204–1272		2 2 2 2	Tomato Tomato Tomato Tomato	35 28 21 14	0.02 0.08 0.08 0.07	GHE-P-10988 CEMS-2287C Rawle, 2005
France, South Limas 2005	Cherry Sweet Million	0.07	834 1211				< 0 0 1	< 0.002[a] 0.82 0.82	GHE-P-10989 CEMS-2288 Rawle, 2005

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
							3 5 7	0.28 0.20 0.14	
France, South Cote d'Azur 2005	Protected Roma	0.07	1031 1053	0.72–0.74	2	Tomato	< 0 0 1 3 5 8	0.03 0.30 0.39 0.18 0.20 0.12	GHE-P-11225 687040D Old, 2008
France, South Rhone Alps 2006	Protected Felicia	0.07	1046 1020	0.72–0.73	2	Tomato	< 0 0 1 3 5 8	< 0.003[a] 0.48 0.23 0.39 0.13 0.11	GHE-P-11225 687040E Old, 2008
France, Nord Baisieux, 2006	Brentyla HFI	0.07	791 816	0.56–0.58	2	Tomato	0 5 7	0.16 0.09 0.10	GHE-P-11542 690320D Livingstone, 2008
France-South Languedoc- Roussillon 2007	Marbonne		983	0.670	1	Tomato	5	0.06	GHE-P-11805 CEMS-3499B Marshall, 2008
France Languedoc- Roussillon 2007	Protected Ondina		1005	0.68	1	Tomato	5	0.03	GHE-P-11805 CEMS-3499E Marshall, 2008
France, North Bretagne 2007	Protected Brazil		1014	0.7	1	Tomato	5	0.08	GHE-P-11805 CEMS-3499H Marshall, 2008
Netherlands Klazienaveen, 2007	Protected Claree		969	0.66	1	Tomato	0 1 3 5	0.25 0.08 0.11 0.09	GHE-P-11805 CEMS-3499K Marshall, 2008
Germany Saxony 2006	Protected Strya	0.07	800	0.57	2	Tomato	< 0 0 1 3 5 7	0.04 0.25 0.14 0.08 0.03 0.02	GHE-P-11543 690336A Livingstone, 2008
Germany Baden- Wurttemberg 2007	Protected Loretto		1017	0.7	1	Tomato	5	0.22	GHE-P-11805 CEMS-3499I Marshall, 2008
Germany Brandenburg 2007	Protected Vanessa		1090	0.7	1	Tomato	5	0.13	GHE-P-11805 CEMS-3499M Marshall, 2008
Greece Thessaloniki 1999	Cherry Supersweet		1250 1215 1245	1.2	3	Tomato	< 0 0 2 3 5	< 0.01 1.3 0.71 0.59 0.31	GHE-P-8660 R99-105A Doran and Craig, 2001
Greece Chalkidiki 2004	Galli F1	0.067	1000		2	Tomato	< 0 0 1 3 5 7	< 0.002[a] 0.08 0.11 0.03 0.02 0.03	GHE-P-10993 CEMS-2292A Rawle, 2005

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
Greece Thessaloniki 2005	Roma	0.067	1000	0.68	2	Tomato	< 0 0 1 3 5 7	< 0.003[a] 0.13 0.11 0.04 0.03 < 0.01	GHE-P-11226 687056C Old, 2006
Greece Thessaloniki 2007	Bobcat		1006	0.68	1	Tomato	5	0.06	GHE-P-11805 CEMS-3499A Marshall, 2008
Hungary Bacs-Kiskun 2007	Protected CarfuF1		1360	1.2	1	Tomato	0 1 3 5	0.43 0.23 0.19 0.20	GHE-P-11805 CEMS-3499N Marshall, 2008
Italy Emilia Romagna 1999	Redceter	(0.24)	502 503 505	1.2	3	Tomato	3	0.24	GHE-P-8661 R99-106A Teasdale, 2000
Italy Bagnarola di Budrio, Bologna 1999	Donador	(0.09)	1084 1290 1272	1.2	3	Tomato	< 0 0 2 3 5	< 0.01 0.54 0.20 0.12 0.07	GHE-P-8664 R99-109A Doran and Craig, 2001
Italy Bologna 1999	Fedra	(0.048)	1980 2000 2578	1.2	3	Tomato	3 5	0.34 0.10	GHE-P-8665 R99-110A Doran and Craig, 2001
Italy S.Felice Circeo 2000	Calida	(0.17)	685 647 681	1.1–1.2	3	Tomato	< 0 0 2 3 5	< 0.002[a] 0.26 0.09 0.05 0.08	GHE-P-9557 000202B Doran and Craig, 2002
Italy Lombardia 2003	Montego	0.04	– –	0.42	2	Tomato	21	< 0.01	GHE-P-10492 682917A Wardman, 2004
Italy Lombardia 2003	Montego	0.04	– –	0.42	2	Tomato	21	< 0.002[a]	GHE-P-10492 682917A Wardman, 2004
Italy Castenaso 2004	Aden	0.067	753 757		2	Tomato	< 0 0 1 3 6 7	0.07 0.24 0.13 0.07 0.05 0.04	GHE-P-10988 CEMS-2287A Rawle, 2005
Italy Bologna 2004	Arletta	0.067	1107 1238		2	Tomato	7	0.22	GHE-P-10988 CEMS-2287E Rawle, 2005
Italy Bologna 2004	Podium	0.067	833 1010		2	Tomato	< 0 0 1 3 4 8	< 0.002[a] 1.6 1.0 1.1 0.92 0.77	GHE-P-10993 CEMS-2292B Rawle, 2005
Italy Bologna 2004	Perfect Peel	0.067	743- 893		2 2 2 2	Tomato Tomato Tomato Tomato	35 28 21 14	< 0.01 0.04 0.13 0.10	GHE-P-10993 CEMS-2292F Rawle, 2005
Italy, Emilia Romagna	Protected Carson	0.07	1029 1039	0.72	2	Tomato	7	0.05	GHE-P-11225 687040A

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
2005									Old, 2008
Italy Lombardia 2005	Protected Nerina	0.07	1022 983	0.7	2	Tomato	< 0 0 1 3 5 7	< 0.003[a] 0.13 0.07 0.02 < 0.01 < 0.01	GHE-P-11225 687040C Old, 2008
Italy Lombardia 2005	H 3402	0.07	998 959	0.70–0.67	2	Tomato	7	0.24	GHE-P-11226 687056A Old, 2008
Italy Emilia Romagna 2005	98-85	0.07	979 974	0.68	2	Tomato	< 0 0 1 3 5 7	< 0.003[a] 0.19 0.13 0.09 0.07 0.08	GHE-P-11226 687056D Old, 2006
Italy Lombardia 2006	Asterix	0.07	795 743	0.53–0.57	2	Tomato	0 5 7	0.12 0.07 0.04	GHE-P-11542 690320B Livingstone, 2008
Italy Ferrara 2007	Stay Green		1020	0.7	1	Tomato	0 1 3 5	0.31 0.08 0.05 0.07	GHE-P-11805 CEMS-3499D Marshall, 2008
Italy Bari 2007	Protected Piccadilly		995	0.63	1	Tomato	0 1 3 5	0.14 0.13 0.08 0.05	GHE-P-11805 CEMS-3499G Marshall, 2008
Poland Wielkopolska 2007	Protected Stefani		928	0.63	1	Tomato	5	0.12	GHE-P-11805 CEMS-3499L Marshall, 2008
Poland Wielkopolska 2007	Protected Malory		1054	0.7	1	Tomato	0 1 3 5	0.06 0.04 0.04 0.10	GHE-P-11805 CEMS-3499O Marshall, 2008
Spain Murcia 1999	Vicar	(0.13)	Chem 480 737 912	1.0–1.2	4	Tomato	< 0 0 2 3 5	< 0.01 0.87 0.47 0.26 0.23	GHE-P-8662 R99-107 Teasdale, 2000
Spain Sevilla 1999	Bon		1006– 1223	1.0– 1.2	4	Tomato	4	0.04	GHE-P-8663 R99-108A Doran and Craig, 2001
Spain Murcia. 1999	Bond	(0.13)	507 700 906	1.2	3	Tomato	2 3 5	0.24 0.16 0.11	GHE-P-8658 R99-103 Doran and Craig, 2001
Spain Granada. 1999	Cherry Rx-335	(0.05)	431 1389 2318	1.1–1.2	3	Tomato	3 5	0.69 0.53	GHE-P-8659 R99-104A Doran and Craig, 2001
Spain Sevilla. 2000	Mina		928– 1145	1.2	3	Tomato	3 5	0.04, 0.05 < 0.01, 0.01	GHE-P-9558 000201A Doran and Craig, 2002
Spain Sevilla. 2000	Sandy Lady	(0.062)	1029– 1928	1.2	3	Tomato	3 5	0.02, 0.04 0.03, 0.05	GHE-P-9558 000201B Doran and Craig, 2002
Spain Funes 2004	Caramba	0.067	1307 1252		2	Tomato Tomato, individual	7 7	0.22 0.02, 0.03, 0.04 (2),	GHE-P-10988 CEMS-2287D Rawle, 2005

Country Region Year	Variety	Application				Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.				
								0.14, 0.15, 0.24 (2), 0.18, 0.27, 0.29, 0.32,	
Spain Funes 2004	H-9036	0.067	1251 1242		2	Tomato Tomato, individual	7 7	0.15 0.02, 0.03, 0.04 (2), 0.05, 0.06, 0.07 (2), 0.11 (2), 0.12, 0.16	GHE-P-10993 CEMS-2292E Rawle, 2005
Spain Grisen, 2004	H9661	0.067	1256 1250		2	Tomato	7 9	0.11 0.17	GHE-P-10993 CEMS-2292G Rawle, 2005
Spain Andalucia 2005	Protected Bond	0.07	1005 1006	0.70	2	Tomato	7	0.02	GHE-P-11225 687040B Old, 2008
Spain Catalonia 2005	Tomate de rama	0.07	1005 1000	0.7	2	Tomato	7	0.12	GHE-P-11226 687056B Old, 2006
Spain Andalucia, 2006	Hector	0.07	798 801	0.57	2	Tomato	< 0 0 1 3 5 7	< 0.003[a] 0.06 0.04 0.02 0.02 < 0.01	GHE-P-11542 690320A Livingstone, 2008
Spain Valencia 2007	Tomatoes Valenciana		1098	0.75	1	Tomato	0 1 3 5	0.33 0.17 0.10 0.06	GHE-P-11805 CEMS-3499C Marshall, 2008
Spain Alicante 2007	Protected Amadeo	(0.069)	989	0.68	1	Tomato	5	0.03	GHE-P-11805 CEMS-3499F Marshall, 2008
United Kingdom 2006	Moneymaker	0.07	803 801	0.57	2	Tomato	< 0 0 1 3 5 7	0.05 0.26 0.21 0.2 0.31 0.07	GHE-P-11542 690320C Livingstone, 2008
United Kingdom Leicestershire, 2007	Protected Ailsa Craig		1017	0.7	1	Tomato	0 1 3 5	0.26 0.21 0.17 0.19	GHE-P-11805 CEMS-3499J Marshall, 2008

[a] limit of detection (LOD)

Peppers

A total of 24 trials conducted in Southern Europe during 1999–2007 in peppers were submitted. The results are shown in Table 46.

Table 46 Results of supervised trials conducted with chlorpyrifos methyl in peppers

Country Region Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
France, south Languedoc-Roussillon 2007	Protected Jordito		959	0.65	1	5	0.14	GHE-P-11801 CEMS-3495B Devine, 2008
France Thezat 2004	Protected Cabeso	0.067	1294 1297		2	7 7	0.33 0.16, 0.14, 0.18 (2), 0.22, 0.28, 0.32, 0.34, 0.40, 0.43, 0.48, 0.78,	GHE-P-10990 CEMS-2289D Rawle, 2005
France Rhone-Alpes 2005	Protected Hannibal	0.07	981 1027	0.69- 0.72	2	7	0.17	GHE-P-11223 687014A Old, 2006
Greece Thessaloniki 2005	Protected r Lenor F1 hybrid	0.067	1000	0.67	2	< 0 0 1 3 5 7	< 0.003[a] 0.65 0.12 0.21 0.16 0.13	GHE-P-11223 687014C Old, 2006
Greece Epanomi 2000	Florinis	(0.17)	700	0.6-1.2	3	< 0 0 2 3 5	< 0.01 1.1 0.33 0.2 0.14	GHE-P-9435 000204A Doran and Craig, 2002
Greece Ionia 2000	Protected Lenor	(0.17)	700– 727	1.2	3	< 0 0 2 3 5	< 0.01 0.84 0.26 0.17 0.09	GHE-P-9435 000204B Doran and Craig, 2002
Greece Thessaloniki 2004	Protected Julia F1	0.067	1000		2	< 0 0 1 3 5 7	0.03 0.74 0.54 0.34 0.16 0.12	GHE-P-10990 CEMS-2289A Rawle, 2005
Greece Thessaloniki 2007	Protected Astrion		963	0.65	1	5	0.03	GHE-P-11801 V2 CEMS-3495A Devine, 2008
Italy Bologna 1999	Cesario		715– 846	1.2	3	3 5	0.56 0.28	GHE-P-8667 R99-112A Doran and Craig, 2001
Italy Bagnarola di Budrio 2004	Protected Sienor	0.067	721 939		2	7	0.05	GHE-P-10990 CEMS-2289E Rawle, 2005
Italy Roncoferraro, Lombardia 2005	Protected Navarro	0.07	1057 1025	742 719	2	7	0.03	GHE-P-11223 687014B Old, 2006
Italy Piemonte 2006	Protected Cuneo	0.07	819 808	0.58	2	0 5 7	0.12 0.04 0.02	GHE-P-11533 690226B Livingstone, 2008
Italy Puglia 2007	Protected Senior		1066	0.67	1	0 1 3	0.14 0.15 0.05	GHE-P-11801 V2 CEMS-3495D Devine, 2008

Country Region Year	Crop Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
						5	0.06	
Spain Sevilla 1999	Negrillo		1055 1883	1.1–1.2	3	< 0 0 2 3 5	< 0.01 0.27 0.13 0.09 0.04	GHE-P-8666 R99-111A Doran and Craig, 2001
Spain Villafrinca 1999	Protected Dulce Italico		997– 1223	1.0–1.2	4	< 0 0 2 3 5	< 0.01 1.2 0.81 0.91 0.52	GHE-P-8668 R99-113A Doran and Craig, 2001
Spain Cordoba 1999	Vidi		Chemig 906– 1544	1.0-1.2	4	3 5	0.13 0.01	GHE-P-8669 R99-114A Doran and Craig, 2002
Spain Sevilla 2000	Negrillo		733– 1527	1.1-1.2	3	3 5	0.11, 0.17 0.07, 0.09	GHE-P-9442 000203A Doran and Craig, 2002
Spain Almeria 2000	Protected Lozano	0.12	1000	1.2	3	3 5	0.32 0.31	GHE-P-9442 000203B Doran and Craig, 2002
Spain Almeria 2000	Protected Lozano	0.12	987– 1025	1.2	3	3 5	0.2 0.19	GHE-P-9442 000203B Doran and Craig, 2002
Spain Dos Hermanas 2004	Protected Negrillo	0.067	1233 1290		2	< 0 0 1 3 5 7	< 0.003[a] 1.0 1.3 0.91 0.72 0.66	GHE-P-10990 CEMS-2289B Rawle, 2005
Spain Los Palacios 2004	Protected Palermo	0.067	920–1140		2 2 2 2	35 28 21 14	0.01 0.02 0.09 0.12	GHE-P-10990 CEMS-2289F Rawle, 2005
Spain Andalucia 2005	Protected Gallego	0.07	983 1000	0.7	2	< 0 0 1 3 5 7	< 0.003[a] 0.55 0.28 0.16 0.06 < 0.01	GHE-P-11223 687014D Old, 2006
Spain Andalucia 2006	Protected Palermo	0.07	799 792	0.57	2	< 0 0 1 3 5 7	< 0.003[a] 0.31 0.09 0.04 0.04 0.01	GHE-P-11533 690226A Livingstone, 2008
Spain Valencia 2007	Protected Adiche		1027	0.7	1	0 1 3 5	0.07 0.05 0.05 0.03	GHE-P-11801 V2 CEMS-3495C Devine, 2008

[a] limit of detection (LOD)

Green beans and peas

A total of six trials conducted in Southern Europe during 2000–2003 were submitted. The results are shown in Table 47.

Table 47 Results of supervised trials conducted with chlorpyrifos methyl in green bens and peas

Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		kg ai/hL	L/ha	kg ai/ha	No			
France Montauban 2000	Green beans Adana	– –	486–518	0.49– 0.52	2	15	< 0.002[a] (5)	GHE-P-9438 000205A Doran and Clements, 2002
Italy Romagna 2000	Green beans Tema	– –	500	0.51	2	15	< 0.002[a] (2)	GHE-P-9438 000205B Doran and Clements, 2002
Italy Lombardia 2003	Peas Gonal	– –	500–530	0.21 0.20	2	10	< 0.01	GHE-P-10490 682896 Wardman, 2004.
Spain Cordoba. 2000	Green beans F-15	– –	805 797	0.52 0.51	2	< 0 0 3 7 10 15	< 0.002[a] 0.65 0.05 < 0.01 < 0.01 < 0.002[a]	GHE-P-9432 000206B Doran and Clements, 2002
Spain Cadiz 2000	Green beans Primel	– –	802 800	0.52 0.51	2	< 0 0 3 7 10 15	< 0.002[a] 0.96 0.03 0.02 0.02 < 0.01	GHE-P-9432 000206C Doran and Clements, 2002

[a] limit of detection (LOD)

Carrots

Four trials conducted in Southern Europe during 2000 were submitted. The results are shown in Table 48.

Table 48 Results of supervised trials conducted with chlorpyrifos methyl in carrots

Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No.			
France St Jory 2000	Maestro	– –	601 602	0.48 0.49	2	< 0 0 2 3	< 0.01 0.04 0.06 0.01	GHE-P-9444 000196A Doran. and Clements, 2002
Italy Emilia Romagna. 2000	Napoli	– –	589 591	0.50 0.52	2	< 0 0 2 3	< 0.01 0.01 0.02 < 0.01	GHE-P-9444 000196C Doran. and Clements, 2002
Spain Paterna del Campo 2000	Navarre F1	– –	547– 614	0.47 0.53	2	3	0.03, 0.04 (2), 0.05, 0.07	GHE-P-9433 000195A Doran. and Clements, 2002
Spain Sanlucar de Barrameda 2000	Ando	– –	581– 686	0.50- 0.52	2	3	0.04 (2)	GHE-P-9433 000195B Doran. and Clements, 2002

Potatoes

A total of 21 trials conducted in Northern and Southern Europe during 2000–2007 were submitted. The results are shown in Table 49.

Table 49 Results of supervised trials conducted with chlorpyrifos methyl in potatoes

. Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No			
France Gontaud de Nogaret 2000	Concurrent	(0.14)	508– 693	0.92 0.99	2	14	< 0.002[a] (2)	GHE-P-9556 000207A Doran. and Clements, 2002
France Velleron 2000	Berbere	(0.14)	575– 633	0.9 1.0	2	14	< 0.002[a] (2)	GHE-P-9556 000207B Doran. and Clements, 2002
France Rhone-Alpes 2006	Mona Lisa	0.07	795 807	0.57 0.58	2	< 0 0 8 15 22 28	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11535 690247A Livingstone, 2008
France Allouagne 2006	Amila	0.07	814 807	0.58	2	0 21 29	< 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11534 690231D Livingstone, 2008
France Alsace 2007	Cicero	(0.067)	820	0.55	1	21	< 0.003[a]	GHE-P-11802 CEMS-3496C Devine, 2008
France Languedoc Roussillon 2007	Mona Lisa	0.07	874	0.57	1	21	< 0.003[a]	GHE-P-11802 CEMS-3496E Devine, H.C.
France Languedoc Roussillon 2007	Potatoes Bea	0.07	822	0.56	1	0 5 11 15 21	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11802 CEMS-3496H Devine, 2008
Germany Motterwitz 2006	Prinzess	0.07	740 776	0.53 0.55	2	< 0 0 7 14 21 28	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11534 690231A Livingstone, 2008
Hungary Fejer 2007	Desiree	(0.067)	822	0.55	1	0 5 10 15 21	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	N232 GHE-P-11802 CEMS-3496B Devine, 2008
Italy Emilia Romagna 2000	Agata	(0.16)	598 598	1.0	2	< 0 0 3 7 10 14	< 0.01 < 0.01 < 0.002[a] < 0.002[a] < 0.002[a] < 0.002[a]	GHE-P-9445 000208B Doran. and Clements, 2002
Italy Emilia Romagna 2000	Primura	(0.067)	600 583	1.0 0.99	2	< 0 0 3 7 10	< 0.01 < 0.01 < 0.002[a] < 0.002[a] < 0.002[a]	GHE-P-9445 000208A Doran. and Clements, 2002

. Country Region Year	Variety	Application				PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		kg ai/hL	L/ha	kg ai/ha	No			
						14	< 0.002[a]	
Italy Lobardia 2003	Hermes	0.04	628– 580	0.23- 0.25	2	15	< 0.002[a] (2)	GHE-P-10491 682901A Wardman, 2004
Italy Emilia Romagna 2007	Potatoes Primura	(0.067)	767	0.52	1	0 5 9 14 21	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11802 CEMS-3496J Devine, 2008
Italy Emilia Romagna 2007	Potatoes Agata	0.07	790	0.54	1	21	< 0.003[a]	GHE-P-11802 CEMS-3496G Devine, 2008
Poland Rozbity Kamien 2006	Irga	0.07	790 823	0.56 0.59	2	0 21 28	< 0.003[a] < 0.003[a] < 0.003[a]	N224 GHE-P-11534 690231B Livingstone, 2008
Poland Wielkopolska 2007	Pasat	0.07	807	0.54	1	20	< 0.003[a]	GHE-P-11802 CEMS-3496A Devine, 2008
Spain Andulucia 2006	Fabula	0.07	788 763	0.56 0.54	2	0 21 28	< 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11535 690247B Livingstone, 2008
Spain Valencia 2007	Martina	0.07	819	0.56	1	21	< 0.003[a]	GHE-P-11802 CEMS-3496F Devine, 2008
Spain Albacete 2007	Potatoes Mona Lisa	0.07	795	0.54	1	0 5 10 14 20	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11802 CEMS-3496I Devine, 2008
United Kingdom Essex 2006	Maris Piper	0.07	803 804	0.57	2	< 0 0 7 14 21 27	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11534 690231C Livingstone, 2008
United Kingdom Staffordshire 2007	Pentland Dell	0.07	807	0.54	1	0 5 10 15 21	< 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a] < 0.003[a]	GHE-P-11802 CEMS-3496D Devine, 2008

[a] limit of detection (LOD)

Sugar Beet

A total of four trials conducted in Southern Europe during 2000–2001 were submitted. The results are shown in Table 50.

Table 50 Results of supervised trials conducted with chlorpyrifos methyl in sugar beet root

Country		Application			PHI		Report No.
Region Year	Variety	L/ha	kg ai/ha	No.	(days)	Residues (mg/Kg)	Trial No. Author(s)
Italy Emilia-Romagna 2000	Rio	413	525	1	120	< 0.002[a]	GHE-P-9428 000198A Doran. and Clements, 2002
Italy Emilia-Romagna 2000	Bushel	402	513	1	120	< 0.002[a]	GHE-P-9428 000198B Doran. and Clements, 2002
Spain Paterna del Campo 2000	Safrane	504–539	460	1	118	< 0.002[a] (5)	GHE-P-9429 000197A Doran. and Clements, 2002
Spain Sevilla 2001	Khazar	409–502	489	1	107	< 0.002[a] (2)	GHE-P-9774 680773A Doran. and Clements, 2002

[a] limit of detection (LOD)

Artichoke (Globe)

A total of four trials conducted in Southern Europe during 2000 were submitted. The results are shown in Table 51.

