ETHEPHON (106)

First draft prepared by Dr Yukiko Yamada, Ministry of Agriculture, Forestry and Fisheries, Tokyo, Japan

EXPLANATION

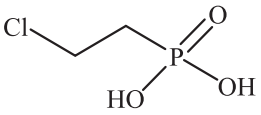
Ethephon, 2-chloroethylphosphonic acid, is a systemic plant growth regulator belonging to the phosphonate family. It is readily absorbed by the plant and releases ethylene, a natural plant hormone. Ethylene not only influences directly several physiological processes, such as ripening and maturation, but also stimulates the endogenous ethylene production. It has been registered in many countries for a variety of crops, including fruits, vegetables, cereals and oilseed crops.

Ethephon was first evaluated by JMPR in 1977 as a new compound, and has been reviewed for residues in 1978, 1983, 1985, 1994 (Periodic Review) and 1994. Currently there are 26 Codex MRLs for ethephon. It was listed in the Priority List by the 46th Session of CCPR in 2014 for toxicological and residue evaluation by the current Meeting in the CCPR Periodic Review Programme.

The Meeting received information on identity, metabolism and environmental fate, residue analysis, use patterns, supervised trials (on apples, cherries, grapes, figs, olives, pineapples, tomatoes, cereals, and cotton), processing, and animal feeding studies.

Matrix	Fortification, mg/kg	n	Range of recoveries, %	Mean recovery, %	CV, %	Ref. method
Blueberry	0.05	3	90–100	96	5.3	
	0.5	4	84–94	89	5.2	

IDENTITY

ISO common name:	Ethephon
Chemical name	
IUPAC:	2-Chloroethylphosphonic acid
CAS:	(2-Chloroethyl)phosphonic acid
CAS Registry No.:	16672-87-0
CIPAC No.:	373
Structural formula:	
Molecular formula:	C2H6ClO3P
Molecular weight:	144.5

PHYSICAL AND CHEMICAL PROPERTIES

Pure active ingredient

Property	Results	Reference
Appearance	White crystalline powder (98.5%)	Mühlberger, 2001 (PA01/031) [M-207237-01-1]
Odour	No characteristic odour (98.5%)	Mühlberger, 2001 (PA01/031) [M-207237-01-1]
Melting point	73.3 °C (98.5%)	Smeykal, 2001 (20010301.01) [M-203841-01-1]
Boiling point	Decomposes at 250–400 °C (under	Smeykal, 2001 (20010301.01)

Property	Results	Reference
	nitrogen) (98.5%)	[M-203841-01-1]
Relative density	1.65 kg/m^3 at 20 °C (98.5%)	Schneider, 2001 (B 031/2001) [M-204865-01-1)]
Vapour pressure	< 1.0×10^{-3} Pa (from 18 to 80 °C) (98.5%)	Smeykal, 2001 (20010301.02) [M-203843-01-1]
Volatility (Henry's law constant)	< 1.45×10^{-7} Pa m^3 mol^{-1}	Bascou, 2002 (C019663) [M-208014-01-1]
Solubility in water	At 21–24 °C pH < 0.2: > 1000 g/L pH 4: 800 g/L pH > 5: decomposition and no solubility could be determined (98.5% and 98.0%)	Mühlberger, 2002 (PA01/018) [M-206704-01-1]
Solubility in organic solvents	Solubility at 20 °C n-Heptane: < 0.3 mg/L p-Xylene: 82.5 mg/L 1,2-Dichloroethane: 832 mg/L Methanol: > 600 g/L Acetone: > 600 g/L Ethyl acetate: > 600 g/L Acetonitrile: > 600 g/L Dimethylsulfoxide: > 600 g/L (98.5%)	Mühlberger, 2001 (PA01/019) [M-204740-01-1]
Partition coefficient	Log P_{ow} at room temperature: pH 2: –0.63 pH 7: –1.89 pH 10: –1.81 (98.5%)	Mühlberger, 2002 (PA01/020) [M-206706-01-1]
Hydrolysis	DT_{50} values at 25 °C: pH 5: 73.5 days pH 7: 2.4 days pH 9: 1.0 day (linear-regression)	Das, 1990 (ISSI 89150) [M-187629-01-1]
Photochemical degradation	Rate constant k at 25 °C and pH 5 from linear regression: k_2 under irradiated conditions, 9.39 10^{-04} h^{-1} (DT_{50} 61 days of 12 hours irradiation/day); k_1 under non-irradiated conditions, 5.22 10^{-04} h^{-1} (DT_{50} 111 days of 12 hours darkness/day). Net rate constant k_3 due to irradiation alone, $k_3 = k_2 - k_1 = 4.17E^{-04}$ h^{-1} (Net DT_{50} 139 days of 12 hours irradiation/day). Degradation product: ethylene (max. 15.3% and 23.1% in non-irradiated and irradiated samples, respectively).	Das, 1990 (ISSI 89151) [M-187632-01-1]
Dissociation constant	At 21 °C $pK_1 = 2.82$ $pK_2 = 7.21$ (98.5%)	Mühlberger, 2002 (PA01/017) [M-206703-01-1]

Technical material

Property	Results	Reference
Active ingredient	Not less than 910 g/kg	FAO Specification 373/TC/S/F (1997) Ethephon technical
Impurities	MEPHA (Mono 2-chloroethyl ester, 2-chloroethyl phosphonic acid): maximum 20 g/kg 1,2-Dichloroethane: maximum 0.5 g/kg	FAO Specification 373/TC/S/F (1997) Ethephon technical
Appearance	Greyish-white coloured, waxy solid without extraneous matter	FAO Specification 373/TC/S/F (1997) Ethephon technical
pH	1.5 to 2.0	FAO Specification 373/TC/S/F (1997) Ethephon technical

Technical concentrate

Property	Results	Reference
Impurities	MEPHA: maximum 2% of declared ethephon content 1,2-Dichloroethane: maximum 0.05% of the declared ethephon content Material insoluble in water: The product shall pass through a 250 µm test sieve and not more than 1 g/kg shall remain on a 150 µm test sieve. Water: shall not be less than the following figure: {1000 – (measured ethephon content in g/kg)/0.91} – 15	FAO Specification 373/TK/S/F (2000) Ethephon technical concentrate
pH	1.5 to 2.0	FAO Specification 373/TK/S/F (2000) Ethephon technical concentrate
Appearance	Viscous colourless liquid (71.5%)	Bascou, 2001 (R&D/CRLD/AN/0015211) [M-184641-01-1]
Odour	No characteristic odour (71.5%)	Bascou, 2001 (R&D/CRLD/AN/0015211