Table 51 Results of supervised trials conducted with chlorpyrifos methyl in artichoke

Country	Variety	Application			PHI	Residues	Report No.
Region Year		L/ha	kg ai/ha	No. of Appl.	(days)	(mg/Kg)	Trial No. Author(s)
Greece Nauplion 2000	Argitiki	1000	1.0	1	5	0.83, 0.95, 1.1, 1.2 (2)	GHE-P-9439 000211A Doran and Clements 2002
Greece Nauplion 2000	Argitiki	1000	1.0	1	5	0.36, 0.40	GHE-P-9439 000211B Doran and Clements 2002
Spain Cantillana 2000	Blanca de Tudela	597	1.0	1	0 1 3 5	1.1 0.37 0.18 0.10	GHE-P-9559 000002A Doran and Clements 2002
Spain Toscana 2000	Teramo	576	0.98	1	0 1 3 5	1.6 0.56 0.16 0.11	GHE-P-9559 000002B Doran and Clements 2002

Cereals—post-harvest use

Twenty four trials were conducted in Europe with a post-harvest use of chlorpyrifos-methyl in barley and wheat submitted. The results are shown in Table 52.

Table 52 Results of post harvest supervised trials conducted with chlorpyrifos methyl in barley

Country Region Year	Crop Variety	Application g ai/tonne seed	PHI (days)	Residues (mg/Kg)	Trial No. Author(s) Reference
France Rhone-Alpes 2006	Barley Winter Caravan	5	0 31 62	2.6 2.9 2.6	GHE-P-11536 690252A Livingstone, 2008

Country Region Year	Crop Variety	Application g ai/tonne seed	PHI (days)	Residues (mg/Kg)	Trial No. Author(s) Reference
			98 181	<u>3.3</u> 3.2	
Poland Siedlce 2006	Barley Winter Prestige	5	0 29 99 121 182	6.2 5.3 10 8.5 6.7	GHE-P-11536 690252D Livingstone, 2008..
Spain Lleida 2006	Barley Winter Kulma	5	0 29 59 89 179	2.9 1.9 1.1 1.5 <u>1.6</u>	GHE-P-11536 690252B Livingstone, 2008
United Kingdom King's Lynn 1994	Barley Puffin	2.5	0 7 28 91 181	1.9 <u>2.0</u> 1.7 1.3 1.0	GHE-P-4372 R94-079A Khoshab and Bolton 1995
United Kingdom King's Lynn 1994	Barley Puffin	4.5	0 7 28 91 181	3.7 3.6 2.6 <u>1.9</u> 1.8	GHE-P-4372 R94-079A Khoshab and Bolton 1995
United Kingdom King's Lynn 1994	Barley Puffin	2.5	0 7 28 91 181	1.9 <u>2.0</u> 1.4 1.2 0.88	GHE-P-4372 R94-079A Khoshab and Bolton 1995
United Kingdom King's Lynn 1994	Barley Puffin	4.5	0 7 28 91 181	3.7 3.9 3.2 <u>2.3</u> 1.9	GHE-P-4372 R94-079A Khoshab and Bolton 1995
United Kingdom Derbyshire 2004	Barley Winter Cellar	5	< 0 0 32 60 95 182	< 0.01 3.2 2.8 3.3 <u>3.2</u> 2.8	GHE-P-11006 CEMS-2305A Rawle, 2006.
United Kingdom Derbyshire 2004	Barley Winter Adoms	5	< 0 0 31 59 94 181	0.03 3.6 3.1 3.0 <u>3.0</u> 2.4	GHE-P-11006 CEMS-2305B Rawle, 2006
United Kingdom Derbyshire 2004	Barley Winter Chalice	5	< 0 0 31 59 94 181	< 0.01 3.9 2.8 3.2 2.8 <u>2.9</u>	GHE-P-11006 CEMS-2305C Rawle, 2006
United Kingdom Derbyshire 2004	Barley Winter Optic	5	0 31 59 94 186	3.2 3.2 2.8 <u>2.6</u> 2.4	GHE-P-11006 CEMS-2305D Rawle, 2006

Country Region Year	Crop Variety	Application g ai/tonne seed	PHI (days)	Residues (mg/Kg)	Trial No. Author(s) Reference
United Kingdom Essex 2006	Barley Winter Pearl	5	0 30 62 91 181	3.6 2.7 2.6 2.7 3.1	GHE-P-11536 690252C Livingstone, 2008.
France Rhone-Alpes 2006	Wheat Winter Cap Horn	5	0 31 62 98 181	3.0 3.2 2.9 3.0 2.7	GHE-P-11537 690268A Livingstone, 2008
Poland Cental Poland 2006	Wheat Winter Kris	5	0 29 99 121 182	4.9 4.9 4.0 3.4 4.7	GHE-P-11537 690268D Livingstone, 2008
Spain Catalunya 2006	Wheat Winter Sarina	5	0 29 59 89 179	3.0 2.4 2.1 1.6 1.9	GHE-P-11537 690268B Livingstone, 2008
United Kingdom King's Lynn 1994	Wheat Riband	2.5	0 7 28 91 181	2.2 1.9 1.6 1.5 1.3	GHE-P-4372 R94-079B Khoshab and Bolton 1995
United Kingdom King's Lynn 1994	Wheat Riband	4.5	0 7 28 91 181	3.7 3.0 3.1 2.4 2.2	GHE-P-4372 R94-079B Khoshab and Bolton 1995.
United Kingdom King's Lynn 1994	Wheat Riband	2.5	0 7 28 91 181	2.2 2.2 1.7 1.3 1.2	GHE-P-4372 R94-079B Khoshab and Bolton 1995
United Kingdom King's Lynn 1994	Wheat Riband	4.5	0 7 28 91 181	3.7 3.6 2.6 2.1 2.2	GHE-P-4372 R94-079B Khoshab and Bolton 1995
United Kingdom Derbyshire 2004	Wheat Winter Consort	5	0 41 59 90 181	3.0 3.8 3.0 3.5 2.5	GHE-P-11005 CEMS-2304A Rawle, N.
United Kingdom Wilson, Derbyshire 2004	Wheat Winter Claire	5	8 41 69 104 191	3.9 3.2 3.5 2.9 2.1	GHE-P-11005 CEMS-2304B Rawle, 2005
United Kingdom Derbyshire 2004	Wheat Winter Biensur	5	0 33 61 96 183	3.6 3.3 3.3 3.1 3.1	GHE-P-11005 CEMS-2304C Rawle, 2005

Country Region Year	Crop Variety	Application g ai/tonne seed	PHI (days)	Residues (mg/Kg)	Trial No. Author(s) Reference
United Kingdom Derbyshire 2004	Wheat Winter Hereward	5	0 32 60 95 182	3.4 3.4 2.6 2.7 3.2	GHE-P-11005 CEMS-2304D Rawle, 2005
United Kingdom Essex 2006	Wheat Winter X119	5	0 30 62 91 181	3.8 3.0 3.1 3.2 3.0	GHE-P-11537 690268C Livingstone, 2008

Corn/Maize

A total of eight trials conducted in Southern Europe during 2000–2007 were submitted. The results are shown in Table 53.

Table 53 Results of supervised trials conducted with chlorpyrifos methyl in maize grain (Report No. GHE-P-11806; Marshall, 2008)

Country		Application			PHI	Residues	
Region, year	Variety	L/ha	kg ai/ha	No.	(days)	(mg/Kg)	Trial No.
France, Midi-Pyrenees	Galactic	403	0.91	1	93	< 0.003[a]	CEMS-3500A
France, Languedoc-Roussillon	PR 35465	417	0.94	1	85	< 0.003[a]	CEMS-3500D
France Languedoc-Roussillon	Anvil ST	417	0.94	1	56	< 0.003[a]	CEMS-3500E
Italy, Piemont	KVS Kandal	410	0.92	1	101	< 0.003[a]	CEMS-3500C
Italy, Piemonte	DKC 5783	395	0.84	1	93	< 0.003[a]	CEMS-3500H
Spain, Albacete	Factor	426	0.96	1	22	< 0.003[a]	CEMS-3500B
Spain, Albacete	N-K Factor	400	0.91	1	22	< 0.003[a]	CEMS-3500F
Spain, Albacete	Milty	391	0.89	1	23	< 0.003[a]	CEMS-3500G

[a] limit of detection (LOD)

Cotton seed

A total of 12 trials conducted in Southern Europe during 2006–2007 were submitted. The results are shown in Table 55.

Table 55 Results of supervised trials conducted with chlorpyrifos methyl in cotton seed

Country	Variety	Application			PHI	Residues	Report No., Trial No.
Region, Year		L/ha	kg ai/ha	No.	(days)	(mg/Kg)	Author(s)
Greece Epanomi, 2006	Kampo	604 595	0.68 0.67	2	29 42	< 0.003[a] < 0.003[a]	GHE-P-11530, 690184A Livingstone, 2008
Greece Epanomia, 2006	Kampo	600 605	0.68	2	29 42	< 0.003[a] < 0.003[a]	GHE-P-11530, 690184C Livingstone, 2008
Greece Thessaloniki 2007	Celia	522	0.71	1	0 5 9 14	0.37 0.01 0.02 < 0.01	GHE-P-11799 CEMS-3493E Devine, 2008
Greece Pella 2007	Celice	498	0.68	1	0 5 10	0.53 0.02 < 0.01	GHE-P-11799 CEMS-3493F Devine, 2008

Country Region, Year	Variety	Application L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No., Trial No. Author(s)
					14	0.02	
Greece Thessaloniki, 2007	Celia	506	0.69	1	14	< 0.003[a]	GHE-P-11799, CEMS-3493A Devine, 2008
Greece Pella, 2007	Volcano	507	0.69	1	14	< 0.01	GHE-P-11799, CEMS-3493B Devine, 2008
Spain Andalucia, 2006	Hermes	602 605	0.72	2	28 54	< 0.003[a] < 0.01	GHE-P-11530, 690184B Livingstone, 2008
Spain Andalucia, 2006	Celia	597 603	0.71– 0.72	2	8 56	< 0.003[a] < 0.01	GHE-P-11530, 690184D Livingstone, 2008
Spain Andalucia, 2007	Lider	503	0.69	1	14	< 0.01	GHE-P-11799, CEMS-3493C Devine, 2008
Spain Andalucia, 2007	Julia	503	0.69	1	14	< 0.003[a]	GHE-P-11799, CEMS-3493D Devine, 2008
Spain Andalucia 2007	Celia	506	0.69	1	0 5 9 14	< 0.01 0.02 0.03 0.02	GHE-P-11799 CEMS-3493G Devine, 2008
Spain Andalucia 2007	Bravo	502	682	1	0 5 11 14	0.01 0.01 < 0.01 < 0.01	GHE-P-11799 CEMS-3493H Devine, 2008

[a] limit of detection (LOD)

Oilseed Rape

A total of 16 trials conducted in Central, Northern and Southern Europe during 2006–2007 were submitted. The results are shown in Table 56.

Table 56 Results of supervised trials conducted with chlorpyrifos methyl in oil seed rape

Country Region, Year	Variety	Application L/ha	kg ai/ha	No.	PHI (days)	Residues (mg/Kg)	Report No., Trial No. Author(s)
France-North Pas de Calais, 2006	Winter Pollen	623	0.49	1	89	< 0.01	GHE-P-11531, 690205A Livingstone, 2007
France-South Rhone-Alpes, 2006	Winter oilseed Exocet	620	0.49	1	94	< 0.002[a]	GHE-P-11532, 690210B Livingstone, 2007
France-North Alsace, 2007	Winter Grizzly	577	0.43	1	75	< 0.003[a]	GHE-P-11800, CEMS-3494A Devine, H.C.
France-South Languedoc Roussillon, 2007	Winter Corail	611	0.46	1	82	< 0.003[a]	GHE-P-11800, CEMS-3494E Devine, 2007
France-South Roussillon, 2007	Winter Stardart	601	0.45	1	82	< 0.003[a]	GHE-P-11800, CEMS-3494H Devine, 2007
Germany Brandenburg, 2006	Winter NK Fair	560	0.44	1	105	< 0.003[a]	GHE-P-11531, 690205D Livingstone, 2007
Germany Brandenburg, 2007	Winter Titan	598	0.45	1	93	< 0.003[a]	GHE-P-11800, CEMS-3494D Devine, 2007
Greece Thessaloniki, 2007	Winter Lycodor	595	0.45	1	51	< 0.003[a]	GHE-P-11800, CEMS-3494G Devine, 2007
Greece Kilkis, 2007	Spring Lycodor	599	0.45	1	50	< 0.003[a]	GHE-P-11800, CEMS-3494J Devine, 2007
Poland 2006	Spring Heros	603	0.48	1	99	< 0.003[a]	GHE-P-11531, 690205C Livingstone, 2007
Poland Wielkopolska, 2007	Winter Californium	637	0.48	1	91	0.02	GHE-P-11800, CEMS-3494C Devine, 2007

Country Region, Year	Variety	Application			PHI (days)	Residues (mg/Kg)	Report No., Trial No. Author(s)
		L/ha	kg ai/ha	No.			
Spain Lleida, 2006	Spring Oban	602	0.48	1	120	< 0.002[a]	GHE-P-11532, 690210A Livingstone, 2007
Spain Valencia, 2007	Spring Tracia	654	0.49	1	54	< 0.003[a]	GHE-P-11800, CEMS-3494F Devine, 2007
Spain Cuenca, 2007	Spring Tracia	603	0.45	1	31	< 0.01	GHE-P-11800, CEMS-3494I Devine, 2007
United Kingdom, Essex, 2006	Winter Winner	570	0.45	1	90	< 0.003[a]	GHE-P-11531, 690205B Livingstone, 2007
United Kingdom Derbyshire, 2007	Spring Apex	601	0.45	1	85	< 0.01	GHE-P-11800, CEMS-3494B Devine, 2007

[a] limit of detection (LOD)

Animal feed

In a total of 51 trials conducted in corn/maize, cotton, rape seed and sugar beet, samples destined as feed for animal consumption were collected and analysed. The results are shown in Tables 57 to 60.

Table 57 Results of supervised trials conducted with chlorpyrifos methyl in corn/maize

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		L/ha	kg ai/ha	No.				
France Larra 2000	Quartal	222	1.0	1	Cob Stover Whole plant	90 90 56	< 0.002[a] (2) < 0.002[a] (2) < 0.002[a] (2)	GHE-P-9443 000212A Doran &Clements, 2002
France Savenes 2000	Cecilia	250	1.0	1	Cob Stover Whole plant	88 88 52	< 0.002[a] (2) < 0.002[a] (2) < 0.002[a] (2)	GHE-P-9443 000212B Doran &Clements, 2002
France Meauzac 2004	604	301 301	0.56	2	Cob Stover	< 0 0 7 14 21 28 < 0 0 7 14 21 28	< 0.002[a] 0.02 < 0.01 < 0.01 < 0.01 < 0.01 < 0.002[a] 11 0.8 0.41 0.12 0.07	GHE-P-10991 CEMS-2290B Rawle, 2005
France Meauzac 2004	Maize604	301	0.56	1	Whole plant	< 0 0 7 14 21 28	< 0.002[a] 15 0.09 0.01 < 0.01 < 0.002[a]	GHE-P-10991 CEMS-2290B Rawle, 2005
France Lizac 2004	Merci	303 298	0.56	2	Cob Stover	28 28	< 0.002[a] 0.04	GHE-P-10991 CEMS-2290C Rawle, 2005
France Lizac 2004	Merci	303	0.57	1	Whole plant	28	< 0.002[a]	GHE-P-10991 CEMS-2290C Rawle, 2005
France Rhone-Alpes 2005	DK315	742 810	0.54–0.59	2	Cob Stover	29 29	< 0.003[a] 0.13	N205 GHE-P-11217 686948A Livingstone, 2006

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		L/ha	kg ai/ha	No.				
France Rhone-Alpes 2005	DK315	742	0.54	1	Whole plant	28	0.01	GHE-P-11217 686948A Livingstone, 2006
France Rhone-Alpes 2005	DK5050	823 880	0.60– 0.64	2	Cob Stover Whole plant	29 29 < 0 0 7 14 21	< 0.003[a] 1.5 0.10 6.7 0.22 1.4 0.76	GHE-P-11217 686948D Livingstone, 2006
France Rhone-Alpes 2005	DK5050	823	0.60	1	Whole plant	0 7 14 21 28	1.7 1.04 0.16 0.30 0.05	GHE-P-11217 686948D Livingstone, 2006
France Midi-Pyrenees 2007	Galactic	403	0.91	1	Rest of plant	93	0.01	GHE-P-11806 CEMS-3500A Marshall, 2008
France Languedoc-Roussillon 2007	PR 35465	417	0.94	1	Rest of plant	85	< 0.01	GHE-P-11806 CEMS-3500D Marshall, 2008
France Languedoc-Roussillon 2007	Anvil ST	417	0.94	1	Rest of plant Silage Whole plant	56 29 0 5 11 14	0.02 0.03 29 0.39 0.04 0.03	GHE-P-11806 CEMS-3500E Marshall, 2008
Italy Emilia-Romagna 2000	Belgrano	613	1.0	1	Cob Stover Whole plant	113 113 0 31 84	< 0.002[a] < 0.002[a] 31 < 0.002[a] 0.04	GHE-P-9440 000213A Doran &Clements, 2002
Italy Lombardia 2000	Aliseo	611	1.0	1	Cob Stover Whole plant	113 113 0 31 79	< 0.002[a] < 0.01 18 < 0.01 < 0.002[a]	GHE-P-9440 000213B Doran &Clements, 2002
Italy Bologna 2004	PR 34 FO2	309 305	0.57– 0.58	2	Cob Stover	28 28	< 0.002[a] 0.04	GHE-P-10991 CEMS-2290D Rawle, 2005
Italy Bologna 2004	PR 34 FO2	309	0.58	1	Whole plant	28	< 0.002[a]	GHE-P-10991 CEMS-2290D Rawle, 2005
Italy Lombardia 2005	DKC6530	837 759	0.55– 0.61	2	Cob Stover	28 28	< 0.003[a] < 0.003[a]	GHE-P-11217 686948B Livingstone, 2006
Italy Lombardia 2005	DKC6530	837	0.61	1	Whole plant	28	< 0.003[a]	GHE-P-11217 686948B Livingstone, 2006
Italy Piemonte 2007	KVS Kandal	410	0.92	1	Rest of plant	101	< 0.003[a]	GHE-P-11806 CEMS-3500C Marshall, 2008
Italy Piemonte, 2007	DKC 5783	395	0.84	1	Rest of plant Silage Whole plant	93 61 0 5	< 0.003[a] < 0.003[a] 8.6 0.13	GHE-P-118061 CEMS-3500H Marshall, 2008

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Reference
		L/ha	kg ai/ha	No.				
						10 15	0.04 0.01	
Spain Calatorao 2004	Dekalb DKC 6575	299 301	0.56	2	Cob Stover	< 0 0 7 14 21 28 < 0 0 7 14 21 28	< 0.002[a] < 0.01 < 0.002[a] < 0.002[a] < 0.002[a] < 0.002[a] < 0.002[a] 2.6 0.15 0.07 0.03 0.02	GHE-P-10991 CEMS-2290A Rawle, 2005
Spain Calatorao 2004	Dekalb DKC 6575	299	0.56	1	Whole plant	< 0 0 7 14 21 28	< 0.002[a] 15 0.02 < 0.01 < 0.01 < 0.002[a]	GHE-P-10991 CEMS-2290A Rawle, 2005.
Spain Catalunya 2005	Oboe	813 843	0.59– 0.62	2	Cob Stover Whole plant	28 28 < 0 0 7 14 21	< 0.003[a] 0.02 < 0.003[a] 0.53 0.24 0.04 < 0.003[a]	GHE-P-11217 686948C Livingstone, 2006
Spain Catalunya 2005	Oboe	813	0.59	1	Whole plant	0 7 14 21 27	12 0.02 < 0.01 < 0.01 0.02	GHE-P-11217 686948C Livingstone, 2006
Spain Albacete 2007	Factor	426	0.96	1	Rest of plant	22	0.53	GHE-P-11806 CEMS-3500B Marshall, 2008
Spain Albacete 2007	N-K Factor	400	0.91	1	Rest of plant Silage Whole plant	22 0 0 5 11 15	1.0 17 11 2.3 3.9 0.45	GHE-P-11806 CEMS-3500F Marshall, 2008
Spain Albacete 2007	Milty	391	0.89	1	Rest of plant Silage Whole plant	23 0 0 5 9 15	0.13 6.8 8.1 0.36 0.35 0.31	GHE-P-11806 CEMS-3500G Marshall, 2008

[a] limit of detection (LOD)

Table 58 Results of supervised trials conducted with chlorpyrifos methyl in cotton animal feed

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		L/ha	kg ai/ha	No.				
Greece Epanomi, 2006	Kampo	604 595	0.68 0.67	2	Whole plant	< 0 0 7 14	0.43 34 1.5 1.6	GHE-P-11530 690184A Livingstone, 2008
Spain Andalucia, 2006	Hermes	602 605	0.72	2	Whole plant	< 0 0 7 14	0.44 12 1.5 0.86	GHE-P-11530 690184B Livingstone, 2008

Table 59 Results of supervised trials conducted with chlorpyrifos methyl in rape animal feed

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		L/ha	kg ai/ha	No.				
France-North Pas de Calais 2006	Winter Pollen	623	0.49	1	Straw Whole plant	89 0 26 53 80	< 0.003[a] 10 0.03 < 0.003[a] < 0.003[a]	GHE-P-11531 690205A Livingstone, 2007
France-South Rhone-Alpes, 2006	Winter oilseed Exocet	620	0.49	1	Straw	94	< 0.002[a]	GHE-P-11532 690210B Livingstone, 2007
France-North Alsace 2007	Winter Grizzly	577	0.43	1	Rest of plant	75	< 0.003[a]	GHE-P-11800 CEMS-3494A Devine, H.C.
France-South Roussillon 2007	Winter Corail	611	0.46	1	Rest of plant	82	0.04	GHE-P-11800 CEMS-3494E Devine, 2007
France-South Roussillon 2007	Winter Stardart	601	0.45	1	Rest of plant Whole plant	82 0 3 7 14 20 27	< 0.003[a] 3.4 0.58 0.10 0.02 0.03 < 0.01	GHE-P-11800 CEMS-3494H Devine, 2007
Germany Brandenburg 2006	Winter NK Fair	560	0.44	1	Straw	105	< 0.01	GHE-P-11531 690205D Livingstone, 2007
Germany Brandenburg 2007	Winter Titan	598	0.45	1	Rest of plant Whole plant	93 0 3 7 13 20 27	< 0.003[a] 5.2 1.6 0.31 0.14 0.05 0.08	GHE-P-11800 CEMS-3494D Devine, 2007
Greece Thessaloniki 2007	Winter Lycodor	595	0.45	1	Rest of plant	51	< 0.003[a]	GHE-P-11800 CEMS-3494G Devine, 2007
Greece Kilkis 2007	Spring Oilseed Rape Lycodor	599	0.45	1	Rest of plant Whole plant	50 0 3 7 14 21	< 0.003[a] 3.6 0.43 0.12 < 0.003[a] < 0.003[a]	GHE-P-11800 CEMS-3494J Devine, 2007

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		L/ha	kg ai/ha	No.				
						28	< 0.003[a]	
Poland 2006	Spring Heros	603	0.48	1	Straw Whole plant	99 0 25 47 71	< 0.003[a] 9.6 < 0.003[a] < 0.003[a] 0.08	GHE-P-11531 690205C Livingstone, 2007
Poland Wielkopolska 2007	Winter Californium	637	0.48	1	Rest of plant	91	< 0.003[a]	GHE-P-11800 CEMS-3494C Devine, 2007
Spain Lleida 2006	Spring Oban	602	0.48	1	Straw Whole plant	120 0 22 46 68	< 0.002[a] 16 < 0.002[a] < 0.002[a] < 0.002[a]	GHE-P-11532 690210A Livingstone, 2007
Spain Valencia 2007	Spring Tracia	654	0.49	1	Rest of plant	54	0.02	GHE-P-11800 CEMS-3494F Devine, 2007
Spain Cuenca 2007	Spring Oilseed Rape Tracia	603	0.45	1	Rest of plant Whole plant	31 0 3 7 14 21 28	0.02 3.5 0.29 0.04 0.02 0.01 0.03	GHE-P-11800 CEMS-3494I Devine, 2007
United Kingdom, Essex 2006	Winter Winner	570	0.45	1	Straw	90	< 0.003[a]	GHE-P-11531 690205B Livingstone, 2007
United Kingdom Derbyshire, 2007	Spring Apex	601	0.45	1	Rest of plant Whole plant	85 0 3 7 14 21 28	0.02 6.9 2.3 0.54 0.09 0.01 < 0.01	GHE-P-11800 CEMS-3494B Devine, 2007

[a] limit of detection (LOD)

Table 60 Results of supervised trials conducted with chlorpyrifos methyl in sugar beet

Country Region Year	Variety	Application			Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
		L/ha	kg ai/ha	No.				
Italy Emilia-Romagna 2000	Rio	413	525	1	Top Whole plant	120 0 30 60 90	< 0.002[a] 0.51 < 0.002[a] < 0.002[a] < 0.002[a]	GHE-P-9428 000198A Doran. and Clements, 2002
Italy Emilia-Romagna 2000	Bushel	402	513	1	Top Whole plant	120 0 30 60 90	< 0.002[a] 1.4 < 0.002[a] < 0.002[a] < 0.002[a]	GHE-P-9428 000198B Doran. and Clements, 2002
Spain Paterna del Campo,2000	Safrane	504–539	460	1	Leaves	118	< 0.002[a] (5)	GHE-P-9429 000197A Doran and Clements, 2002

Country Region Year	Variety	Application L/ha	kg ai/ha	No.	Portion Analysed	PHI (days)	Residues (mg/Kg)	Report No. Trial No. Author(s)
Spain Sevilla 2001	Khazar	409–502	489	1	Leaves	107	< 0.002[a] (2)	GHE-P-9774 680773A Doran. and Clements, 2002

[a] limit of detection (LOD)

FATE OF RESIDUES IN PROCESSING

The effect of processing on chlorpyrifos-methyl residues was investigated in oranges, apples, peach, grape, tomato, barley, wheat, maize, cotton and rape seed. When residues in the processed commodity were < LOQ, the LOQ was used to determine the processing factor (PF), and was expressed as below the calculated value. When the residues in the raw commodity was < LOQ and they concentrated in the processed commodity, PF was expressed as higher than the calculated. No PF was calculated when the residues in both the raw and processed commodities were < LOQ.

Residues of total TCP (mg/kg) were reported as TCP. The TCP method involves an alkaline hydrolysis step that would convert any conjugates and parent chlorpyrifos-methyl to TCP.

Oranges

Two processing studies (Reports GHE-P-11003 and GHE-P-11219) on oranges were conducted in Spain during 2004–2005 to determine the residue of chlorpyrifos-methyl and total TCP in whole orange, peel, pulp, juice and essential oil. Two applications of chlorpyrifos-methyl were made to orange trees at a nominal rate of 2.7 kg ai/ha and fruits harvested 21 days after the last application. Orange fruits were washed and juice extracted using an industrial processing machine. The water/oil emulsion with rests of pulp was centrifuged to obtain the essential oil fraction. The raw juice was pasteurised at 85–100 °C for 1–2 min. and immediately cooled down. Residues in the samples are summarized in Table 61.

Table 61 Processing studies on oranges

	GHE-P-11003, D, 2004 Rawle, 2002			GHE-P-11219, E, 2005 Old, 2007			Mean
	CPM	PF	TCP	CPM	PF	TCP	CPM PF
Whole fruit	0.13	–	0.15	0.24	–	0.23	
Juice	0.01	0.08	0.01	< 0.003[a]	< 0.012	< 0.003[a]	0.046
Essential oil	5.2	40	7.6	9.7	40.4	8.3	40.2

[a] limit of detection (LOD)

Apples

Three processing studies on apple were conducted in France to determine the residue of chlorpyrifos-methyl and total TCP in whole apple, juice, puree and dry pomace. Two applications of chlorpyrifos-methyl were made to apple trees at a nominal application rate of 0.6 or 0.78 kg ai/ha and processed according to Figure 3. Residues in the samples are summarized on Table 62.

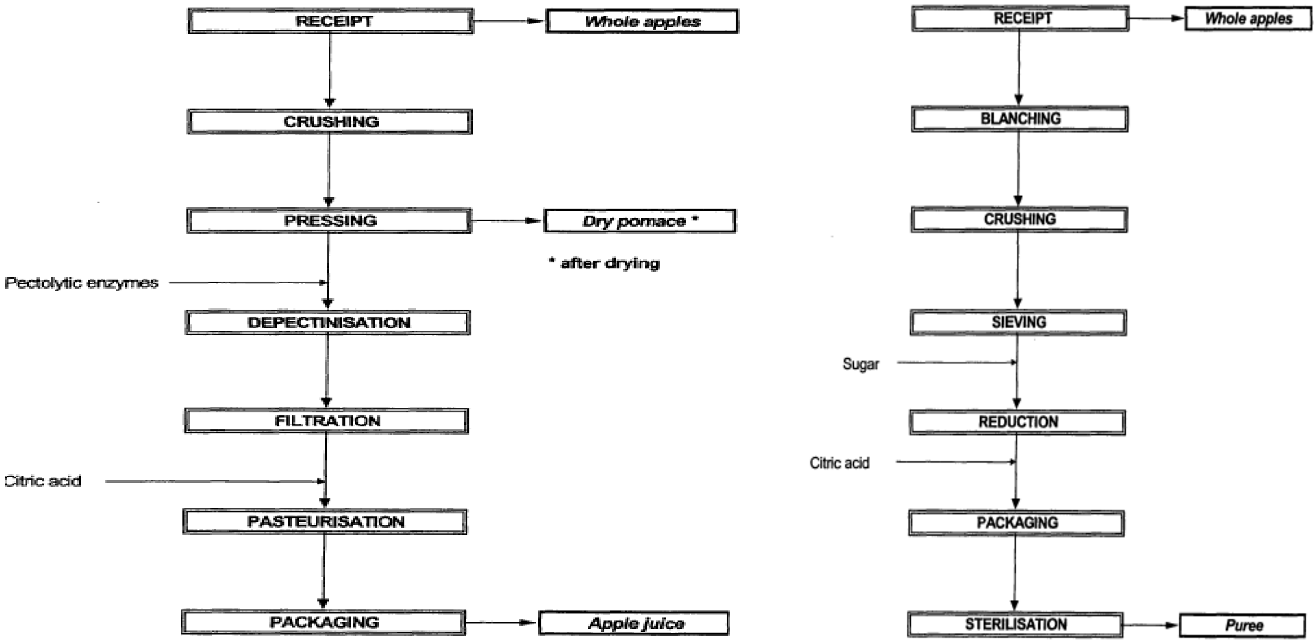


Figure 3 Scheme of the processing of apples to apple juice and puree (GHE-P 10994)

Table 62 Processing studies on apples

	GHE-P-8643 Doran and Craig, 2001		GHE-P-10994, D Rawle, 2005			GHE-P-10995, D Rawle, 2005			Mean
	CPM	PF	CPM	PF	TCP	CPM	PF	TCP	CPM PF
Fruit	0.04	–	0.07	–	0.06	0.02	–	0.02	–
Juice	< 0.002[A]	< 0.05	< 0.003[a]	< 0.04	< 0.01	< 0.003[a]	< 0.15	< 0.01	< 0.08
Pomace wet	0.26	6.5	–	–	–	–	–	–	6.5
Pomace, dried	–	–	0.16	2.29	0.45	0.08	4.0	0.23	3.1
pure	< 0.01	< 0.25	< 0.003[a]	< 0.04	0.01	< 0.003[a]	< 0.15	0.01	< 0.15

[a] limit of detection (LOD)

Peaches

One processing trial (Report GHE-P-10992, Rawle, 2005) on peaches was conducted in France during 2004 to determine the residue of chlorpyrifos-methyl and total TCP in whole fruit, juice and dry pomace. Two applications of chlorpyrifos-methyl were made to peach trees at a nominal application rate of 0.833 and 0.904 kg ai/ha. The last application was made 28 days before harvest. The peaches were stoned, crushed and put into an automatic sieve to obtain the juice. Sugar was added to the purée, the purée heated until brix reaches 24%. The pH of the puree was corrected, if necessary, to approximately 3.5 with citric acid and the puree samples put into glass containers and sterilized at 115 to 120 °C for 10 minutes. Residues in the samples are summarised on Table 63.

Table 63 Processing study on peaches

Substrate	Chlorpyrifos methyl (mg/kg)	PF	TCP (mg/kg)
Whole fruit	< 0.01	–	0.02
Juice	< 0.003[a]	–	0.01
Dried pomace	0.01	< 1	0.23
Puree	< 0.003[a]	–	0.01

[a] limit of detection (LOD)

Grapes

Seven studies on grapes were conducted in France during 2004 to determine the residue of chlorpyrifos-methyl and total TCP in grapes and processing fractions. The field conditions of the trials are shown in Table 41 and the description of the processing procedure on Figure 4. Residues found in the samples are summarised in Table 64a and b.

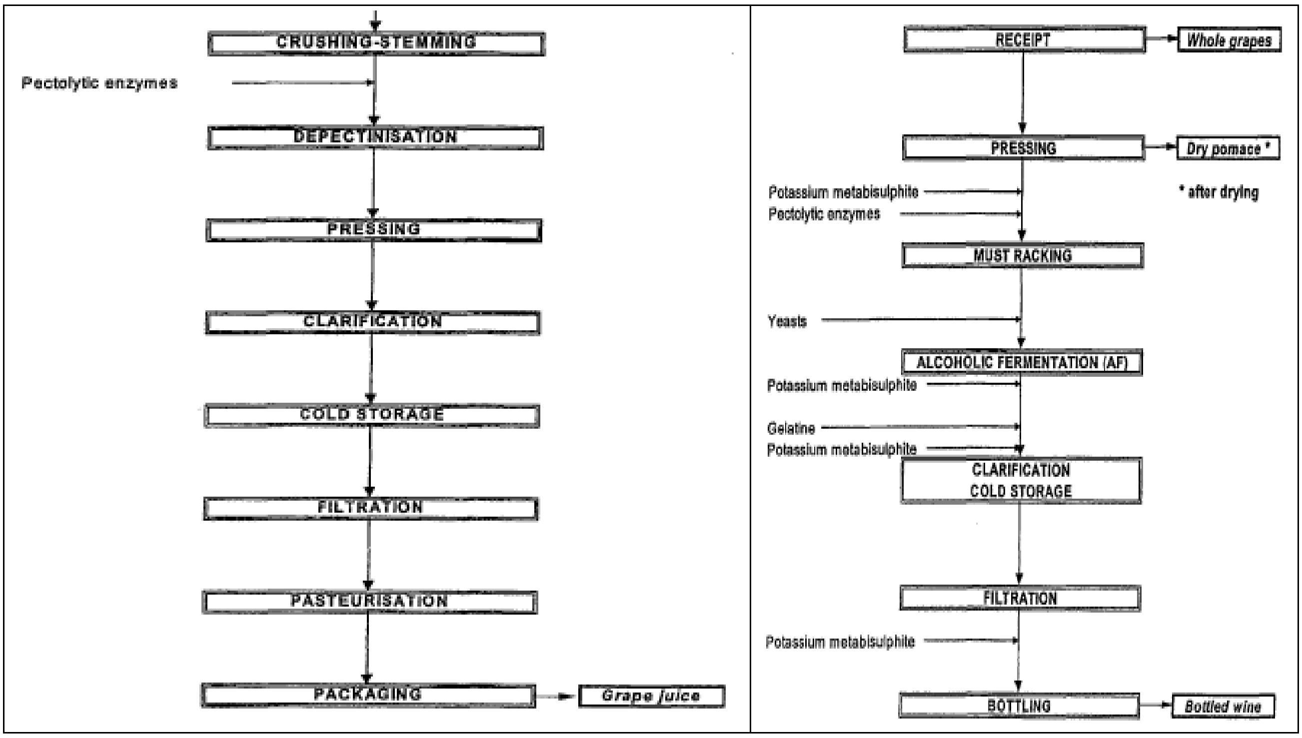


Figure 4 Scheme of the processing of grapes

Table 64a Processing studies on grapes

	GHE-P-8651 Doran and Craig, 2001		GHE-P-8655 Doran and Craig, 2001		GHE-P-11001, C Rawle, 2006		GHE-P-11002, C Rawle, 2006		GHE-P-11228, A Old, 2006		Mean or median
	CPM	PF	CPM	PF	CPM	PF	CPM	PF	CPM	PF	PF
Grapes	0.02	–	0.01	–	0.01	–	< 0.01	–	< 0.01	–	–
Must	< 0.002[a]	< 0.1	< 0.002[a]	< 0.2	< 0.002[a]	< 0.2	< 0.01, < 0.003[A]	–	< 0.003[A]	–	< 0.15
Pomace, wet	0.05	2.5	0.06	6	–	–	–	–	–		4.2
Pomace, dried	–	–	–	–	0.03	3	0.08, 0.07	> 8, > 7	0.22	> 22	> 7.5
Wine at bottling	< 0.002[a]	< 0.1	< 0.002[a]	< 0.2	< 0.002[a]	< 0.2	< 0.002[a], < 0.003[a]	–	< 0.003[A]	–	< 0.15
Wine after 4 months	< 0.002[a]	< 0.1	< 0.002[a]	< 0.2	< 0.002[a]	< 0.2	< 0.002[a], < 0.003[a]	–	< 0.003[A]	–	< 0.15

[a] limit of detection (LOD)

Table 64b Processing studies on grapes

	GHE-P-10999, C Rawle, 2005			GHE-P-11000, C Rawle, 2005			Mean CPM	GHE-P-11001, C, 2004	GHE-P-11002, C, 2004	GHE-P-11228, A, 2005
	CPM	PF	TCP	CPM	PF	TCP	PF	TCP	TCP	TCP
Grapes	< 0.01		0.08	0.11		0.17		0.06	0.04	0.06
Raisins	< 0.002[b]	–	0.29	< 0.01	< 0.09	0.05	< 0.09	–	–	–
Must	–	–	–	–	–	–	–	< 0.01	0.06, 0.04[a]	0.02
Pomace, dried	–	–	–	–	–	–	–	0.20	0.34, 0.33	0.64
Wine at bottling	–	–	–	–	–	–	–	< 0.01	0.04, 0.03[b]	0.03
Wine after 4 months	–	–	–	–	–	–	–	< 0.01	0.03, 0.03[b]	0.04

[a] Produced by heating. All other process fractions produced by maceration;

[b] limit of detection (LOD)

Tomatoes

Three studies were conducted to determine residues of chlorpyrifos-methyl and TCP in tomatoes and process fractions. The field conditions of the trials are shown in Table 45. The tomatoes were weighed and blanched (plunged into boiling water for one minute maximum then immediately plunged into cool water) and peeled. The proportions of canned tomatoes were two thirds of peeled tomatoes and one third of juice. The peeled tomatoes and juice were filled into glass jars and sterilized at 115 to 120 °C for 10 minutes. Table 65 shows the residues found in the samples analysed

Table 65 Processing studies on tomatoes

	GHE-P-8661, Italy Teasdale, 2000		GHE-P-10988, E, Italy, Rawle, 2005			GHE-P-10993, G, Spain Rawle, 2005			Mean
	CPM	PF	CPM	PF	TCP	CPM	PF	TCP	CPM PF
Tomato	0.24	–	0.22	–	0.03	0.17	–	0.15	–
Washed	0.18	0.75	–	–	–	–	–	–	0.75
Canned	< 0.01	< 0.04	–	–	–	< 0.003[a]	< 0.01	0.03	< 0.025
Juice	< 0.01	< 0.04	< 0.01	< 0.05	0.10	< 0.003[a]	< 0.01	0.03	< 0.033
Puree	0.11	0.46	–	–	–	0.02	0.09	0.08	0.27

[a] limit of detection (LOD)

Barley

Two trials (Reports GHE-P-11006 and GHE-P-11536) were conducted during 2004–2006 to determine residues of chlorpyrifos-methyl, TCP and des-methyl chlorpyrifos-methyl in stored malting barley grain and process fractions (malt sprouts, brewing malt, spent grains, brewer’s yeast and beer) stored under conditions and practice typical of Northern and Southern European Zones. Chlorpyrifos-methyl was applied to the post-harvest grain, prior to storage in a rotary mixer using hand held trigger application equipment or Hege 14 seed dresser equipment at a nominal rate of 5 g ai/tonne grain. Samples were taken after 0 or 6 months of storage and processed according to Figure 5. Residues of chlorpyrifos-methyl and metabolites found in barley and processing products are shown in Table 66.

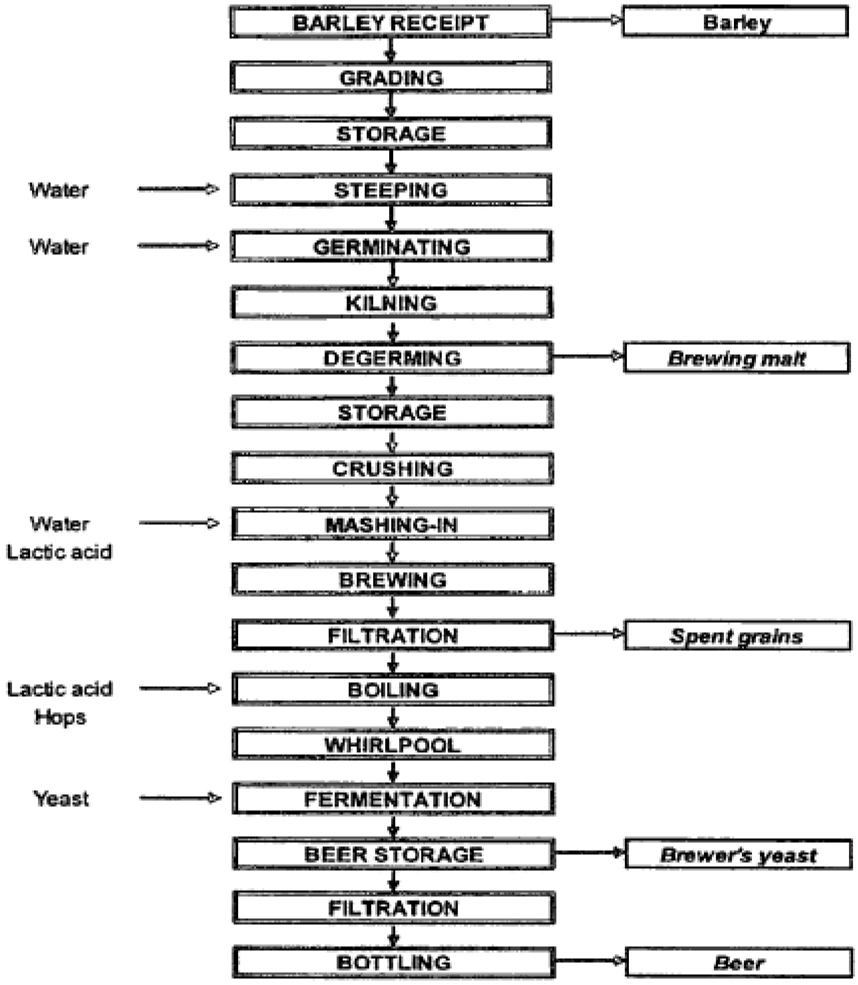


Figure 5 Scheme for processing barley

Table 66 Processing studies in barley

	GHE-P-11006, Trial D, UK 2004, 6 months storage			GHE-P-11536 France, 0 day storage				GHE-P-11536 France, 6 months storage				Mean
	CPM	PF	TCP	CPM	PF	TCP	Des-Me	CPM	PF	TCP	Des-Me	CPM PF
Grain	2.1	–	1.6	2.6	–	1.5	0.03	3.2		2.6	0.52	–
Beer	< 0.002[a]	< 0.001	0.08	< 0.003[c]	< 0.001	0.10	0.02	< 0.003[c]	< 0.001	0.10	0.03	< 0.001
Malt sprouts	0.19	0.09	0.89	0.18[c]	0.07	0.80	0.18	0.28[c]	0.09	0.96	0.22	0.08
Derooted malt	0.32	0.16	1.2									
Spent grains	0.16	0.08	0.24	0.12[b]	0.05	0.22	0.03	0.30[b]	0.09	0.39	0.07	0.06
Flocs	< 0.002[a]	< 0.001	0.15									
Yeast	< 0.002[a]	< 0.001	0.68	< 0.003[c]	< 0.001	0.17	0.04	< 0.003[c]	< 0.001	0.15	0.04	< 0.001

[a] brewing malt and malt sprouts

[b] spent grain including flocs

[c] limit of detection (LOD)

Maize

In one processing study conducted in France, the grain treated twice at 0.56 kg ai/ha was processed according to commercial practices to flour and oil (Rawle, 2005; GHE-10991). No residues of chlorpyrifos-methyl (< LOD of 0.002 mg/kg) was detected in maize flour and oil. Residues in grain were not reported.

Wheat

Two trials were conducted during 2004–2006 to determine residues of chlorpyrifos-methyl, TCP and des-methyl chlorpyrifos-methyl in stored wheat grain and process fractions (flour, bran, wholemeal flour, bread and wholemeal bread). The trials took place in UK and Southern France in typical European wheat grain storage areas. Chlorpyrifos methyl was applied to the post-harvest grain, prior to storage in a rotary mixer using hand held trigger application equipment or Hege 14 seed dresser equipment at a nominal rate of 5 g ai/tonne grain (Figure 6). Process fractions were generated immediately after application and after 6 months of storage. Residues found in the samples are shown in Table 67.

Table 67 Processing studies on wheat treated post harvested with chlorpyrifos-methyl

	GHE-P-11005, Trial D, UK, 2004, 6 months of storage				GHE-P-11537, France, 2006 0 day of storage				GHE-P-11537, France, 2006 6 months storage				
	CPM	PF	TCP	Des-Me	CPM	PF	TCP	Des-Me	CPM	PF	TCP	Des-Me	Mean CPM PF
Grain	3.2	–	2.4	–	3.0	–	2.3	0.03	2.7	–	2.4	0.33	–
White flour	0.70	0.22	0.43	–	0.72	0.24	0.47	0.02	0.59	0.22	0.43	0.08	0.23
White bread	0.27	0.08	0.23	–	0.27	0.09	0.28	0.17	0.21	0.08	0.22	0.21	0.08
Wholemeal flour	2.6	0.8	2.0	–	3.2	1.0	2.2	0.05	3.2	1.2	2.2	0.34	1
Wholemeal bread	1.0	0.33	1.0	–	2.0	0.65	1.3	0.44	1.2	0.47	1.3	0.42	0.48
Wheat germ	9.6	3.0	9.1	–	2.5	0.83	3.4	1.7	5.0	1.9	4.8	2.5	1.9
Bran	9.3	2.9	9.2	–	9.4	3.1	6.2	0.19	7.8	2.9	6.6	0.95	3

In one study conducted by Morel (1975; GHE-P 326), wheat grains were treated post harvested at 1.25 to 3.75 g/tonne and samples collected 7 days after treatment were processed. Residues found in the raw and processed commodities are shown in Table 68.

Table 68 Processing studies on wheat treated post harvested with chlorpyrifos-methyl

Rate	Wheat	Flour	PF	Middlings	PF	Bran	PF	Bread	PF
1.25	0.52	0.16	0.31	1.4	2.69	0.96	1.85	0.01	0.02
2.5	0.92	0.22	0.24	2.2	2.39	1.6	1.74	0.01	0.01
3.75	1.0	0.30	0.30	3.3	3.30	2.2	2.20	0.02	0.02
		Mean PF	0.28	Mean PF	2.8	Mean PF	1.9	Mean PF	0.02

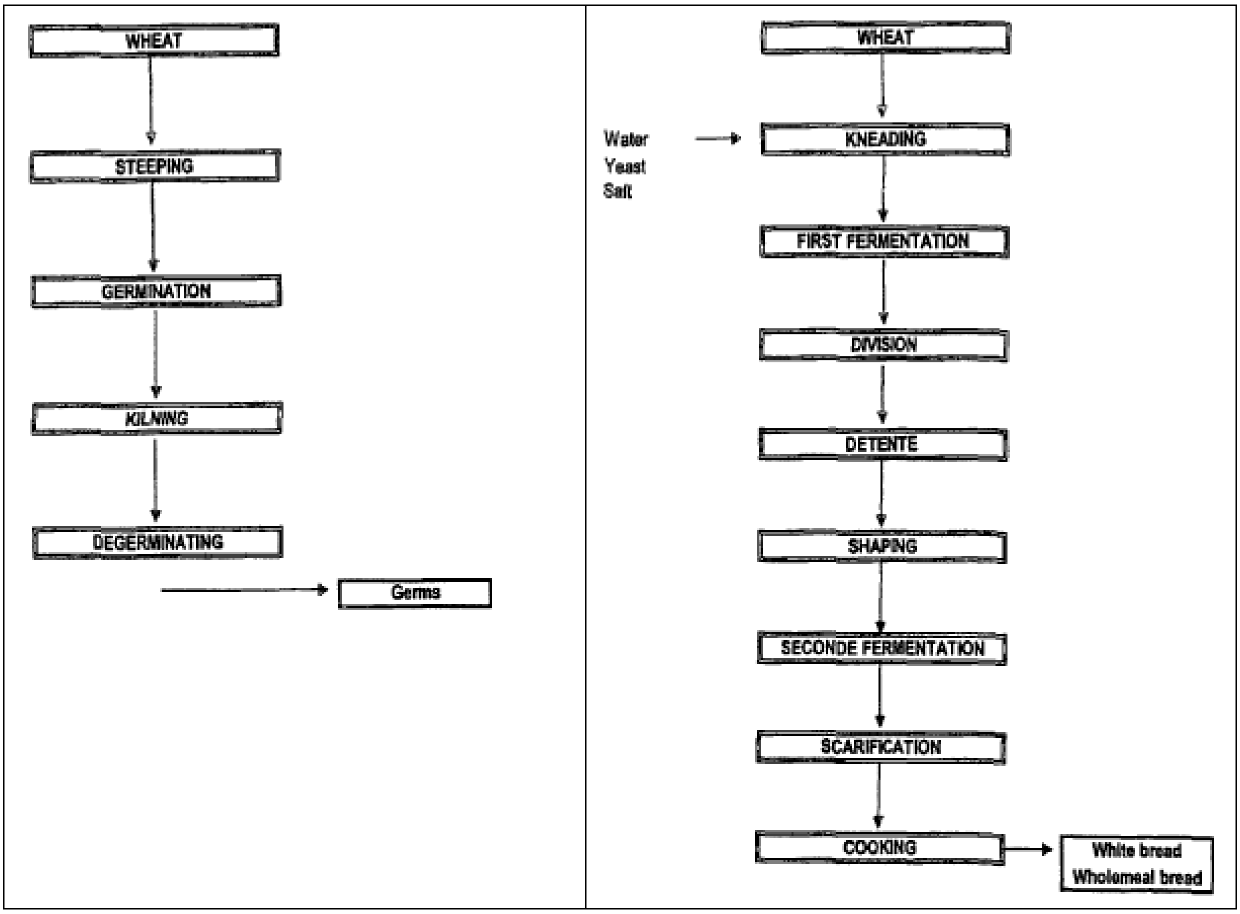


Figure 6 Scheme for processing wheat

Cotton

One trial was conducted to determine residues of chlorpyrifos-methyl and TCP in seed and process fractions (pressed cake, raw oil and refined oil) following two applications of chlorpyrifos-methyl at 0.675 kg ai/ha. Seed samples were collected 56 days after the last application and processed according to commercial practices. Residues in samples are summarised on Table 69.

Table 69 Processing studies on cotton treated with chlorpyrifos-methyl

Study	Substrate	Chlorpyrifos-methyl (mg/kg)	TCP (mg/kg)
GHE-P-11530, D Spain Livingstone, 2008	Seed	< 0.01	0.025
	Pressed Cake	< 0.003[a]	0.020
	Raw Oil	< 0.01	0.030
	Refined Oil	< 0.003[a]	0.025

[a] limit of detection (LOD)

Oil Seed Rape

Two studies were conducted to determine residues of chlorpyrifos-methyl and TCP in seed, and process fractions following a single application of chlorpyrifos-methyl at 0.45 kg ai/ha. Seed samples were collected 105 days after the last application and processed according to commercial practices. Residues in seed and processing fractions samples are summarised in Table 70.

Table 70 Processing studies on wheat treated post harvested with chlorpyrifos-methyl

Study Report (GHE-P-), Trial, Year	Substrate	Chlorpyrifos-methyl (mg/kg)	Total TCP Residue (mg/kg)
11531, D, 2006 Germany, Livingstone, 2007	Seed	< 0.003[a]	0.021
	Pressed cake	< 0.01	0.018
	Raw oil	< 0.01	< 0.003[a]
	Refined oil	< 0.003[a]	0.013
11532, B, 2006 S France Livingstone, 2007	Seed	< 0.002[a]	< 0.01
	Pressed cake	< 0.002[a]	0.025
	Raw oil	< 0.002[a]	< 0.003[a]
	Refined oil	< 0.002[a]	< 0.003[a]

[a] limit of detection (LOD)

RESIDUES IN ANIMAL COMMODITIES

Farm animal feeding studies

Cattle

In a feeding study conducted by Kuper (1978; GH-C-1161), cows were fed 0, 1, 3, 10, 30, and 100 ppm chlorpyrifos-methyl in the diet starting at the lowest level and increasing the dosage every two weeks. The highest feeding level was followed by a two week period where no chlorpyrifos-methyl was added to the feed. Milk samples from each cow were obtained by combining equal amounts of milk from two successive milkings starting with the evening milking. Samples were taken twice during the first week of feeding at each level and three times the second week. Cream samples were obtained by combining 1.5 gal of milk from each of the three cows at one milking. The composite milk was sampled and then put in a separator. The resulting cream was also sampled. Milk samples were analysed for residues of chlorpyrifos-methyl and TCP using methodology validated for concentrations as low as 0.01 ppm. The results are shown in Table 72.

Table 72 Residues (mean) of chlorpyrifos-methyl and TCP found in composite milk and cream samples

Feeding level		Chlorpyrifos-methyl		TCP	
ppm	days	milk	cream	milk	cream
3	13	< 0.01	–	< 0.01	–
10	11 13	– < 0.01	– –	< 0.01 < 0.01	– –
30	9 11 13	0.01 0.01 < 0.01	0.08 0.09 0.06	0.01 0.01 0.01	0.02 0.02 0.02
100	9 11 13	0.03 0.02 0.02	0.40 0.26 0.42	0.04 0.04 0.04	0.05 0.06 0.05

In another study conducted by Kuper (1978; GH-C 1118), calves were fed rations containing 1, 3, 10, 30 and 100 ppm chlorpyrifos-methyl for 28 days. Tissue samples were analysed for chlorpyrifos-methyl and TCP using GC/FPD (LOQ of 0.01 and 0.05 ppm, respectively). The results are shown in Table 73.

Table 73 Average residues of chlorpyrifos-methyl and TCP found in tissues of calves fed chlorpyrifos-methyl for 28 days

Feed	Chlorpyrifos-methyl				TCP [c]			
level, ppm	muscle	liver	kidney	fat	muscle	liver	kidney	fat
1	–	–	–	< 0.01(3)	–	0.07	< 0.05	–
3	–	–	–	0.01, < 0.01 (2)	–	0.15	0.07	–
10	–	–	–	0.02 (2), 0.03	< 0.05	0.44	0.21	< 0.05
30	< 0.01 (3)	< 0.01(3)	< 0.01 (2), 0.01	0.03, 0.05, 0.12	< 0.05	1.2	0.63	0.06
100	< 0.01(3)	< 0.01(3)	0.02, 0.03, 0.05	0.52, 0.59, 0.73	0.08	2.2	1.2	0.08
100 [a]	< 0.01(3)	< 0.01(3)	< 0.01(3)	< 0.01(3)	< 0.05	< 0.05	< 0.05	< 0.05
100 [b]	–	–	–	< 0.01(3)	–	< 0.05	< 0.05	–

[a] after seven-day withdrawal from treated feed

[b] after 14 days withdrawal from treated feed

[c] only the mean values are reported

Swine

Swine were fed rations containing 1, 3, 10, 30 or 100 ppm of chlorpyrifos-methy for 28 days (Kuper and Kutschinski, 1979; GH-C-1233). Tissue samples were analysed for chlorpyrifos-rnethyl and TCP using GC/FPD, validated at 0.01 and 0.05 mg/kg, respectively. The results are shown in Table 74.

Table 74 Average residues of chlorpyrifos-methyl and TCP found in tissues of swine fed chlorpyrifos-methyl for 28 days

Feed	Chlorpyrifos-methyl				TCP [a]			
level, ppm	muscle	liver	kidney	fat	muscle	liver	kidney	fat
1	< 0.01 (3)	–	–	< 0.01(3)	< 0.05	< 0.05	< 0.05	< 0.05
3	< 0.01(3)	–	–	0.02 (3)	< 0.05	0.05	0.05	< 0.05
10	< 0.01(3)	< 0.01(3)	< 0.01(3)	0.05, 0.06, 0.11	< 0.05	0.17	0.14	< 0.05
30	0.03(3)	< 0.01(3)	< 0.01(3)	0.19, 0.22, 0.17	0.08	0.40	0.38	0.06
100	0.14	< 0.01(3)	< 0.01(3)	0.70, 0.62, 0.91	0.23	1.2	1.4	0.22
100 [a]	< 0.01	< 0.01(3)	< 0.01(3)	< 0.01(3)	< 0.05	< 0.05	< 0.05	< 0.05

[a] only mean values are reported

Poultry

Chickens were fed rations containing 1, 3, 10, 30 and 100 ppm chlorpyrifos-methyl for 28 days (Kupper, 1978; GH-C-1155). Eggs were collected on alternate days throughout the test and muscle, fat and liver samples were taken at 0, 7 and 14 days after withdrawal from treated feeds and analysed for chlorpyrifos-methyl and TCP using GC/FPD (LOQ of 0.01 and 0.05 mg/kg, respectively). Residue in tissues and eggs are shown in Table 74.

Table 74 Average residues of chlorpyrifos-methyl and TCP found in tissues of chickens fed chlorpyrifos-methyl for 28 days

Feed	Chlorpyrifos-methyl				TCP[f]			
level, ppm	muscle	fat	liver	eggs	muscle	fat	liver	eggs
10	< 0.01 (6)	< 0.01(6)	–	< 0.01(6)	< 0.05	–	< 0.05	< 0.05
30	< 0.01(6)	0.01 (5), 0.02	< 0.01(6)	< 0.01(6)	< 0.05	< 0.05	0.05	< 0.05
100	0.01	0.06 (2), 0.07 (2), 0.08, 0.04	< 0.01(6)	0.02	< 0.05	< 0.05	0.05	0.06
100	< 0.01(6)[a]	< 0.01[a] (6)	< 0.01[a](6)	0.01[b]	< 0.05[a]	< 0.05[a]	< 0.05[a]	< 0.05[b]
100				< 0.01[c]			< 0.05[e]	< 0.05[c]
100				< 0.01[d]				< 0.05[d]

[a] after seven-day withdrawal from treated feed

[b] after two-day withdrawal from treated feed

[c] after four-day withdrawal from treated feed

[d] after six-day withdrawal from treated feed

[e] after fourteen-day withdrawal from treated feed

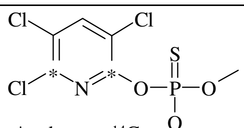
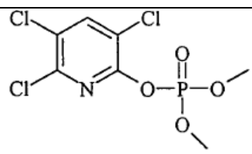
f only mean levels are reported

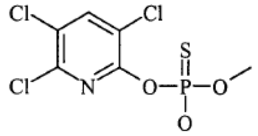
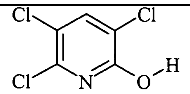
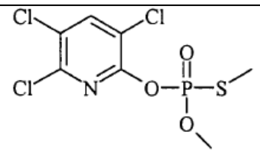
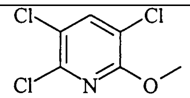
RESIDUES IN FOOD IN COMMERCE AND CONSUMPTION

Monitoring data of chlorpyrifos-methyl in various crops is available from Working Party on Pesticide Residues (WPPR) annual reports over years 1995 to 2007 (http://www.pesticides.gov.uk), the report of the U.S. Food and Drug Administration's (FDA) on pesticide residue monitoring program over 2004 to 2006 (http://www.cfsan.fda.gov) and the European Commission Staff Working Document on Monitoring of Pesticide Residues over 1996 to 2006 (www.europa.eu.int/comm/food/fvo/specialreports/pesticides_index_en.htm).

APPRAISAL

Chlorpyrifos-methyl, an organophosphate insecticide has been evaluated by the JMPR several times since 1975. The compound was listed at the Thirty-ninth Session of the CCPR for periodic review by the 2009 JMPR for both toxicology and residues. An ADI of 0–0.01 mg/kg bw and a ARfD of 0.1 mg/kg bw was established by the Meeting. The manufacturer submitted data on metabolism of chlorpyrifos-methyl in farm animals and plants, environmental fate, methods of analysis, GAP information, supervised residue trials on citrus, pome fruit, stone fruits, cherries, grapes, strawberries, kiwi fruit, onion, tomato, peppers, sugar beet, potato, carrot, artichoke, green beans, oilseed rape, cotton and cereals, and processing studies on various crops. Additionally, metabolism studies on chlorpyrifos in plants and of TCP and TMP in soils were submitted. The structure of the parent compounds and main metabolites are shown below.

^{14}C-labelled chlorpyrifos-methyl (O,O-dimethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate)	 * - denotes ^{14}C	OXM - Chlorpyrifos-methyl oxon	

DEM Des-methyl chlorpyrifos-methyl		TCP 3,5,6-trichloro-2-pyridinol	
S-methyl isomer chlorpyrifos-methyl		TMP 2-methoxy-3,5,6-trichloropyridine	

Animal metabolism

The metabolism of chlorpyrifos-methyl in rats was evaluated by the WHO panel at the present Meeting. The compound was found to be rapidly and extensively absorbed in the rat following a single oral dose (16 or 30 mg/kg bw). Excretion was rapid (largely within 24 hours) and primarily in the urine. Urinary metabolites were identified as the glucuronide conjugate of TCP (68.6%), free TCP (13.8%) and DEM (17.8%). The fate of the phosphorothioate moiety was not investigated.

Two lactating goats were fed [^{14}C]chlorpyrifos-methyl at 32 mg/kg feed, administered in gelatin capsules, twice a day for 7 days then sacrificed 14 h after the final dose and samples taken. Liver, kidney, fat and milk fat were extracted with acetonitrile (ACN), the extract partitioned with hexane and the ACN layer analysed by radio TLC and HPLC. The non-extracted residue (NER) was subject to base hydrolysis. Recovery was > 91% of administered dose and approximately 95% of recovered radioactivity was in the urine (~22 mg/kg chlorpyrifos-methyl eq.). Highest total radioactive residues (TRR) were found in kidney and liver (0.62 and 0.40 mg/kg chlorpyrifos-methyl eq., respectively). Residues in fat and skeletal muscle were 0.14 and 0.047 mg/kg, respectively. In milk, residues concentrated in milk fat (0.115 mg/kg), with levels over 4 times that found in whole milk. The majority of the residues found in liver and kidney were TCP, 66.7% TRR (0.24 mg/kg) and 74.2% TRR (0.45 mg/kg) respectively. In fat and milk fat, the parent compound was predominant (55.3 and 61.8% TRR, respectively), at levels of 0.06 mg/kg. The S-methyl isomer and DEM were also detected in all matrices, at levels < 10% TRR each. Base extracts of liver and kidney showed no parent compound and only TCP as metabolite (10.56% TRR in liver and 6.8% TRR in kidney). Base extracts of insoluble tissue showed traces of chlorpyrifos-methyl (up to 0.2% TRR), TCP plus S-methyl isomer (up to 9% TRR) and up to 1% TRR of DEM in kidney.

Four laying hens received a daily dose of labelled [^{14}C]chlorpyrifos-methyl at a dietary intake level equivalent to 25 mg/kg feed for 10 days. The birds were sacrificed approximately 16 h after the tenth dose for tissue collection. Tissue and egg samples were extracted using ACN, the extracts partitioned with hexane and analysed by TLC and HPLC. The unextracted residues in egg yolk and kidney were subjected to base hydrolysis and the extracts analysed by LSC. The majority of the radioactivity (approximately 70% applied radioactivity) was present in the excreta. Radioactivity was low in tissues, exceeding 0.1 mg/kg only in fat (0.07–0.35 mg/kg chlorpyrifos-methyl eq.), kidney (0.09–0.15 mg/kg) and egg yolk (< 0.01–0.10 mg/kg). The highest level in muscle was 0.02 mg/kg. The majority of the residues present in kidney were the TCP (approximately 77% TRR) and DEM metabolites (22% TRR). Fat contained mainly the parent (approximately 75% TRR) and egg yolk contained roughly equal quantities of all three components (16 to 23% TRR).

In summary, chlorpyrifos-methyl is metabolized in goats and hens primarily to TCP (over 60% TRR). Residues concentrated in fat tissue and milk fat. This metabolic pathway was also found in rats.

Plant metabolism

The Meeting received plant metabolism studies with chlorpyrifos-methyl on tomato and cereal grains, and chlorpyrifos on citrus, cabbage, peas and radish.

Structurally, chlorpyrifos (O,O-diethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate) differs from chlorpyrifos-methyl (O,O-dimethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate) only in the phosphorothioester moiety, as the first is a diethyl and the second a dimethyl ester. Consequently, knowledge of chlorpyrifos metabolism in plants is useful in determining the relevant residues of chlorpyrifos-methyl, for enforcement purposes.

Chlorpyrifos-methyl

In a tomato study [^{14}C]chlorpyrifos-methyl was applied to plants at a rate equivalent to 0.99 kg ai/ha, within the seasonal label rate range of 0.5 to 3.0 kg ai/ha. Fruit and leaf samples were collected at 0, 5, 13, 26 and 42 days after application (DAT), rinsed first with dichloromethane (DCM) and then with ACN. A concentrate of the 26 DAT fruit extracted aqueous phase was subjected to treatment using ß-glucosidase. The stability of DEM during extraction was evaluated by adding [^{14}C]-DEM (76% purity) to a 5 DAT rinsed control tomato fruit sample. An aliquot of a [^{14}C]-DEM solution (74.8% purity) was also subjected to the enzyme procedure. In rinsed fruit, the radioactivity decreased from 86.7% TRR at 0 DAT to 0.8% TRR at 26 DAT. TRR values also declined over the time in leaves. By 13 DAT, 15% remained in the tissues. About 100% of the [^{14}C]-DEM radioactivity was recovered during the procedure. Up to 5 DAT, most of the residues were identified as chlorpyrifos-methyl, which was metabolized primarily to TCP (11.3% TRR at 13 DAT) and polar residues (19.6% TRR at 13 DAT). For all fruit samples, no more than 2.5% of TRR was found in the region where DEM was expected to elute. TMP, the S-methyl isomer, and OXN were not detected in any sample. The β-g1ucosidase treatment liberated 6.5% TRR, eluting in the TCP region. About 62 and 24% TRR of [^{14}C]-DEM solution submitted to the enzyme procedure eluted in the DEM and TCP regions, respectively; about 17% of the radioactivity was lost during the procedure. As was found for fruit extracts, chlorpyrifos-methyl was metabolized in leaf rinses primarily to TCP and to polar residues.

An EC formulation of [^{14}C]chlorpyrifos-methyl was applied to wheat and maize grain at a rate equivalent to 32.4 mg ai/kg grain with samples of the treated grain stored at 25±1 °C for 180 days. At the end of the experiment, the parent compound represented about ⅓ of the applied radioactivity (AR) in maize and 45% in wheat. TCP and DEM represented 39 and 24% AR in maize, respectively, and 19% AR each in wheat.

Chlorpyrifos

A single orange tree (Washington navel) was sprayed with [^{14}C]chlorpyrifos at a rate equivalent to 3.97 kg ai/ha. TRR levels in both leaves and fruit declined by 50% or more after 21 days after treatment. Over 99% of the whole fruit TRR remained associated with the peel, mostly as chlorpyrifos. OXON, TCP and DES were found at low levels (up to 0.5% TRR; 0.22 mg/kg chlorpyrifos eq.). Enzyme hydrolysis of the leaf aqueous soluble fraction, approximately 60% of the sample radioactivity was extracted into organic solvent, being 32.0% TCP. A base hydrolysis of this same fraction showed 80% of the residues as TCP. About 5% of NER was solubilised by enzyme digestion, 15% by acid hydrolysis; approximately 85% of the bound radioactivity remained associated with the acid detergent fibre. About 90% of the leaf NER was solubilised by base hydrolysis. Subsequent partitioning of the aqueous phase from this step resulted in the extraction of 82.9% of the solubilised radioactivity into organic solvent, composed of at least seven components, with TCP representing 36.7% TRR.

Cabbage plants received one foliar spray application of [^{14}C]chlorpyrifos at a rate equivalent to 1.43 kg ai/ha. Plants were sampled at 0, 7, 14, 21 and 42 days after application (DAT) with TRR values declining over the 42 days. At 7 DAT, organic extracts contained 42% of TRR, mostly as chlorpyrifos. TCP levels increased from 2% TRR at 7 DAT to 6.1% TRR at 21 DAT. The maximum level of DES was found at 14 DAT (5.3% TRR). Chlorpyrifos appears to be metabolized to TCP, which is extensively conjugated with glucose and malonic acid.

Potted pea plants were treated with one application of [^{14}C]chlorpyrifos, applied at a rate equivalent to 1.9 kg ai/ha, with samples collected weekly up to 28 DAT. Radioactivity declined rapidly during the first 7 days; in pods, the levels had reached 0.25% of TRR at the end of the study. There was a steady decrease of chlorpyrifos over time (from 89.6% of TRR at 0 DAT to 3.8% of TRR by day 28 in pea pods), while TCP and TCP conjugates increased during this period (8.7 and 42.5% of TRR, respectively). Conjugates consisted of at least five different sugar or sugar plus malonic acid conjugates of TCP.

A single foliar spray of [^{14}C]chlorpyrifos was applied to radish plants at rate equivalent to 1.92 kg ai/ha then sampled weekly up to 35 days DAT. TRR in the rinsed tops decreased from 58.7 mg/kg chlorpyrifos eq. on Day 0 to 1.6 ma/kg at 35 DAT. Whereas the levels in roots remained relatively unchanged during the course of the study at about 2 mg/kg. Residues in the aqueous phase increased during the course of the experiment (from 0.06 to 38.5% of TRR in roots), representing mostly TCP conjugates. Chlorpyrifos residues decreased to 14.8% TRR in tops and 41.5% of TRR in roots at 35 DAT, while TCP reached 2.5% of TRR in tops at the end of the experiment. Enzyme digestion was more effective at releasing NER residues (up to 20% of TRR), with over 80% of this radioactivity being aqueous soluble.

In summary, metabolism studies conducted with chlorpyrifos-methyl and chlorpyrifos in plants indicates a single primary metabolic pathway that involves hydrolysis of the phosphate ester to give primarily TCP and polar residues, mainly TCP conjugates of glucose and malonic acid.

Environmental fate

The Meeting received information on soil aerobic metabolism and soil photolysis.

In four agricultural soils [^{14}C]Chlorpyrifos-methyl, at a rate equivalent to 0.5 kg ai/ha, was incubated under aerobic conditions at 40% moisture-holding capacity (MHC) and 20 °C. Samples were taken at regular intervals up to 100 DAT, extracted with solvent and analysed by LSC and HPLC. The initial degradation product in all soils was TCP, accounting for up to 65% of applied radioactivity (AR) within 7 days, which was subsequently mineralised to $^{14}CO_2$ (23–69% of AR at 100 days, depending upon soil type). Nine minor degradation products were also observed (up to 16% of AR), one of which at approximately 2% of AR co-chromatographed with TMP. Levels of NER reached 17–26% of AR at 100 days, and little or no organic volatiles were observed. Soil half-lives, estimated by best-fit kinetics, ranged from 0.63 days (sandy clay loam) to 3.6 days (loamy sand).

The route of aerobic degradation of [^{14}C]TCP was investigated in the laboratory in four European soils treated at 250 g/ha in a soil depth of 5 cm and a soil bulk density of 1.5 g/cm^3, adjusted to 40% maximum water holding capacity (WHC_{max}) and incubated at 20 °C in the dark. The amounts of TCP and its degradation products in the extracts were determined by HPLC and confirmed by TLC. For the non-sterile soils, the overall recovery ranged between 83.1 and 103.7% of AR. The level of radioactivity in the soil extracts declined to between 6.6 and 50.8% of AR after 120 days. The level of NER and of evolved $^{14}CO_2$ increased throughout the incubation period (up to 58% of AR), whilst the levels of ^{14}C organic volatiles were very low throughout (< 0.5% of AR). TCP was the major component present in all soil extracts, dropping to about 32% of AR after 120 days in the Marcham sandy clay loam soil. At this time, TMP level reached 13% of AR.

In top soil taken from three USA sites [^{14}C]TMP was assayed at a concentration of approximately 1.0 mg/kg of soil at 100% or 35% moisture content, ⅓ bar soil moisture tension and 25 °C. Extensive mineralization to CO_2 (in the order of 70% of AR) was observed in the two silty soils but not in the sandy soil, a known poor degrader, where TMP accounted for about 70% of AR after 300 days. Low levels of TCP (about 10% of AR) were observed in all three soils.

The aerobic degradation of [^{14}C]Chlorpyrifos-methyl was investigated in sandy loam and clay loam water/sediments treated at 0.5 kg ai/ha. The samples were incubated under an aerobic/anaerobic gradient in the dark at 17–20 °C. $^{14}CO_2$ and other volatile organic compounds accounted for up to 11% of AR. The radioactivity associated with surface water declined from about 80% at time zero to 21–38% at the end of the experiment. Degradation of chlorpyrifos-methyl was rapid in both systems with less than 2% of AR remaining after 100 days. DT_{50} values in the sandy loam and clay loam systems were 2.6 and 25.4 days, respectively. The principal degradation product was TCP, which was detected at maximum levels of 83 and 62% in 30 day sandy loam and clay loam samples, respectively.

The aqueous photolytic degradation rate and quantum yield of [^{14}C]chlorpyrifos-methyl solutions (8.8–13.7 mg/L) in water/ACN (9:1) were determined at 20 °C irradiated under a 450 W Xenon high-pressure lamp at 290 nm for periods of up to eight hours. Chlorpyrifos-methyl degraded with a calculated quantum yield of 2.6×10^{-3} and DT_{50} varying according to season and weather conditions, from 1.8 days to 3.8 months.

In summary, chlorpyrifos-methyl is degraded in soils and sediments to TCP, which is either directly mineralized to CO_2, or via TMP.

Methods of residue analysis

The Meeting received data on analytical methods for chlorpyrifos-methyl in various plant and animal commodities. In general, for plant commodities the methods involved extraction with acetone/water. The extract was partitioned into hexane and quantified by GC/FPD or cleaned-up with C_{18} SPE and quantified by HPLC/MS/MS or GC/NCI-MS. The methods were satisfactorily validated at a LOQ of 0.01 mg/kg, with a LOD of 0.002 or 0.003 mg/kg.

In kidney, liver, milk, muscle and egg the compound was extracted with acetone, the extract cleaned-up in a C_{18} SPE and chlorpyrifos-methyl quantified by GC/NCI-MS. LOQ for chlorpyrifos-methyl was 0.01 mg/kg.

Although a multiresidue method to analyse chlorpyrifos-methyl was not provided, the Meeting is aware of the availability of multiresidue methods that include the compound.

Stability of pesticide residues in stored analytical samples

The Meeting received data on the stability of residues in various plant and animal commodities.

In one study conducted with oranges, grapes, wine, tomato, tomato juice and wheat fortified at 0.10 mg/kg chlorpyrifos-methyl, from 80 to 106% of the compound remained after 90 days of storage at -20 °C. Another study on various plant commodities, fortified at 0.10 mg/kg, chlorpyrifos-methyl was shown to be stable for up to 18 months when stored at -18 °C, with over 70% of the compound remaining on completion of the study.

In a study conducted with cattle tissues and milk, chlorpyrifos-methyl remained stable (75–85% remained) in samples fortified at 0.10 mg/kg after 90 days under frozen conditions (-20 °C). Almost half of chlorpyrifos-methyl present in fortified egg samples was lost during storage, suggesting instability of the compound in this matrix.

Definition of the residue

Chlorpyrifos-methyl was shown to metabolize in animals and plants primarily to TCP. This metabolite is the major residue in goat liver and kidney and hen kidney; it represented over 20% TRR in tomato 26 days after the last treatment and 39% TRR in maize after 180 days of storage. TCP is also the main metabolite in plants treated with chlorpyrifos.

Residues of chlorpyrifos-methyl were found to concentrate in fat tissue and milk fat. The compound has a log K_{ow} of 4.

Even though TCP can be a significant part of the residues in plant and animals treated with chlorpyrifos-methyl, it is also a major metabolite formed following the application of chlorpyrifos. As a consequence, TCP is not considered as a specific residue marker of the use of chlorpyrifos-methyl.

TCP lacks the phosphate ester moiety, responsible for the cholinesterase inhibiting capacity of chlorpyrifos-methyl. Data from repeated dose studies show that TCP is about 10 times less toxic than the parent compound. Also, TCP levels in crops and animal products are generally not higher than those of the parent compound. As a consequence the Meeting agreed that dietary human exposure to this metabolite is not considered of toxicological concern.

The current residue definition for chlorpyrifos-methyl in plant and animal commodities, for both enforcement and dietary risk assessment purposes is: *Chlorpyrifos-methyl (fat-soluble).*

The Meeting agreed to confirm this residue definition of chlorpyrifos-methyl: *Chlorpyrifos-methyl*.

The residue is fat soluble.

Results of supervised trials on crops

The NAFTA calculator was used as a tool in the estimation of the maximum residue level from the selected residue data set obtained from trials conducted according to GAP. As a first step, the Meeting reviewed all relevant factors related to each data set in arriving at a best estimate of the maximum residue level using expert judgment. The NAFTA calculator was then employed. If use of the statistical calculation spreadsheet resulted in the derivation of a different value from that recommended by the JMPR, a brief explanation of the deviation is provided.

As no chlorpyrifos-methyl residue trial data was submitted for the following crops; cabbage head, Chinese cabbage, common beans, date, lettuce head, mushrooms, radish, rice and tea green black, the Meeting withdrew its previous maximum residue level recommendations.

Citrus fruits

Chlorpyrifos-methyl is registered in oranges, mandarins, clementines and lemons in Italy at a GAP rate of 0.055 kg ai/hL. In Spain, the approved rate is 0.068–0.09 kg ai/hL. In both countries the PHI is 15 days. Residue data from 51 trials conducted on various citrus fruits conducted from 1991 to 2006 were submitted.

Fifteen trials were conducted in Italy in oranges, mandarins and clementines. In seven trials conducted according to maximum Spanish GAP rate, residues (whole fruit) at 15 days PHI in mandarins and clementines were 0.18, 0.23 and 0.52 mg/kg and in oranges 0.16, 0.26, 0.58 and 0.89 mg/kg. Residues in mandarin pulp were < 0.01 (< LOD of 0.003 mg/kg) and 0.01 mg/kg. Eight trials did not match GAP.

Thirty six trials were conducted in Spain in lemons, oranges, mandarins and clementines. In eight trials conducted according to the maximum Spanish GAP rate, residues at 15 days PHI (whole fruit) were 0.09, 0.21, 0.33 and 0.69 mg/kg in mandarins and 0.09, 0.11, 0.11 and 0.18 mg/kg in oranges. Residues were < 0.01 (< LOD of 0.003 mg/kg) and 0.01 mg/kg in mandarin pulp. Twenty eight trials did not mach GAP.

The Meeting noted that the residue populations of chlorpyrifos-methyl in mandarins, clementine and oranges from 15 trials conducted according to Spanish GAP are within the same range and agreed to use a combined data set of: 0.09, 0.09, 0.11, 0.11, 0.16, 0.18, 0.18, 0.21, 0.23, 0.26, 0.33, 0.52, 0.58, 0.69 and 0.89 mg/kg. Residues in pulp from four trials were < 0.01 (2) (< LOD of 0.003 mg/kg) and 0.01 (2) mg/kg.

There is no current GAP for chlorpyrifos-methyl covering the citrus crop group; however the GAPs for the individual crops within the group are comparable. The Meeting agreed that as the registered uses cover the main crops within the group an estimate could be done for citrus crop group.

The Meeting estimated a maximum residue level of 2 mg/kg for chlorpyrifos-methyl in citrus fruit. The Meeting also estimated a HR of 0.01 mg/kg and a STMR of 0.01 mg/kg based on the residue data in citrus pulp.

A maximum residue level estimate of 1.4 mg/kg was derived from the use of the NAFTA calculator. The Meeting applied the JMPR procedure of using one significant figure for residues below 10 mg/kg.

The Meeting withdraws its previous recommendation of 0.5 mg/k for chlorpyrifos-methyl in oranges.

Pome fruits

Chlorpyrifos-methyl is registered in apples and pears in Italy (maximum rate of 0.077 kg ai/hL), in pome fruit in Spain (maximum rate of 0.09 kg ai/hL) and in Hungary (maximum rate of 0.76 kg ai/ha; 800–1000 L/ha), with a 15 day PHI. It is also approved for use in pome fruit in Switzerland, (maximum rate of 0.76 kg ai/ha), Poland (maximum rate of 0.6 kg ai/ha; 500–750 L/ha) and Greece (maximum rate of 0.056 kg ai/hL), with a PHI of 21 days. A total of 72 trials conducted in Europe from 1999 to 2007 in apple and pears were submitted. Decline studies showed that residues were still decreasing between 15 and 21 days after application

In two trials conducted in Austria, residues were 0.02 mg/kg in apple at 21 days PHI, matching GAP in Poland, and 0.05 mg/kg in pear at 14 days PHI, matching GAP in Hungary.

Two trials conducted in Belgium did not match GAP.

Thirty six trials were conducted in France (north and south). In 14 trials conducted in the south matching Spanish GAP, residues at 15 days PHI were: < 0.01 (< LOD of 0.003 mg/kg), 0.03 and 0.16 mg/kg in pears and 0.02, 0.03, 0.04, 0.07 (2), 0.08, 0.10 (2), 0.19, 0.20, 0.22 mg/kg in apples. In 13 trials matching Swiss or Polish GAP, residues at 21 days PHI were: < 0.01 (< LOD of 0.003 mg/kg), < 0.01, 0.02, 0.03, 0.05, 0.07 and 0.08 mg/kg in pears and 0.02, 0.03, 0.04, 0.08, 0.09 and 0.15 mg/kg in apples. Eighteen trials did not match any GAP.

Seven trials were conducted in Germany in apples. In four trials matching Hungarian GAP, residues within 15 days PHI were 0.02 (2), 0.05 and 0.56 mg/kg. One trial matched Swiss GAP with residues at 21 days PHI of 0.03 mg/kg. Two trials did not match GAP.

Four trials were conducted in Greece matched Spanish GAP. Residues at 15 days PHI were 0.02 and 0.04 mg/kg in pear and 0.15 and 0.19 mg/kg in apple.

Seven trials were conducted in Italy. In five trials matching Spanish GAP, residues at 15 days PHI were 0.02 (2) mg/kg in pears and 0.03, 0.06 and 0.08 mg/kg in apple. Two trials did not match GAP.

In three trials conducted in Poland according to GAP, residues at 21 days PHI were < 0.01 (< LOD of 0.003 mg/kg) and 0.01 mg/kg in apple and 0.02 mg/kg in pears.

Nine trials were conducted in Spain. In two trials conducted according to GAP, residues at 15 days PHI were 0.03 mg/kg in apple and 0.08 mg/kg in pears. Seven trials did not match GAP.

Two trials conducted in the United Kingdom did not match GAP.

Residues in pears from nine trials with a PHI of 15 days were: < 0.01 (< LOD of 0.003 mg/kg), 0.02 (3), 0.03, 0.04, 0.05, 0.08 and 0.16 mg/kg.

Residues in apples from 21 trials conducted at a 15 day PHI were: 0.02 (2), 0.03 (3), 0.04, 0.05, 0.06, 0.07 (3), 0.08 (2), 0.10 (2), 0.15, 0.19 (2), 0.20, 0.22 and 0.56 mg/kg

Residues in pears from nine trials conducted at a 21 day PHI were: < 0.01 (< LOD of 0.003 mg/kg), < 0.01, 0.02 (3), 0.03, 0.05, 0.07 and 0.08 mg/kg

Residues in apples from nine trials conducted at a 21 day PHI were: < 0.01 (< LOD of 0.003 mg/kg), 0.01, 0.02, 0.03 (2), 0.04, 0.08, 0.09 and 0.15 mg/kg.

The Meeting decided that data from trials in apples and pears, done according to GAP, were from different populations (Mann-Whitney U test) and could not be combined. The Meeting agreed that the residue data from apples at a PHI of 15 days, which had the highest residues and reflected the critical GAP in Europe, could be used for the estimation for pome fruits.

The Meeting estimated a maximum residue level of 1 mg/kg, a HR of 0.56 mg/kg and a STMR of 0.07 mg/kg for chlorpyrifos-methyl in pome fruits.

The maximum residue level estimate derived from use of the NAFTA calculator was 0.6 mg/kg. The Meeting noted that the majority of trials were conducted at the lower 25% range of the GAP rate, including the trial that gave rise to the highest residue (0.56 mg/kg). As a consequence the Meeting considered that the estimate derived from the calculation using the NAFTA spreadsheet may not accommodate all uses of chlorpyrifos-methyl in pome fruit that followed GAP.

The Meeting agreed to withdraw its previous recommendations of 0.5 mg/kg for chlorpyrifos-methyl in apple

Stone fruits

Chlorpyrifos-methyl is registered in Italy peaches and in Spain in peaches and nectarines at a maximum rate of 0.09 kg ai/h, with a PHI of 15 days. In Bulgaria, the rate is up to 0.055 kg ai/hL for stone fruits with a PHI of 14 days. In Greece, the PHI for stone fruit is 21 days (0.056 kg ai/hL) and 30 days (0.6 kg ai/ha) in Hungary for peaches and apricots. A total of 34 European trials were submitted for peaches and apricots completed between 1992 and 2007. Decline studies showed that residues were still decreasing between 15 and 21 days after application

Ten trials were conducted in southern France. In five trials matching Spanish GAP, residues in whole fruit at 14–15 days PHI were < 0.01 and 0.02 mg/kg in apricots and < 0.01, 0.01 and 0.02 mg/kg in peaches; residues in pulp (pitted fruit) were < 0.01 (2), 0.01 and 0.02 (2) mg/kg. Three trials matched GAP in Greece, with residues in whole fruit and pulp of apricots (1 trial) and peaches at 21 days PHI of < 0.01 (3) mg/kg. Two trials did not match GAP

From five trials conducted in Greece, according to Italian GAP, residues in whole fruit at a PHI of 15 days were: < 0.01 (< LOD of 0.003 mg/kg), 0.01 and 0.04 mg/kg in apricots and < 0.01 and 0.17 mg/kg in peaches. Residues in pulp were < 0.01 (< LOD of 0.003 mg/kg), 0.01 and 0.04 mg/kg in apricot and < 0.01 mg/kg in peaches.

Eleven trials were conducted in Italy. In eight trials conducted according to GAP, residues at a PHI of 15 days were: < 0.01 mg/kg in apricots and 0.01, 0.02 (3), 0.06, 0.07 and 0.08 mg/kg in peaches; residues in pulp were < 0.01 mg/kg in apricot and 0.01, 0.02 (3), 0.06, 0.07 and 0.09 mg/kg in peaches. One trial matching Greek GAP, residues at a PHI of 21 days was < 0.01 mg/kg in peach whole fruit and pulp.

Eight trials were conducted in Spain. In three trial matching GAP, residues in whole fruit at a PHI of 15 days were: < 0.01 mg/kg (< LOD of 0.003 mg/kg) in apricots and 0.02 and 0.23 mg/kg in peaches; in pulp, residues were < 0.01 mg/kg (< LOD of 0.003 mg/kg) in apricots and 0.02 and 0.26 mg/kg in peaches. Five trials matched Greek GAP with residues at a PHI of 21 days of < 0.01 (2) (< LOD of 0.002 mg/kg) and < 0.01 in apricots and 0.02 and 0.03 mg/kg in peaches; in pulp, residues were < 0.01 (2) (< LOD of 0.002 mg/kg), < 0.01 and 0.02 mg/kg.

Residues in whole fruit and pulp of apricots from seven trials matching GAP with a PHI of 15 days were: < 0.01 (2) (< LOD of 0.003 mg/kg), < 0.01 (2), 0.01, 0.02 and 0.04 mg/kg.

Residues in whole fruit of peaches from 14 trials matching GAP with a PHI of 15 days were: < 0.01 (2), 0.01 (2), 0.02 (5), 0.06, 0.07, 0.08, 0.17 and 0.23 mg/kg. In pulp (pitted fruit), residues were: < 0.01 (3), 0.01 (2), 0.02 (5), 0.06, 0.07, 0.09 and 0.26 mg/kg.

Residues in whole fruit and pulp of apricots from four trials according to GAP at 21 days PHI were: < 0.01 (2) (< LOD of 0.002 mg/kg) and < 0.01 (2) mg/kg,

Residues in peaches from five trials matching GAP at a PHI of 21 days were: < 0.01 (3), 0.02 and 0.03 mg/kg. In pulp, residues were < 0.01 (2) (< LOD of 0.002 mg/kg), < 0.01 (2) and 0.02 mg/kg.

Chlorpyrifos-methyl is registered for use in cherries in Hungary at 0.6 kg ai/ha and 800–1000 L/ha (0.048–0.072 kg ai/hL) with a 30 day PHI. Eleven trials were conducted in Austria, Germany, Hungary and Poland in 2006/2007. Decline studies showed that residues declined rapidly during the first 5 days following application then relatively slowly thereafter. Consequently, data from samples collected 21 days after application (30% shorter PHI than GAP of 30 days) were accepted as being comparable to GAP. Residues from the 11 trials were < 0.01 (9) (< LOD of 0.003 mg/kg) and < 0.01 (2) mg/kg in whole fruit and pulp.

The Meeting agreed that the residue population from trials conducted at a PHI of 15 days in peaches had the highest residues and could be used for the estimation of a maximum residue level for stone fruit.

The Meeting estimated a maximum residue level of 0.5 mg/kg for chlorpyrifos-methyl in stone fruits. Based on the residue data in peach pulp (pitted fruit), the Meeting also estimated a HR of 0.26 mg/kg and a STMR of 0.02 mg/kg.

The maximum residue level estimate derived from use of the NAFTA calculator was 0.15 mg/kg. However, the Meeting noted that most of the trials were conducted at the lower 25% range of the GAP rate, including the trial that gave rise to the highest residue (0.23 mg/kg). The Meeting considered that the estimate derived from the NAFTA spreadsheet calculation may not accommodate all uses of chlorpyrifos-methyl in stone fruit that followed maximum GAP.

The Meeting withdraws its previous recommendations of 0.5 mg/kg for chlorpyrifos-methyl in peaches.

Grapes

Chlorpyrifos-methyl is registered in grapes in Italy at a rate up to 0.045 kg ai/hL and in Spain at up to 0.09 kg ai/hL, both with a PHI of 15 days. In France, the PHI is 21 days (0.338 kg ai/ha) and in Hungary 30 days (0.52–0.60 kg ai/ha; 800–1000L/ha). In Chile, the compound is recommended as a post-harvest treatment. Data was submitted from 63 trials conducted in red and white grapes (table and wine) from 1998 to 2007.

Three trials were conducted in Austria, from which one matched French GAP, with residues at a PHI of 21 days of < 0.01 mg/kg.

One trial conducted in Chile using foliar application did not matched GAP.

Twenty three trials were conducted in France. In two trials conducted in the south according to Spanish GAP, residues at a 15 day PHI were: < 0.01 and 0.07 mg/kg. Nine trials matched the French or Hungarian GAP, and residues were: < 0.01 (2) (< LOD of 0.003 mg/kg), < 0.01 (2), 0.01 (2), 0.03, and 0.04 mg/kg at a 21 day PHI and < 0.01 mg/kg at a 30 day PHI. The remaining trials did not match GAP.

Eleven trials were conducted in Germany, from which seven matched the French or Hungarian GAP, where residues found were: < 0.01 (2), 0.01 and 0.02 (3) mg/kg at a 21 day PHI and < 0.01 mg/kg at a 30 day PHI. The remaining trials did not match GAP.

Five trials were conducted in Greece, two matched the Italian GAP with residues at a 15 day PHI of 0.03 and 0.07 mg/kg. One trial matching French GAP gave residues at a 21 day PHI of < 0.01 mg/kg (< LOD of 0.003 mg/kg). Two trials did not match southern European GAP.

Two trials were conducted in Hungary, one matching French GAP, with residues at a PHI of 21 days of 0.01 mg/kg. One trial did not match any GAP from northern Europe.

Six trials were conducted in Italy, of which four matched GAP, where residues found at a PHI of 15 days were: < 0.01 (< LOD of 0.003 mg/kg), < 0.01, 0.01 and 0.12 mg/kg. One trial conducted in the north matched French GAP with residues at a 21 day PHI of < 0.01 mg/kg. One trial did not match GAP.

One trial was conducted in Poland according to French GAP with residues at a 21 day PHI of 0.04 mg/kg.

Twelve trials were conducted in Spain. In nine trials conducted according to GAP, residues at a 15 day PHI were: < 0.01 (< LOD of 0.003 mg/kg) (3), < 0.01 (< LOD of 0.003 mg/kg), < 0.01 (2), 0.04, 0.05 and 0.53 mg/kg. The remaining three trials did not match GAP.

Residues in grapes from 17 combined trials matching GAP at a 15 day PHI were: < 0.01 (4) (< LOD of 0.003 mg/kg), < 0.01 (< LOD of 0.002 mg/kg), < 0.01 (4), 0.01, 0.03, 0.04, 005, 0.07 (2), 0.12 and 0.53 mg/kg

Residues in grapes from 20 trials according to GAP at PHIs of 21 and 30 days could be also combined resulting in residues of: < 0.01 (3) (< LOD of 0.003 mg/kg), < 0.01 (8), 0.01 (4), 0.02 (3), 0.03 and 0.04 mg/kg

The residue populations from trials conducted according to 15 days PHI gave the highest levels and were used as the basis for the maximum residue level estimation for grapes.

The Meeting estimates a maximum residue level of 1 mg/kg, a HR of 0.53 mg/kg and a STMR of 0.01 mg/kg for chlorpyrifos-methyl in grapes.

The maximum residue level estimate derived from use of the NAFTA calculator was 0.70 mg/kg. The Meeting noted that most of the trials were conducted at the lower 25% range of the GAP rate, including the trial that gave rise to the highest residue (0.53 mg/kg). The Meeting considered that the estimate derived from the NAFTA spreadsheet calculation may not accommodate all uses of chlorpyrifos-methyl in grapes following the critical GAP.

Strawberries

Chlorpyrifos-methyl is registered for use in strawberries at a rate of 0.068–0.09 kg ai/hL in Italy and Spain, with PHIs of 15 and 5 days, respectively. No GAP information for northern Europe was provided. Data from 23 European trials were submitted.

Of five trials conducted in France, three were conducted in the south and matched Spanish GAP, residues found were: < 0.01 and 0.02 (2) mg/kg at 5 days PHI. Two trials conducted in northern France gave residues in the same range. Eight trials conducted in Italy and Spain at GAP rate, resulted in residues at 5 days PHI of: < 0.01 (< LOD of 0.003 mg/kg), < 0.01 (2), 0.02 (2), 0.01 (2), and 0.04 mg/kg. Ten trials were conducted in northern Europe (Austria, Germany, Hungary, Poland and the UK) matching southern Europe GAP, giving residues in the same range.

From 11 trials conducted in southern Europe matching Spanish GAP residues found were: < 0.01 (< LOD of 0.003 mg/kg), < 0.01 (3), 0.01 (2), 0.02 (4) and 0.04 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg, a HR of 0.04 mg/kg and a STMR of 0.01 mg/kg for chlorpyrifos-methyl in strawberries.

The maximum residue level estimate derived from use of the NAFTA calculator (> 10% of non-detects; maximum likelihood estimation (MLE) approach) was 0.08 mg/kg. The Meeting noted that all the trials were conducted at the lower 25% range of the GAP rate, including the one that gave rise to the highest residue (0.04 mg/kg). The Meeting considered that the estimate derived using the NAFTA spreadsheet calculator may not accommodate all uses of chlorpyrifos-methyl in strawberries following critical GAP.

Kiwifruit

Four European trials were submitted where 2 applications of chlorpyrifos-methyl were made at a rate of 0.049 kg ai/hL. Residues after 15 days ranged from 0.07 to 0.30 mg/kg and dropped to < 0.01 mg/kg (< LOD of 0.003 mg/kg) after 21 days. However, chlorpyrifos-methyl is currently not approved for use on kiwifruit in Europe.

As there was no GAP provided to support the trials, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in kiwifruit.

Onions

Chlorpyrifos-methyl is registered for use in onions at a rate of 0.48 kg ai/ha in Hungary (PHI of 30 days) and at 0.36 kg ai/ha in Poland (PHI of 21 days). Six trials in onions were submitted however none were according to GAP.

As there was no GAP information provided to support the trials, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in onions.

Tomatoes

Chlorpyrifos-methyl is registered in Italy, at a rate of 0.028–0.04 kg ai/hL (PHI of 15 days) and in Spain at up to 0.068–0.09 kg ai/hL (PHI of 5 days). Fifty five field and protected trials were conducted in Europe from 1999 to 2007. Ten trials were conducted in France. In seven trials conducted in southern France matching the Spanish GAP rate, residues at a PHI of 5 days were: 0.06, 0.20 and 0.42 mg/kg in field trials and 0.03, 0.08, 0.13 and 0.20 mg/kg in protected cropping trials. Three trials did not match GAP.

In four field trials conducted in Greece matching Spanish GAP, residues at a PHI of 5 days were: 0.03 (2), 0.06 and 0.31 mg/kg.

Seventeen trials were conducted in Italy. In nine trials conducted matching Spanish GAP, residues at 5 days PHI were: 0.05 (2), 0.07 (3), 0.08 and 0.92 mg/kg in field trials and < 0.01 and 0.05 mg/kg in protected cropping trials. Six trials did not match any GAP.

Fourteen trials were conducted in Spain. In six trials matching GAP, residues at 5 days PHI were: 0.01, 0.02, 0.04, 0.05 and 0.06 mg/kg in field trials and 0.03 mg/kg in protected cropping trials. Eight trials did not match GAP.

Ten trials conducted in northern Europe (the Czech Republic, Hungary, Germany, Poland and the UK) could not be evaluated due to the lack of an approved GAP for the region.

Residues on tomato from 19 trials conducted according to GAP in the field at 5 days PHI were: 0.01, 0.02, 0.03 (2), 0.04, 0.05 (3), 0.06 (3), 0.07 (3), 0.08, 0.20, 0.31, 0.42 and 0.92 mg/kg.

Residues on tomato from eight trials conducted matching GAP in the protected cropping at 5 days PHI were: < 0.01 (2), 0.03 (2) and 0.05 (2), 0.13 and 0.20 mg/kg.

Trials conducted matching Spanish GAP in field and protected cropping situations were not similar (Mann-Whitney U test) and could not be combined. The Meeting agreed that the residues coming from the field trials, having the highest residue population, could be used for the maximum residue level estimation.

The Meeting estimates a maximum residue level of 1 mg/kg, a HR of 0.92 mg/kg and a STMR of 0.06 mg/kg for chlorpyrifos-methyl in tomato.

The maximum residue level estimate derived from use of the NAFTA calculator was 0.90 mg/kg. The Meeting noted that most of the trials were conducted at the lower 25% range of the most critical GAP rate and that the NAFTA calculator value was lower than the highest residue found in the trials (0.92 mg/kg). The Meeting agreed that the value derived from the use of the NAFTA calculator spreadsheet may not accommodate all uses of chlorpyrifos-methyl in tomatoes where chlorpyrifos-methyl is applied according to critical GAP.

Peppers

Chlorpyrifos-methyl is registered to be used in peppers and egg plant in Italy at a rate of 0.34–0.45 kg ai/ha (PHI of 15 days) and 0.068–0.09 kg ai/hL in Spain for peppers (PHI of 5 days). Twenty four trials were conducted in Europe from 1999 to 2007 in the field and protected cropping.

Three trials were conducted in southern France, with one in protected cropping matching Spanish GAP, with residues of 0.14 mg/kg at a 5 day PHI.

Five trials were conducted in Greece. In three protected cropping trials matching Spanish GAP, residues at 5 days PHI were 0.03 and 0.16 (2) mg/kg. Three trials conducted at double rate gave residues in the same range.

Five trials were conducted in Italy. In two protected cropping trials matching Spanish GAP, residues at 5 days PHI were 0.04 and 0.06 mg/kg.

Fourteen trials were conducted in Spain. Five protected trials matching GAP gave residues at a PHI of 5 days were: 0.03, 0.04, 0.06, 0.52 and 0.72 mg/kg and three field trials conducted at GAP gave residues of 0.01, 0.04 and 0.09 mg/kg. Six trials conducted at double rate or higher PHI gave residues in the same range.

Residues from protected cropping trials, conducted according to Spanish GAP were: 0.03 (2), 0.04 (2), 0.06 (2), 0.14, 0.16 (2), 0.52 and 0.72 mg/kg.

Residues found from field trials, conducted according to Spanish GAP, were: 0.01, 0.04 and 0.09 mg/kg.

Trials conducted according to Spanish GAP in the field and protected cropping were not similar (Mann-Whitney U test) and could not be combined. The Meeting agreed that as the residues coming from the protected cropping had the highest residue population, they be used for the maximum residue level estimation.

The Meeting estimated a maximum residues level of 1 mg/kg, a HR of 0.72 mg/kg and a STMR of 0.06 mg/kg for chlorpyrifos-methyl in peppers.

The maximum residue level estimate derived from use of the NAFTA calculator was 0.5 mg/kg. The Meeting noted that most of the trials were conducted at the lower 25% range of the most critical GAP rate and that NAFTA calculator value was lower than the highest residue found in the trials (0.72 mg/kg). The Meeting agreed that value derived from the use of the NAFTA calculator might not accommodate all uses in peppers where chlorpyrifos-methyl is applied according to critical GAP.

Using the default dehydration factor of 10 to extrapolate from peppers to dried chilli peppers, the Meeting estimated a maximum residue level of 10 mg/kg (based on a highest residue of 7.2 mg/kg) and a STMR of 0.6 mg/kg for chlorpyrifos-methyl in Peppers, chilli dried.

In Italy, the approved GAP is for both peppers and egg plant. The Meeting agreed to use the residue data in peppers and estimates a maximum residues level of 1 mg/kg, a HR of 0.72 mg/kg and a STMR of 0.06 mg/kg for chlorpyrifos-methyl in egg plants.

The Meeting withdraws its previous chlorpyrifos-methyl recommendations of 5 mg/kg in peppers, chilli dry and of 0.1 mg/kg in egg plant

Green beans and peas

The Meeting received data from six residue trials in green beans and peas conducted in Europe at a rate of 2 × 0.20 to 0.52 kg ai/ha. Residues at 10 or 15 days after the last application ranged from < 0.01 (< LOD of 0.002 mg/kg) to 0.02 mg/kg.

However, as there was no GAP information provided to support the trials, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in green beans or peas.

Carrot

The Meeting received data from four trials conducted in carrots in France, Italy and Spain, at a rate of 2 ×× 0.48 to 0.52 kg ai/ha. Residues after 3 days of the last application ranged from < 0.01 to 0.07 mg/kg.

However, as there was no GAP information provided to support the trials, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in carrots.

Potatoes

Chlorpyrifos-methyl is approved for use in potatoes in Italy at a rate up 0.045 kg ai/hL or 0.45 kg ai/ha and in Spain up to 0.09 kg ai/hL. In both countries the PHI is 15 days. Data from 21 trials conducted in Europe from 2000 to 2007 were provided to the Meeting.

Seven trials were conducted in South of France. In two trials matching Spanish GAP, residues at a PHI of 15 days were: < 0.01 mg/kg (2) (< LOD of 0.003 mg/kg). No residues were detected in trials conducted at double rate (two trials), lower (one trial) or higher PHI (two trials).

Five trials were conducted in Italy. In three trials matching either the Italian or Spanish GAP rate, residues at a PHI of 15 days were: < 0.01 (2) (< LOD of 0.002 mg/kg) and < 0.01 mg/kg (< LOD of 0.003 mg/kg). No residues were detected in two trials conducted at doubled rate or one at a lower PHI.

Three trials were conducted in Spain. One trial matching GAP, resulted in residues at the 15 day PHI of < 0.01 mg/kg (< LOD of 0.003 mg/kg). No residues were detected in two trials conducted at lower or higher PHIs.

Six trials were conducted at 0.07 kg ai/hL in northern Europe (Germany, Poland, Hungary and the UK), for which no GAP information was provided. No residues were detected at any sampling point (0 to 21 days).

In six trials conducted in southern Europe according to GAP residues found were: < 0.01 (< LOD of 0.002 mg/kg) and < 0.01 (4) mg/kg (< LOD of 0.003 mg/kg). In all trials submitted, no residues were detected at the day of the last application, indicating that it is unlikely the use of chlorpyrifos-methyl, at the GAP rate, will leave detectable residues in potato tubers.

The Meeting estimated a maximum residue for chlorpyrifos-methyl of 0.01(*) mg/kg and a HR and STMR of 0 for chlorpyrifos-methyl in potato.

The NAFTA calculator was not used to derive an estimate as all residue values considered by the Meeting were below the LOQ, making its application unsuitable.

Sugar beet

Chlorpyrifos-methyl is registered for use on sugar beet in Poland at a rate of 0.36 kg ai/ha (PHI of 30 days) and up to 0.05 kg ai/hL in Spain (PHI of 15 days). Data from four trials conducted in Italy and Spain in 2000/2001 were submitted where sampling occurred at more than harvest interval of greater than 100 days.

As no trials were conducted that matched GAP, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in sugar beet.

Artichoke (globe)

No GAP information on the use of chlorpyrifos-methyl in artichokes was provided to the Meeting. Four trials were conducted in Greece and Spain, at a 1 kg ai/ha. Residues at a PHI of 5 days ranged from 0.11 to 1.2 mg/kg.

As there is no GAP to support the trials, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in artichoke.

The Meeting withdraws its previous recommendations of 0.1 mg/kg for chlorpyrifos-methyl in artichoke, globe

Cereal grains – post-harvest use

Chlorpyrifos-methyl is registered for use as a grain storage treatment in a number of countries. The application rate for cereal grains ranges from 2.5 g ai/tonne seed (storage interval of 21 days in Hungary to 120 days in Belgium) to 4.5 g ai/tonne seed (storage interval of 90 days) in the UK. In Spain, the GAP for wheat, barley and maize is 2.2 g ai/tonne seed with no storage interval specified.

Twelve trials were conducted in barley in Europe from 1994 to 1995. The formulation was applied to the grain in a rotary mixer using hand-held trigger application equipment at the GAP use rates and timings. Nine trials conducted at 4.5–5 g ai/tonne seed, gave residues within 90 days storage interval of 1.6, 1.9, 2.3, 2.6, 2.9, 3.0, 31, 3.2 and 3.3 mg/kg. One trial conducted at the GAP rate gave a large variation of residues during the period of storage, starting with 6.2 mg/kg at the day of treatment, reaching a highest residue of 10 mg/kg at 99 days of storage and dropping to 6.7 mg/kg after 182 days. The highest value from this trial is twice the application rate (5g ai/tonne), an unexpected in large scale post-harvest application in cereals. The Meeting agreed that this variation indicates a lack of homogeneity in mixing during treatment and the trial should not be considered in the estimation.

In two trials conducted at 2.5 g ai/tonne seed matching Spanish GAP, samples were collected from 0 to 181 days after the treatment; the highest residues were found after 7 days at 2.0 (2) mg/kg.

Twelve trials were conducted in wheat in Europe. Ten trials conducted at 4.5–5 g ai/tonne seed, gave residues within 90 days storage interval of 1.9, 2.2, 2.4, 2.9, 3.0, 3.1, 3.2 (2), 3.5 and 4.7 mg/kg.

In two trials conducted at 2.5 g ai/tonne seed matching Spanish GAP, samples were collected from 0 to 181 days after the treatment; the highest residues were found at 0 days were 2.2 (2) mg/kg.

Residue data from 19 trials conducted at the highest application rate in barley and wheat can be combines as follow: 1.6, 1.9 (2), 2.2, 2.3, 2.4, 2.6, 2.9 (2), 3.0 (2), 3.1 (2), 3.2 (3), 3.3, 3.5 and 4.7 mg/kg.

Residues from trials conducted in wheat and barley at 2.5 g ai/tonne seed are 2.0 (2) and 2.2 (2) mg/kg

Based on the residue data from the highest application rate, the Meeting estimated a maximum residue level of 5 mg/kg, a HR of 4.7 mg/kg and a STMR of 3.0 mg/kg for chlorpyrifos-methyl in cereal grain group, post-harvest.

Long-term dietary risk assessment indicates an exceedance of the ADI for 10 of the 13 GEMS/Food Consumption Cluster Diets (up to 260% ADI).

Taking the alternative GAP approach, the Meeting considered the residue data set coming from trials conducted according to Spanish GAP in wheat and barley for maximum residue level estimation. The Meeting estimated a maximum residue level of 3 mg/kg, a HR of 2.2 mg/kg and a STMR of 2.1 mg/kg for chlorpyrifos-methyl in wheat, barley and maize, post-harvest.

The maximum residue level estimate derived from use of the NAFTA calculator was 2.5 mg/kg. The normal JMPR procedure is to use one significant figure for maximum residue levels below 10 mg/kg. Rounding up the value obtained from the calculator results in 3 mg/kg which corresponds to the recommendation of the current Meeting.

The Meeting withdraws its previous recommendations of 10 mg/kg for chlorpyrifos-methyl in wheat and sorghum, post-harvest

Maize

Chlorpyrifos-methyl is registered to be used in maize in Italy (0.06 kg ai/hL) and Spain (0.068–0.09 kg ai/hL), with a 15 days PHI.

Eight trials were conducted with maize in France, Italy and Spain in 2007 at a rate of 0.84–0.94 kg ai/ha (0.225 kg ai/hL). Samples collected from 22 to 93 days after the application gave residues < 0.01 mg/kg (< LOD of 0.003 mg/kg).

As no trial was conducted according to GAP, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in maize.

Cotton

Chlorpyrifos-methyl is registered to be used in cotton in Spain (up to 0.09 kg ai/hL, 15 days PHI) and in Greece (up to 0.67 kg/ha; 500–800 L/ha with a 21 day PHI). Twelve trials were conducted in Greece and Spain in 2006/2007 at the Greek GAP rate, with residues in cotton seed ranging from < 0.003 to 0.02 mg/kg 15 days after the last application (eight trials) and < 0.01 mg/kg (< LOD of 0.003 mg/kg) 28 days after the last application.

As no trial was conducted according to GAP, the Meeting could not estimate a maximum residue level for chlorpyrifos-methyl in cotton seed.

Rape seed

The Meeting received no information on registered GAP for chlorpyrifos-methyl in rape seed. Data was submitted from 16 trials conducted in 2006/2007 where chlorpyrifos was applied at a rate of 0.45 to 0.49 kg ai/ha, which resulted in no detectable residues in samples collected at harvest intervals of 31 to 120 days.

As there was no GAP provided to support the trials, the Meeting could not recommend a maximum residue level for chlorpyrifos-methyl in rape seed.

Animal feed

Chlorpyrifos-methyl is registered for pre-harvest use in maize in Italy (0.06 kg ai/hL) and Spain (0.068–0.09 kg ai/hL), with a PHI of 15 days. In 28 trials conducted in Europe, samples of cobs, whole plant and stover (rest of the plant) were analysed. In four trials conducted in southern France and Spain, matching Spanish GAP, residues in maize whole plant, at a PHI of 15 days were: < 0.01, 0.04, 0.16 and 1.4 mg/kg. Twenty four trials were conducted at double rate and or samples were collected 28 days after the last application, i.e., did not match GAP

The trials matching GAP with chlorpyrifos-methyl in maize were considered insufficient for making estimations for chlorpyrifos-methyl in animal feed.

In two trials conducted in cotton in Spain, matching Greek GAP, residues in cotton, whole plant, at a 15 day PHI were: 0.86 and 1.6 mg/kg.

The trials conducted with chlorpyrifos-methyl in cotton were considered insufficient to make estimations for chlorpyrifos-methyl in animal feed.

In 16 trials conducted with rape seed, samples of animal feed were analysed. As no registered GAP information for use in rape seed was provided, the trials could not be evaluated. Four trials were conducted in sugar beet and samples of animal feed were analysed (tops/leaves and whole plant).

As no registered GAP information was provided to support the trials, the Meeting could not make estimations for chlorpyrifos-methyl in animal feed from sugar beet.

Fate of residues during processing

Two processing studies on oranges were conducted in Spain in 2004–2005. Orange trees received 2 applications of chlorpyrifos-methyl at 2.7 kg ai/ha. The fruit was harvested 21 days after the second application and underwent processing that simulated standard industrial procedures. Residues of chlorpyrifos-methyl in whole fruit were 0.13 and 0.24 mg/kg. Mean (n = 2) processing factors (PF) for chlorpyrifos-methyl were calculated as 0.046 for orange juice and 40.2 for essential oil.

In three French studies, two applications were made to apple trees at 0.6 or 0.78 kg ai/ha with harvested fruit processed following standard commercial practices. Residues of chlorpyrifos-methyl in the fruit ranged from 0.02 to 0.07 mg/kg. No residues were detected in apple juice, PF estimated as < 0.05, < 0.04 and < 0.15 (mean of < 0.08). No residues of chlorpyrifos-methyl were detected in apple purée, with a mean PF of < 0.15.

In a study conducted in 2004 on peaches in France, trees received two applications of chlorpyrifos-methyl at 0.833 and 0.904 kg ai/ha. Treated fruit was sampled 28 days after the last application and processed to juice and purée according to commercial practices. Chlorpyrifos-methyl residues in whole fruit were < 0.01 mg/kg. No residues were found in juice and purée, but were detected in dry pomace at the LOQ level. No PF for chlorpyrifos-methyl could be estimated as no residues were detected in the raw commodity.

In seven studies conducted on grapes, chlorpyrifos-methyl was applied twice at 0.07 kg ai/hL. Samples were taken 21 or 28 days after the last application and were processed to raisins and wine according to commercial practices. Residues of chlorpyrifos-methyl in grapes ranged from < 0.01 to 0.11 mg/kg but were not detected in wine (PF < 0.15), raisins (PF < 0.09) and must (PF < 0.15). Residues concentrated in grape wet pomace (mean PF of 4.2, n = 2) and in dry pomace (median of > 7.5, n = 4).

Three processing studies were conducted in tomatoes in Italy and Spain. Tomatoes were treated with chlorpyrifos-methyl at 0.24 or 0.07 kg ai/hL with samples processed according do commercial practice. Residues in tomatoes ranged from 0.17 to 0.22 mg/kg but were not detected in the juice (mean PF < 0.033) or the canned tomato (mean PF < 0.025). Residues were reduced in purée, with a mean PF of 0.27 and in washed tomato (PF of 0.75).

Two processing studies were conducted during 2004–2006 on barley grain stored for 6 months after receiving chlorpyrifos-methyl at 5 g ai/tonne grain. Residues of chlorpyrifos-methyl in grain at 0 or 180 days after treatment ranged from 2.1 to 3.2 mg/kg and were not detected in beer (mean PF < 0.001).

In one processing study conducted in France, maize treated twice at 0.56 kg ai/ha was processed according to commercial practices to flour and oil. Residues in grain were not reported and no residues of chlorpyrifos-methyl (< LOD of 0.002 mg/kg) were detected in the processed commodities.

Four processing studies were conducted on wheat grain stored for up to 6 months after being treated with chlorpyrifos-methyl at 1.25 to 5 g ai/tonne grain. Residues of chlorpyrifos-methyl in grain after treatment ranged from 0.52 to 3.2 mg/kg. Residues were reduced in white flour (mean PF of 0.25; n = 6), white bread (mean PF of 0.05; n = 6) and wholemeal bread (mean PF of 0.48, n = 3). Residues remained unchanged in wholemeal flour (n = 3) and concentrated in wheat germ (mean PF=1.9; n = 3) and in bran (mean PF=2.45 n = 6).

One processing study was conducted cotton after the plant was treated twice with chlorpyrifos-methyl at 0.675 kg ai/ha. Seed samples were collected 56 days after the last application and processed according to commercial practices. No residues were detected in cotton seed, pressed cake, raw oil or refined oil.

Two processing studies were conducted in rape seed treated with chlorpyrifos-methyl at a rate of 0.45 kg ai/ha. Seed samples were collected 105 days after treatment and processed according to commercial practices. No residues were detected in seed, pressed cake, raw or refined oil.

Summary of processing factors from the processing of Raw Agricultural Commodities (RACs)

Processed commodity	Processing factor	Residue in the raw commodity	STMR-P, mg/kg	HR-P, mg/kg	Maximum residue level, mg/kg
Orange juice	0.046	0.21 (median, citrus)	0.01		-
Apple juice	< 0.08	0.07 (STMR, pome)	0.0056		-
Apple wet pomace	6.5	0.07 (STMR, pome)	0.455		-
Apple dried pomace	3.1	0.56 (HR, pome)	-		2
Grape pomace, wet	4.2	0.01 (STMR)	0.042		-
Grape pomace, dry	>7.5	0.53 (HR)	-		5
Grape Wine	< 0.15	0.01 (STMR)	0.002		-
Raisins	< 0.09	0.01 (STMR)	0.001		-
Tomato juice	< 0.033	0.06 (STMR)	0.002		-
Beer	< 0.001	2.1 (STMR, barley)	0.002		-
Wheat bran	2.45	2.1 (STMR, wheat) 2.2 (HR, wheat)	5.14	5.39	6
Wheat white flour	0.25	2.1 (STMR, wheat) 2.2 (HR, wheat)	0.525	0.55	-
Wheat germ	1.9	2.1 (STMR, wheat) 2.2 (HR, wheat)	3.99	4.18	5
Wheat wholemeal	1	2.1 (STMR, wheat) 2.2 (HR, wheat)	2.1	2.2	-
Wheat white bread	0.05	2.1 (STMR, wheat) 2.2 (HR, wheat)	0.105	0.11	-
Wheat wholemeal bread	0.48	2.1 (STMR, wheat) 2.2 (HR, wheat)	1.01	1.06	-

Residues in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of chlorpyrifos-methyl in farm animals on the basis of the diets listed in Annex 6 of the 2006 JMPR Report (OECD Feedstuffs Derived from Field Crops), the STMR or highest residue levels estimated at the present Meeting. Dietary burden calculations are provided in Annex 6. Only residue values for grain and fruit pomace, wet were available for use in the calculation of the dietary burden

		Animal dietary burden for chlorpyrifos-methyl, ppm of dry matter diet		
		US-Canada	EU	Australia
Beef cattle	max	3.95	3.59	4.2[a]
	mean	3.77	3.42	3.77[b]
Dairy cattle	max	3.69 [c]	2.95	3.56
	mean	3.52[d]	2.85	3.4
Swine breed	max	5.04[a]	4.31[a]	3.95
	mean	4.8	4.11 [b]	3.77
Swine finish	max	4.31	4.31	3.95
	mean	4.11	4.11	3.77
Poultry broiler	max	4.31[e]	2.98	1.6
	mean	4.11[f]	2.84	1.53
Poultry layer	max	3.68[g]	1.97	2.96
	mean	3.52[h]	1.88	2.84

[a.] Highest maximum cattle or swine dietary burden suitable for maximum residue level estimates for mammalian meat

[b]. Highest mean cattle or swine dietary burden suitable for STMR estimates for mammalian meat.

[c]. Highest maximum dairy cattle dietary burden suitable for MRL estimates for mammalian milk

[d]. Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

[e]. Highest maximum poultry dietary burden suitable for MRL estimates for poultry meat and eggs.

[f.] Highest mean poultry dietary burden suitable for STMR estimates for poultry meat and eggs.

[g]. Highest maximum poultry dietary burden suitable for MRL estimates for eggs.

[h]. Highest mean poultry dietary burden suitable for STMR estimates for eggs.

The chlorpyrifos-methyl dietary burdens for animal commodity MRL estimation (residue levels in animal feeds expressed on dry weight) reached a maximum of 5 ppm for swine and of 3.68 ppm for poultry. The chlorpyrifos-methyl dietary burdens for animal commodity STMR estimation (residue levels in animal feeds expressed on a dry weight basis) reached a maximum of 4.11 ppm for swine and of 3.52 ppm for poultry.

Animal feeding studies

In one feeding study conducted in dairy cows, the animals were fed 0, 1, 3, 10, 30, and 100 ppm chlorpyrifos-methyl in the diet starting at the lowest level and increasing the dosage every two weeks. The highest feeding level was followed by a two week period where no chlorpyrifos-methyl was added to the feed. In milk, chlorpyrifos-methyl was not detected 13 days after 3 and 10 ppm dosing but was detected at the LOQ level 9–11 days after dosing at 30 ppm. In milk cream, the levels detected at 30 ppm were 0.08–0.09 mg/kg. Cream samples from the 3 or 10 ppm dose levels were not analysed.

In another study, calves were fed rations containing 1, 3, 10, 30 and 100 ppm chlorpyrifos-methyl for 28 days. Residues of chlorpyrifos-methyl in fat samples were 0.01 mg/kg at 3 ppm, 0.03 mg/kg at 10 ppm and 0.09 mg/kg at 30 ppm. Muscle, liver and kidney samples were only analysed from the 30 or 100 ppm feeding level, and were not detected (< 0.01 mg/kg).

In a study on swine, animals were fed rations containing 1 to 100 ppm of chlorpyrifos-methyl for 28 days. In muscle, residues were only found above the LOQ (0.01 mg/kg) at the 30 ppm level or 100 ppm (0.03 and 0.14 mg/kg). No residues were found at any feeding level in liver or kidney. In fat, residues increased proportionally with the feeding level (mean/high levels at 3 ppm: 0.02/0.02 mg/kg; 10 mg/kg: 0.07/011 mg/kg).

In one study conducted with laying poultry, the birds were fed rations containing 1, 3, 10, 30 and 100 ppm chlorpyrifos-methyl for 28 days. No residues of chlorpyrifos-methyl were detected (< 0.01) in muscle, fat and eggs at or below the feeding level of 10 mg/kg. At 30 ppm, residues were detected only in fat at the LOQ and at 100 ppm in fat (0.15 mg/kg) and eggs (0.02 mg/kg).

Animal commodity maximum residue levels

Dietary burden (mg/kg) Feeding level [ppm]		Chlorpyrifos-methyl residues, mg/kg					
		Milk	Milk cream	Muscle	Liver	Kidney	Fat
mrl cattle beef, highest residue	(4.2) [1; 3; 10; 30]			(< 0.01) [-; -; -; < 0.01]	(< 0.01) [-; -; -; < 0.01]	(< 0.01) [-; -; -; < 0.01]	(0.013) [< 0.01;0.01; 0.03; 0.12]
STMR cattle beef, mean residue	(3.8) [1; 3; 10; 30]			(0) [-; -; -; < 0.01]	(0) [-; -; -; < 0.01]	(0) [-; -; -; < 0.01]	(0.013) [< 0.01; 0.01; 0.03 0.09]
mrl milk, mean residue	(3.7) [3; 10; 30]	(< 0.01) [-; < 0.01; < 0.01]	(0.009) [-; -; 0.07]				
STMR milk, mean residue	(3.5) [3; 10; 30]	(0) [-; < 0.01; < 0.01]	(0.008) [-; -; 0.07]				

Dietary burden (mg/kg) Feeding level [ppm]		Chlorpyrifos-methyl residues, mg/kg			
		Muscle	Liver	Kidney	Fat
mrl swine highest residue	(5.0) [3; 10]	(< 0.01) [< 0.01; < 0.01]	(< 0.01) [< 0.01; < 0.01]	(< 0.01) [< 0.01; < 0.01]	(0.055) [0.02; 0.11]
STMR swine mean residue	(4.1) [3; 10]	(0) [< 0.01; < 0.01]	(0) [< 0.01; < 0.01]	(0) [< 0.01; < 0.01]	(0.03) [0.02; 0.07]

Dietary burden (mg/kg) Feeding level [ppm]		Chlorpyrifos-methyl residues, mg/kg			
		Eggs	Muscle	Liver	Fat
mrl poultry meat highest residue	(4.3) [10; 30]		(< 0.01) [< 0.01; < 0.01]	(< 0.01) [-; < 0.01]	(0.004) [0.01; < 0.01]
STMR poultry meat, mean residue	(4.1) [3; 10]		(0) [< 0.01; < 0.01]	(0) [-; < 0.01]	(0.004) [0.01; < 0.01]
mrl eggs highest residue	(3.7) [10; 30]	(< 0.01) [< 0.01; < 0.01]			
STMR eggs, mean residue	(3.5) [3; 10]	(0) [< 0.01; < 0.01]			

Feeding study and the dietary burden calculations for cattle were the basis for the estimations in milk. Based on the residues on milk cream (0.009 and 0.008 mg/kg) and the default assumption that milk cream is 50% fat, the Meeting recommends a maximum residue level of 0.02 mg/kg and a STMR of 0.016 mg/kg for chlorpyrifos-methyl in milk fats. The Meeting estimated a maximum residue level of 0.01(*) mg/kg in milks; assuming milk to contain 4% fat, the Meeting estimated a STMR of 0.0006 mg/kg for chlorpyrifos-methyl in milks (4% of milk fat STMR of 0.016 mg/kg).

Based on the feeding studies and the dietary burden calculations for swine, the Meeting recommends a maximum residue level of 0.01(*) mg/kg, a STMR and a HR of 0 mg/kg for chlorpyrifos-methyl in edible offal (mammalian); a maximum residue level of 0.1 mg/kg (fat) for meat (from mammalian other than marine mammals); a STMR of 0.03 mg/kg and HR of 0.055 mg/kg in the fat portion of the meat and a STMR and HR of 0 in the muscle portion of the meat.

Based on the feeding study and the dietary burden calculation for chickens, the Meeting estimates a maximum residue level of 0.01(*) mg/kg and a STMR and HR of 0 mg/kg for chlorpyrifos-methyl in eggs and poultry edible offal; a maximum residue level of 0.01 mg/kg in poultry meat (fat), a STMR and HR of 0.004 mg/kg in the fat portion of the poultry meat and a STMR and HR of 0 in the muscle portion of the poultry meat.

The Meeting withdraws its previous recommendations for chlorpyrifos-methyl in cattle fat, cattle meat, cattle edible offal, chicken fat, chicken meat, chicken edible offal, milks and eggs.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMR values shown below. The maximum residue levels are recommended for use as maximum residue limits.

For plants and animals, definition of the residue for compliance with maximum residue level and estimation of dietary intake: *chlorpyrifos-methyl*.

The residue is fat soluble.

CCN	Commodity name	Recommended MRL (mg/kg)		STMR (P)	HR
		New	Previous	mg/kg	mg/kg
FP 0226	Apple	W [a]	0.5		
	Apple juice			0.005	
AB 0226	Apple pomace, dry	2		0.22	
	Apple pomace, wet			0.455	
VS 0620	Artichoke, Globe	W	0.1		
GC 0640	Barley	3		2.1	2.2
	Beer			0.002	
VB 0041	Cabbages, Head	W	0.1		
MF 0812	Cattle fat	W [a]	0.05		
MM 0812	Cattle meat	W [a]	0.05		
MO 0812	Cattle, Edible offal of	W [a]	0.05		
PF 0840	Chicken fat	W [a]	0.05		
PM 0840	Chicken meat	W [a]	0.05		
PO 0840	Chicken, Edible offal of	W [a]	0.05		
VL 0467	Chinese cabbage (type pe-tsai)	W	0.1		
FC 0001	Citrus	2		0.01	0.01
VP 0526	Common bean (pods and/or immature seeds)	W	0.1		
FT 0295	Date	W	0.05		
MO 0108	Edible offal (mammalian)	0.01*		0	0
VO 0440	Egg plant	1	0.1	0.06	0.72
PE 0112	Eggs	0.01*	0.05	0	0
FB 0269	Grapes	1	0.2	0.02	0.53
	Raisins			0.001	0.001
	Wine			0.002	
AB 0226	Grape pomace, dry	5		0.075	
	Grape pomace, wet			0.042	
VL 0482	Lettuce, Head	W	0.1		
GC 0645	Maize	3		2.1	2.2
MM 0095	Meat (from mammals other than marine mammals)	0.1 (fat)		0.03 (fat) 0 (muscle)	0.055 (fat) 0 (muscle)
ML 0106	Milks	0.01*	0.01	0.0006	
FM 0183	Milk fats	0.02		0.01	
VO 0450	Mushrooms	W	0.01		
FC 0004	Oranges, Sweet, Sour	W [a]	0.5		
	Orange juice			0	
FS 0247	Peach	W [a]	0.5		
VO 0051	Peppers	1	0.5	0.06	0.72
VO 0444	Peppers, Chili (dry)	10	5	0.6	
FP 0009	Pome fruits	1		0.06	0.56
VR 0589	Potato	0.01*		0	0
PO 0111	Poultry edible offal	0.01*		0	0
PO 0110	Poultry meat	0.01 (fat)		0.004 (fat) 0 (muscle)	0.004 (fat) 0 (muscle)
VR 0494	Radish	W	0.1		
GC 0649	Rice	W	0.1		
GC 0651	Sorghum	W	10 Po		
FS012	Stone fruit	0.5		0.02	0.26
FB 0275	Strawberry	0.06		0.01	0.04
DT 1114	Tea, Green, Black	W	0.1		
VO 0448	Tomato	1	0.5	0.06	0.92
	Tomato juice			0.002	
	Tomato pure			0.016	
GC 0654	Wheat	3	10 Po	2.1	2.2
CM 0654	Wheat bran, Unprocessed	6 PoP	20 PoP	5.14	5.39
CF 1211	Wheat flour	W	2 PoP	0.525	0.55

CCN	Commodity name	Recommended MRL (mg/kg)		STMR (P)	HR
		New	Previous	mg/kg	mg/kg
CF 1210	Wheat germ	5 PoP		3.99	4.18
CF 1212	Wheat wholemeal			2.1	2.2
CP 1211	White bread	W	0.5 PoP	0.105	0.11
CP 1212	Wholemeal bread	W	2 PoP	1.01	1.06

[a] replaced by an estimation for the group

DIETARY RISK ASSESSMENT

Long-term intake

The ADI for chlorpyrifos-methyl is 0–0.01 mg/kg bw. The International Estimated Daily Intakes (IEDI) for chlorpyrifos-methyl was estimated for the 13 GEMS/Food Consumption Cluster Diets using the STMR or STMR-P values estimated by the current Meeting. The results are shown in Annex 3 of the 2009 JMPR Report. The IEDI ranged from 20 to 140% of the ADI. The information provided to the JMPR precludes an estimate that the long-term intake of residues of chlorpyrifos-methyl would be below the ADI.

The IEDI exceeded the maximum ADI for the Cluster diets C (110% ADI) and H (140% ADI), with 42.7 and 72.8% of the total intake, respectively, coming from the consumption of maize. The estimation of a STMR made by the Meeting considered the alternative GAP approach. However, in the absence of suitable information this could not be done. To refine the long-term intake estimates information on expected residues in maize processed commodities, such as maize flour and cooked maize would need to be assessed. The ADI for chlorpyrifos-methyl was established by the present Meeting on the basis of a NOAEL of 1 mg/kg bw/d from a 2-year study in rats and a safety factor of 100. However, two other studies had LOAELs of 3 mg/kg bw/d, suggesting it is unlikely that the ADI itself could be refined.

Short-term intake

The ARfD for chlorpyrifos-methyl is 0.1 mg/kg bw. The International Estimated Short Term Intake (IESTI) for chlorpyrifos-methyl was calculated for the plant and animal commodities for which STMR(P)s and HR(P)s were estimated and for which consumption data were available. The results are shown in Annex 4 of the 2009 JMPR Report. The IESTI ranged from 0 to 30% of the ARfD for the general population and from 0 to 40% for children. The Meeting concluded that the short-term intake of residues from the uses of chlorpyrifos-methyl considered by the Meeting is unlikely to present a public health concern.

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GHE-P-11796 ver. 2	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in apples and pears at intervals and at harvest following a single application of GF-1684—Southern Europe 2007 (N230). Dow AgroSciences. GLP. Unpublished.
GHE-P-11797 ver. 2.	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in apricots and peaches at intervals and at harvest following a single application of GF-1684—Southern Europe 2007 (N229). Dow AgroSciences. GLP. Unpublished.
GHE-P-11799	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in cotton seeds at intervals and at harvest following a single application of GF-1684—Southern Europe 2007 (N236). Dow AgroSciences. GLP. Unpublished.
GHE-P-11801 ver. 2	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in indoor peppers at intervals and at harvest following a single application of GF-1684—Southern Europe 2007 (N231). Dow AgroSciences. GLP. Unpublished.
GHE-P-11800	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in oilseed rape at intervals and at harvest following a single application of GF-1684—Northern, Central and Southern Europe 2007 (N237). Dow AgroSciences. GLP. Unpublished.
GHE-P-11802 ver. 2	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in potatoes at intervals and at harvest following a single application of GF-1684—Northern, Central and Southern Europe 2007 (N232). Dow AgroSciences. GLP. Unpublished.
GHE-P-11804	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in strawberries at intervals and at harvest following a single application of GF-1684—Northern, Central and Southern Europe 2007 (N238). Dow AgroSciences. GLP. Unpublished.
GHE-P-11803 ver. 2	Devine, HC	2008	Residues of chlorpyrifos-methyl and TCP in wine grapes at intervals and at harvest following two applications of GF-1684—Northern, Central and Southern Europe 2007 (N228) Dow AgroSciences. GLP. Unpublished.
GHE-P-9436	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in apples at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N156) Dow AgroSciences. GLP. Unpublished.
GHE-P-9552	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in apples at intervals following two applications of EF-1066 (RELDAN 22) Northern Europe—2000 (N165) Dow AgroSciences. GLP. Unpublished.
GHE-P-9551	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in apples at intervals following two applications of EF-1066 (RELDAN 22) Southern Europe—2000 (N164) Dow AgroSciences. GLP. Unpublished.
GHE-P-9433	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in carrots at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N154) Dow AgroSciences. GLP. Unpublished.
GHE-P-9444	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in carrots at intervals following two applications of EF-1066 (RELDAN 22) Southern Europe—2000 (N161) Dow AgroSciences. GLP. Unpublished.
GHE-P-9439	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in globe artichokes at harvest under open field conditions following a single application of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N130). Dow AgroSciences. GLP. Unpublished.
GHE-P-9559	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in globe artichokes at intervals grown under open field conditions following a single application of RELDAN 22

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			(EF-1066), Southern Europe—2000 (N167) Dow AgroSciences. GLP Unpublished.
GHE-P-9437	Doran, A and Clements, B	2002	.Residues of chlorpyrifos-methyl in grapes at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Northern France—2000 (N134) Dow AgroSciences. GLP. Unpublished.
GHE-P-9446	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in grapes at intervals following two applications of RELDAN 22 (EF-1066), Southern Europe—2000 (N135) Dow AgroSciences. GLP. Unpublished.
GHE-P-9438	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in green beans at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N157). Dow AgroSciences. GLP. Unpublished.
GHE-P-9432	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in green beans at intervals following two applications of RELDAN 22 (EF-1066), Southern Europe—2000 (N131) Dow AgroSciences. GLP. Unpublished.
GHE-P-9443	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in maize at harvest following a single application of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N160) Dow AgroSciences. GLP. Unpublished.
GHE-P-9440	Doran, A. and Clements, B	(2002).	. Residues of chlorpyrifos-methyl in maize at intervals following a single application of EF-1066 (RELDAN 22) Southern Europe—2000 (N158). Dow AgroSciences. GLP. Unpublished
GHE-P-9447	Doran, A. and Clements, B	2002	Residues of chlorpyrifos-methyl in onions at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N163) Dow AgroSciences. GLP. Unpublished.
GHE-P-10013	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in onions at intervals following two applications of RELDAN 22 (EF-1066), Southern Europe—2001 (N169) Dow AgroSciences. GLP. Unpublished.
GHE-P-9442	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in peppers at harvest grown under glass and under open field conditions following multiple applications of EF-1066 (RELDAN 22) or GF-71 Southern Europe—2000 (N159) Dow AgroSciences. GLP. Unpublished.
GHE-P-9435	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in peppers at intervals grown under glass and under open field conditions following multiple applications of EF-1066 (RELDAN 22) Southern Europe—2000 (N155) Dow AgroSciences. GLP. Unpublished.
GHE-P-9556	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in potatoes at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N166). Dow AgroSciences. GLP. Unpublished.
GHE-P-9445	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in potatoes at intervals following two applications of EF-1066 (RELDAN 22) Southern Europe—2000 (N162). Dow AgroSciences. GLP. Unpublished.
GHE-P-9429	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in sugar beet at harvest following a single application of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N152). Dow AgroSciences. GLP. Unpublished.
GHE-P-9774	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in sugar beet at harvest following a single application of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2001 (N168). Dow AgroSciences. GLP. Unpublished.
GHE-P-9428	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in sugar beet at intervals following a single application of EF-1066 (RELDAN 22) Southern Europe—2000 (N151). Dow AgroSciences. GLP. Unpublished.
GHE-P-9558	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in tomatoes at harvest under open field conditions following multiple applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N136). Dow AgroSciences. GLP. Unpublished.
GHE-P-9557	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in tomatoes at intervals grown under cover following multiple applications of RELDAN 22 (EF-1066), Southern Europe—2000 (N133). Dow AgroSciences. GLP. Unpublished.
GHE-P-9441	Doran, A and Clements, B	2002	Residues of chlorpyrifos-methyl in wine grapes at harvest following two applications of EF-1066 (RELDAN 22) or GF-71, Southern Europe—2000 (N137). Dow AgroSciences. GLP. Unpublished.
GHE-P-8643	Doran, A.and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at harvest and processed fractions (pomace, juice and puree) following multiple applications of RELDAN 22 (EF-1066), Northern France—1999 (N121). Dow AgroSciences. GLP. Unpublished.

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GHE-P-8645	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at harvest following multiple applications of RELDAN 22 (EF-1066), Germany—1999 (N125). Dow AgroSciences. GLP. Unpublished.
GHE-P-8647	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at harvest following multiple applications of RELDAN 22 (EF-1066), Southern France—1999 (N127). Dow AgroSciences. GLP. Unpublished.
GHE-P-8649	Doran, A and Craig, A	2001)	Residues of chlorpyrifos-methyl in apples at harvest following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N124). Dow AgroSciences. GLP. Unpublished
GHE-P-8644	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at intervals following two applications of RELDAN 22 (EF-1066), Germany—1999 (N122). Dow AgroSciences. GLP. Unpublished.
GHE-P-8648	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at intervals following two applications of RELDAN 22 (EF-1066), Italy—1999 (N123). Dow AgroSciences. GLP. Unpublished
GHE-P-8642	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at intervals following two applications of RELDAN 22 (EF-1066), Northern France—1999 (N120). Dow AgroSciences. GLP. Unpublished
GHE-P-8646	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in apples at intervals following two applications of RELDAN 22 (EF-1066), Southern France—1999 (N126). Dow AgroSciences. GLP. Unpublished.
GHE-P-8659	Doran, A.and Craig, A	2001	Residues of chlorpyrifos-methyl in cherry tomatoes at harvest grown under cover following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N111). Dow AgroSciences. GLP. Unpublished
GHE-P-8660	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in cherry tomatoes at harvest grown under open field conditions following multiple applications of RELDAN 22 (EF-1066), Greece—1999 (N112). Dow AgroSciences. GLP. Unpublished.
GHE-P-8651	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at harvest and processed fractions (wet pomace, must and wine) following applications of RELDAN 22 (EF-1066), Northern France - 1999 (N102). Dow AgroSciences. GLP. Unpublished.
GHE-P-8655	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at harvest and processed fractions (wet pomace, must and wine) following applications of RELDAN 22 (EF-1066), Southern France—1999 (N103). Dow AgroSciences. GLP. Unpublished.
GHE-P-8656	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at harvest following applications of RELDAN 22 (EF-1066), Italy—1999 (N104). Dow AgroSciences. GLP. Unpublished.
GHE-P-8652	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at intervals following applications of RELDAN 22 (EF-1066), Germany—1999 (N107). Dow AgroSciences. GLP. Unpublished.
GHE-P-8650	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at intervals following applications of RELDAN 22 (EF-1066), Northern France—1999 (N106). Dow AgroSciences. GLP. Unpublished
GHE-P-8657	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in grapes at intervals following applications of RELDAN 22 (EF-1066), Spain—1999 (N105). Dow AgroSciences. GLP. Unpublished.
GHE-P-8671	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in onions at harvest following multiple applications of RELDAN 400 (EF-1256), Hungary—1999 (N129). Dow AgroSciences. GLP. Unpublished.
GHE-P-8670	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in onions at intervals following multiple applications of RELDAN 400 (EF-1256), Hungary—1999 (N128). Dow AgroSciences. GLP. Unpublished.
GHE-P-8669	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in sweet peppers at harvest grown under cover following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N119). Dow AgroSciences. GLP. Unpublished.
GHE-P-8667	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in sweet peppers at intervals following three applications of RELDAN 22 (EF-1066), Italy—1999 (N117). Dow AgroSciences. GLP. Unpublished.
GHE-P-8668	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in sweet peppers at intervals grown under cover following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N118). Dow AgroSciences. GLP. Unpublished. May 2001.

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GHE-P-8666	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in sweet peppers at intervals grown under open field conditions following three applications of RELDAN 22 (EF-1066), Spain—1999 (N116). Dow AgroSciences GLP. Unpublished.
GHE-P-8654	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in table grapes at intervals following applications of RELDAN 22 (EF-1066), Southern France—1999 (N108). Dow AgroSciences. GLP. Unpublished.
GHE-P-8665	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in tomatoes at harvest grown under cover following multiple applications of RELDAN 22 (EF-1066), Italy—1999 (N115). Dow AgroSciences. GLP. Unpublished.
GHE-P-8663	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in tomatoes at harvest grown under cover following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N113). Dow AgroSciences. GLP. Unpublished.
GHE-P-8658	Doran, A. and Craig, A.	2001	Residues of chlorpyrifos-methyl in tomatoes at intervals following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N110). Dow AgroSciences. GLP. Unpublished.
GHE-P-8664	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in tomatoes at intervals grown under cover following multiple applications of RELDAN 22 (EF-1066), Italy—1999 (N114). Dow AgroSciences. GLP. Unpublished.
GHE-P-8653	Doran, A and Craig, A	2001	Residues of chlorpyrifos-methyl in wine grapes at harvest following applications of RELDAN 22 (EF-1066), Germany—1999 (N109). Dow AgroSciences. GLP. Unpublished.
GH-C 5482	Graper, LK	2002	Nature of the Residue Study with ^{14}C-Labeled Chlorpyrifos Applied to Cabbage (Dursban L017). Dow AgroSciences. GLP. Unpublished.
GH-C 5483	Graper, LK	2002	Nature of the Residue Study with ^{14}C-Labeled Chlorpyrifos-Methyl Applied to Tomatoes (L07). Dow AgroSciences. GLP. Unpublished.
50020	Graper, LK, Riccio, R and Balcer, JL	2006	Nature of the Residue Study with ^{14}C-Labeled Chlorpyrifos Applied to Radishes (L021). Dow AgroSciences. GLP. Unpublished.
GHE-P-9032	Jackson, R	2000	The generation and identification of water and soil degradation products of chlorpyrifos-methyl. Dow AgroSciences. GLP. Unpublished.
GHE-P-4495	Khoshab, A	1995	Residues of chlorpyrifos-methyl and its pyridinol metabolite in whole Lemon at harvest following a single application of Reldan 22E (EF-1066), Spain—1994 (N088). Dow AgroSciences. GLP. Unpublished.
GHE-P-4496	Khoshab, A	1995	Residues of chlorpyrifos-methyl and its pyridinol metabolite in whole Mandarin at harvest following a single application of Reldan 22E (EF-1066), Spain—1994 (N089). Dow AgroSciences. GLP. Unpublished.
GHE-P-4497	Khoshab, A	1995	Residues of chlorpyrifos-methyl and its pyridinol metabolite in whole Orange at harvest following a single application of Reldan 22E (EF-1066), Spain—1994 (N090). Dow AgroSciences. GLP. Unpublished.
GHE-P-3722	Khoshab, A and Berryman, T	1994	Residues of chlorpyrifos-methyl in peaches at harvest following a single application of Reldan 22E (EF 1066)—Italy 1993 (N085). Dow AgroSciences. GLP. Unpublished.
GHE-P-3631	Khoshab, A and Berryman, T	1994	Residues of chlorpyrifos-methyl in whole lemon at harvest following a single application of Reldan 22E (EF 1066)—Spain 1993 (N086). Dow AgroSciences. GLP. Unpublished.
GHE-P-3630	Khoshab, A and Berryman, T	1994	Residues of chlorpyrifos-methyl in whole Mandarins at harvest following a single application of Reldan 22E (EF 1066 or EF 815)—Spain 1993 (N087). Dow AgroSciences GLP. Unpublished.
GHE-P-3632	Khoshab, A and Berryman, T	1994	Residues of chlorpyrifos-methyl in whole orange at harvest following a single application of Reldan 22E (EF 1066)—Spain 1993 (N084). Dow AgroSciences. GLP. Unpublished.
GHE-P-4372	Khoshab, A and Bolton, A	1995	Residues of chlorpyrifos-methyl in post-harvest stored Wheat and Barley grain following treatment with RELDAN 22 (EF-1066) or RELDAN 50 (EF-917) at two different rates of application (N091). Dow AgroSciences. GLP. Unpublished.
GHE-P-2905	Khoshab, A and Chen, S	1993	Residues of chlorpyrifos-methyl in lemon peel and pulp at intervals following a single application of Reldan 22E (EF 815)—Spain 1991 (N080). Dow AgroSciences. GLP. Unpublished.
GHE-P-2906	Khoshab, A and Chen, S	1993	Residues of chlorpyrifos-methyl in mandarin peel and pulp at intervals following a single application of Reldan 22E (EF 815)—Spain 1991 (N076). Dow AgroSciences. GLP. Unpublished.
GHE-P-2907	Khoshab, A and	1993	Residues of chlorpyrifos-methyl in orange peel and pulp at intervals

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	Chen, S		following a single application of Reldan 22E (EF 815)—Spain 1991 (N075). Dow AgroSciences Ref. No. GLP. Unpublished.
GHE-P-3089	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in peaches at intervals following a single application of Reldan 22E (EF 815)—Greece 1992 (N079). Dow AgroSciences Ref. No. GLP. Unpublished.
GHE-P-3120	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in peaches at intervals following a single application of Reldan 22E (EF 815)—Italy 1992 (N077). Dow AgroSciences. GLP. Unpublished.
GHE-P-3088	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in peaches at intervals following a single application of Reldan 22E (EF 815)—Spain 1992 (N078). Dow AgroSciences. GLP. Unpublished.
GHE-P-3096	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in whole lemon at intervals and in peel and pulp at harvest following a single application of Reldan 22E (EF 815)—Spain 1992 (N083). Dow AgroSciences GLP. Unpublished.
GHE-P-3229	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in whole mandarins at intervals and in peel and pulp at harvest following a single application of Reldan 22E (EF 815)—Spain 1992 (N082). Dow AgroSciences. GLP. Unpublished.
GHE-P-3230	Khoshab, A and Laurie, D	1993	Residues of chlorpyrifos-methyl in whole orange fruit at intervals and in peel and pulp at harvest following a single application of Reldan 22E (EF 815)—Spain 1992 (N081) Dow AgroSciences GLP. Unpublished.
ERC93.1	Khoshab, Aand Laurie, D	1993	Analytical Method. Determination of Chlorpyrifos-methyl in Lemons, Mandarins and Oranges. (OR09). Dow AgroSciences. Ref. No. Non-GLP. Unpublished.
ERC 92.27	Khoshab, A and Laurie, D	1993	Analytical Method. Determination of Chlorpyrifos-methyl in Peaches (OR10). Dow AgroSciences. Non-GLP. Unpublished. 22 July 1993.
GHE-P-2500	Knowles, SJ	1991a	Determination of flammability of chlorpyrifos-methyl technical. Dowelanco Europe. GLP. Unpublished.
GHE-P-2500	Knowles, SJ	1991b	Determination of explosive properties of chlorpyrifos-methyl technical. Dowelanco Europe. GLP. Unpublished.
GHE-P-2500	Knowles, SJ	1991c	Determination of oxidizing properties of chlorpyrifos-methyl technical. Dowelanco Europe. GLP. Unpublished.
GHE-P-3085	Knowles, SJ	1993	Determination of Solvent Solubility of Chlorpyrifos-Methyl (Pure) Dowelanco. GLP. Unpublished.
GH-C-1155	Kuper, AW	1978	Residues of chlorpyrifos-methyl and 3,5,6,-trichloro-2-pyridinol in tissues and eggs of chickens fed chlorpyrifos-methyl (N144). Dow AgroSciences. Non-GLP. Unpublished.
GH-C 1118	Kuper, AW	1978	Residues of chlorpyrifos-methyl and 3,5,6,-trichloro-2-pyridinol in tissues from calves fed chlorpyrifos-methyl (N143). Dow AgroSciences. Non-GLP. Unpublished.
GH-C-1233	Kuper, AW and Kutschinski, AH	1979	Residues of chlorpyrifos-methyl and 3,5,6,-trichloro-2-pyridinol in tissues of swine fed chlorpyrifos-methyl (N146). Dow AgroSciences. Non-GLP. Unpublished.
GH-C-1161	Kuper, AW	1978	Residues of chlorpyrifos-methyl and 3,5,6,-trichloro-2-pyridinol in milk and cream from cows fed chlorpyrifos-methyl (N145). Dow AgroSciences. Non-GLP. Unpublished
GH-C 964	Laskowski, DA, Comeaux, LB and Bidlack, HD	1977	Aerobic soil decomposition of ^{14}C-labeled 3,5,6-trichloro-2-methoxypiridine. Dow AgroSciences. GLP. Unpublished.
GHE-P-11217	Livingstone, K.	2006	Residues of chlorpyrifos-methyl in maize at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N205). Dow AgroSciences. GLP. Unpublished.
GHE-P-11531	Livingstone, K.	2007	Residues of chlorpyrifos-methyl in spring or winter oilseed rape at intervals, at harvest and in process fractions following a single applications of GF-1684—Northern and Central Europe—2006 (N209). Dow AgroSciences. GLP. Unpublished. November 2007.
GHE-P-11529	Livingstone, K	2008	Residues of chlorpyrifos-methyl in cherries at intervals and at harvest following multiple applications of GF-1684—Central Europe—2006 (N226). Dow AgroSciences. GLP. Unpublished.
GHE-P-11530	Livingstone, K	2008	Residues of chlorpyrifos-methyl in cotton at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N223). Dow AgroSciences. GLP. Unpublished.

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GHE-P-11545	Livingstone, K	2008	Residues of chlorpyrifos-methyl in mandarins at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N212). Dow AgroSciences. GLP. Unpublished. January 2008.
GHE-P-11544	Livingstone, K	2008	Residues of chlorpyrifos-methyl in oranges at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N213). Dow AgroSciences. GLP. Unpublished.
GHE-P-11533	Livingstone, K	2008)	Residues of chlorpyrifos-methyl in peppers (protected) at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N222). Dow AgroSciences. GLP. Unpublished.
GHE-P-11527	Livingstone, K	2008	Residues of chlorpyrifos-methyl in pome fruit at intervals and at harvest following multiple applications of GF-1684—Southern Europe—2006 (N241). Dow AgroSciences. GLP. Unpublished.
GHE-P-11526	Livingstone, K	2008	Residues of chlorpyrifos-methyl in pome fruit at intervals, at harvest following multiple applications of GF-1684—Northern and Central Europe—2006 (N214). Dow AgroSciences. GLP. Unpublished.
GHE-P-11534	Livingstone, K	2008	Residues of chlorpyrifos-methyl in potatoes at intervals, at harvest following multiple applications of GF-1684—Northern and Central Europe—2006 (N224). Dow AgroSciences. GLP. Unpublished.
GHE-P-11535	Livingstone, K	2008)	Residues of chlorpyrifos-methyl in potatoes at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N225). Dow AgroSciences. GLP. Unpublished.
GHE-P-11528	Livingstone, K	2008	Residues of chlorpyrifos-methyl in stone fruit at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N215). Dow AgroSciences. GLP. Unpublished.
GHE-P-11536	Livingstone, K	2008	Residues of chlorpyrifos-methyl in stored barley grain at intervals and harvest following application of GF-1684—Northern, Southern and Central Europe—2006 (N234). Dow AgroSciences. GLP. Unpublished.
GHE-P-11537	Livingstone, K	2008	Residues of chlorpyrifos-methyl in stored wheat grain at intervals and harvest following application of GF-1684—Northern, Southern and Central Europe—2006 (N233). Dow AgroSciences. GLP. Unpublished.
GHE-P-11541	Livingstone, K	2008	Residues of chlorpyrifos-methyl in strawberries at intervals, at harvest following multiple applications of GF-1684—Northern and Central Europe—2006 (N218). Dow AgroSciences. GLP. Unpublished.
GHE-P-11540	Livingstone, K	2008	Residues of chlorpyrifos-methyl in strawberries at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N219). Dow AgroSciences. GLP. Unpublished.
GHE-P-11542	Livingstone, K	2008	Residues of chlorpyrifos-methyl in tomatoes (field and protected) at intervals, at harvest following multiple applications of GF-1684—Northern and Southern Europe—2006 (N220). Dow AgroSciences. GLP. Unpublished.
GHE-P-11543	Livingstone, K	2008	Residues of chlorpyrifos-methyl in tomatoes (protected) at intervals, at harvest following multiple applications of GF-1684—Central Europe—2006 (N221). Dow AgroSciences. GLP. Unpublished.
GHE-P-11539	Livingstone, K	2008	Residues of chlorpyrifos-methyl in white and red table grapes at intervals, at harvest following multiple applications of GF-1684—Southern Europe—2006 (N217). Dow AgroSciences. GLP. Unpublished.
GHE-P-11538	Livingstone, K	2008	Residues of chlorpyrifos-methyl in white and red wine grapes and red table grapes at intervals, at harvest following multiple applications of GF-1684—Central Europe—2006 (N216). Dow AgroSciences. GLP. Unpublished.
GH-C 5484	Magnussen, JD	2002	^{14}C Chlorpyrifos Citrus Nature of Residue Study (Dursban L018). Dow AgroSciences. GLP. Unpublished.
50021	Magnussen, JD and Balcer, JL	2006	Nature of the Residue Study with ^{14}C-Chlorpyrifos Applied to Peas (L020). Dow AgroSciences. GLP. Unpublished.
GH-C 5429	Maliani, N	2002a	Independent laboratory validation of Dow AgroSciences LLC Method GRM 00.10—Determination of residues of chlorpyrifos-methyl residues in crops and process fractions with a high water content (OR17A). Dow AgroSciences. GLP. Unpublished.
GH-C 5437	Maliani, N	2002b	Independent laboratory validation of Dow AgroSciences LLC Method GRM 02.01—Determination of residues of chlorpyrifos-methyl and chlorpyrifos in animal tissues by gas chromatography with negative-ion chemical ionisation mass spectrometry (O34A). Dow AgroSciences. GLP.

Code	Author	Year	Report
			Unpublished.
GHE-P-11798	Marshall, L	2008	Residues of chlorpyrifos-methyl and TCP in cherries at intervals and at harvest following a single application of GF-1684—Central Europe—2007 (N235). Dow AgroSciences. GLP. Unpublished.
GHE-P-11806	Marshall, L	2008	Residues of chlorpyrifos-methyl and TCP in maize at intervals and at harvest following a single application of GF-1684—Southern Europe—2007 and 2008 (N240). Dow AgroSciences. GLP. Unpublished.
GHE-P-11805	Marshall, L	2008	Residues of chlorpyrifos-methyl and TCP in outdoor and indoor tomatoes at intervals and at harvest following a single application of GF-1684—Northern, Central and Southern Europe—2007 and 2008 (N239). Dow AgroSciences. Version 3. GLP. Unpublished.
33688	McConnell, AB, Servatius, LJ, Herrer, RE, Bache, B and Wilkes, LC	1982	Determination of the metabolic fate of ^{14}C chlorpyrifos-methyl in lactating goats (H18). Dow AgroSciences. Ref. No. GH-C 1578. Non-GLP. Unpublished.
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20075010/11-FPKI	Miserocchi, G	2008	Residues decay of chlorpyrifos-methyl in Kiwi following applications of GF-1684 Italy, 2007 (N227). Dow AgroSciences. GLP. Unpublished.
GHE-P-326	Morel, JL	1975	Determination of residues of chlorpyrifos-methyl in bread following treatment of grain in a silo with Reldan insecticide (N013). Dow AgroSciences, Non-GLP. Unpublished.
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GHE-P-11215	Old, J	2006	Residues of chlorpyrifos-methyl in apples at intervals and harvest following multiple applications of GF-1325—Northern Europe—2005 (N198). Dow AgroSciences. GLP. Unpublished. November 2006.
GHE-P-11214	Old, J	2006	Residues of chlorpyrifos-methyl in apples at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N195). Dow AgroSciences GLP. Unpublished.
GHE-P-11216	Old, J	2006	Residues of chlorpyrifos-methyl in apricots at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N199). Dow AgroSciences GLP. Unpublished.
GHE-P-11220	Old, J	2006	Residues of chlorpyrifos-methyl in peaches at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N200). Dow AgroSciences GLP. Unpublished.
GHE-P-11222	Old, J	2006	Residues of chlorpyrifos-methyl in pears at intervals and harvest following multiple applications of GF-1325—Northern Europe—2005 (N202). Dow AgroSciences. GLP. Unpublished.
GHE-P-11221	Old, J	2006	Residues of chlorpyrifos-methyl in pears at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N201). Dow AgroSciences. GLP. Unpublished.
GHE-P-11223	Old, J	2006	Residues of chlorpyrifos-methyl in protected peppers at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N203). Dow AgroSciences Ref. No. GLP. Unpublished.
GHE-P-11224	Old, J	2006	Residues of chlorpyrifos-methyl in red and white table grapes at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N196). Dow AgroSciences. GLP. Unpublished.
GHE-P-11228	Old, J	2006)	.Residues of chlorpyrifos-methyl in red wine grapes at intervals and harvest and in process fractions following multiple applications of GF-1325—Southern Europe—2005 (N206). Dow AgroSciences. GLP. Unpublished.
GHE-P-11226	Old, J	2006	Residues of chlorpyrifos-methyl in tomatoes at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N204). Dow AgroSciences Ref. No. GLP. Unpublished.
GHE-P-11227	Old, J	2006	Residues of chlorpyrifos-methyl in white wine grapes at intervals and harvest following multiple applications of GF-1325—Northern Europe—2005 (N197). Dow AgroSciences. GLP. Unpublished.

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GHE-P-11219	Old, J	2007	Residues of chlorpyrifos-methyl in oranges at intervals and harvest following multiple applications of GF-1325—Southern Europe—2005 (N208). Dow AgroSciences Ref. No. GLP. Unpublished.
GHE-P-11225	Old, J	2008	Residues of chlorpyrifos-methyl in protected tomatoes at intervals, at harvest and in process fractions following multiple applications of GF-1325—Southern Europe—2005 (N211). Dow AgroSciences. GLP. Unpublished.
GHE-P-11532	Livingstone K	2007	Residues Of Chlorpyrifos-Methyl In Spring or Winter Oil Seed Rape at and In Process Fractions Following of Application of Gf-1684—Southern Europe—2006 (N210). Dow AgroSciences. GLP. Unpublished.
GHE-P-3756	Phillips, M and Hall, BE	1994	Aerobic Degradation of Chlorpyrifos-methyl in Natural Waters and Associated Sediments (K12). Dow AgroSciences. GLP. Unpublished.
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GHE-P-10994	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in apples and process fractions at intervals and at harvest following multiple applications of GF-1325, Germany and Northern France—2004 (N183). Dow AgroSciences. GLP. Unpublished.
GHE-P-10995	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in apples and process fractions at intervals and at harvest following multiple applications of GF-1325, Greece, Southern France and Spain (N186). Dow AgroSciences. GLP. Unpublished.
GHE-P-10996	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in apricots at intervals and at harvest following multiple applications of GF-1325, Greece, Southern France and Spain (N187). Dow AgroSciences. GLP. Unpublished.
GHE-P-10989	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in cherry tomatoes grown under cover at intervals following multiple applications of GF-1325, Southern France—2004 (N189). Dow AgroSciences. GLP. Unpublished.
GHE-P-10991	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in maize and process fractions at intervals and at harvest following multiple applications of GF-1325, Spain, Southern France and Italy—2004 (N181). Dow AgroSciences. GLP. Unpublished.
GHE-P-11004	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in mandarins at intervals and at harvest following multiple applications of GF-1325, Italy and Spain—2004 (N179). Dow AgroSciences. GLP. Unpublished.
GHE-P-10992	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in peaches and process fractions at intervals and at harvest following multiple applications of GF-1325, Italy, Southern France and Spain (N185). Dow AgroSciences. GLP. Unpublished
GHE-P-10997	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in pears at intervals and at harvest following multiple applications of GF-1325, Greece, Southern France and Spain—2004 (N177). Dow AgroSciences. GLP. Unpublished.
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GHE-P-11000	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in red table grapes and process fractions at intervals and at harvest following multiple applications of GF-1325, Spain and Southern France—2004 (N178). Dow AgroSciences. GLP. Unpublished.
GHE-P-10990	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in sweet peppers grown under cover at intervals and at harvest following multiple applications of GF-1325, Greece, Spain, Southern France and Italy—2004 (N180). Dow AgroSciences. GLP. Unpublished.
GHE-P-10993	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in tomatoes and process fractions at intervals and at harvest following multiple applications of GF-1325, Greece, Italy and Spain—2004 (N182). Dow AgroSciences. GLP. Unpublished.

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GHE-P-10988	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in tomatoes and tomato juice grown under cover at intervals and at harvest following multiple applications of GF-1325, Italy, Southern France and Spain—2004 (N176). Dow AgroSciences. GLP. Unpublished.
GHE-P-10999	Rawle, N	2005	Residues of chlorpyrifos-methyl and TCP in white table grapes and process fractions at intervals and at harvest following multiple applications of GF-1325, Spain and Southern France (N188). Dow AgroSciences. GLP. Unpublished.
GHE-P-11003	Rawle, N	2006	Residues of chlorpyrifos-methyl and TCP in oranges and process fractions at intervals and at harvest following multiple application of GF-1325, Italy and Spain—2004 and 2005 (N194). Dow AgroSciences. GLP. Unpublished. 2006.
GHE-P-11002	Rawle, N	2006	Residues of chlorpyrifos-methyl and TCP in red wine grapes and process fractions at intervals and at harvest following multiple applications of GF-1325, Spain, Italy, Southern France and Greece (N191). Dow AgroSciences. GLP. Unpublished.
GHE-P-11006	Rawle, N	2006	Residues of chlorpyrifos-methyl and TCP in stored malting barley grain and process fractions at intervals following a single application of GF-1325, UK—2004 (N193). Dow AgroSciences. GLP. Unpublished.
GHE-P-11005	Rawle, N	2006	Residues of chlorpyrifos-methyl and TCP in stored wheat grain and process fractions at intervals following a single application of GF-1325, UK—2004 (N190). Dow AgroSciences. GLP. Unpublished.
GHE-P-11001	Rawle, N	2006	Residues of chlorpyrifos-methyl and TCP in white wine grapes and process fractions at intervals and at harvest following multiple applications of GF-1325, Germany and Northern France (N192). Dow AgroSciences. GLP. Unpublished.
GHE-P-3638	Reeves, GL	1994	Aerobic soil degradation of ^{14}C-chlorpyrifos-methyl (K13). Dow AgroSciences. GLP. Unpublished.
GHE-P-4045	Richardson, N	1995	Chlorpyrifos-Methyl (Technical) Determination Of Auto-Ignition Temperature. Dow AgroSciences. GLP. Unpublished.
GHE-P-6453	Sydney, P	1997	Determination of physical-chemical properties (surface tension and partition coefficient) (A45). Dow AgroSciences. GLP. Unpublished.
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GRM 00.10	Teasdale, R	2000	Determination of residues of chlorpyrifos-methyl residues in crops and process fractions with high water content (OR17). Dow AgroSciences. GLP. Unpublished.
GHE-P-8661	Teasdale, R	2000	Residues of chlorpyrifos-methyl in tomatoes at harvest and processed fractions (canned tomatoes, juice and puree) following multiple applications of RELDAN 22 (EF-1066), Italy—1999 (N100). Dow AgroSciences. GLP. Unpublished.
GHE-P-8662	Teasdale, R	2000	Residues of chlorpyrifos-methyl in tomatoes at intervals grown under cover following multiple applications of RELDAN 22 (EF-1066), Spain—1999 (N101). Dow AgroSciences. GLP. Unpublished.
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GHE-P-9749	Watson, P	2002	Chlorpyrifos-Methyl Calculation of Henry's Law Constant (H) Dow AgroSciences. GLP. Unpublished.
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GHE-P-10492	Wardman, JP	2004	Residues of cypermethrin, alpha-cypermethrin and chlorpyrifos in tomatoes at harvest following multiple applications of GF-875 or EF-1153,

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GHE-P-3982	Yon, DA and Muller, J	1994	Aqueous hydrolysis of chlorpyrifos-methyl (K17). Dow AgroSciences. GLP. Unpublished.
GHE-P-3981	Yon, DA and Muller, J	1994	Aqueous photolysis of chlorpyrifos-methyl K18). Dow AgroSciences. GLP. Unpublished.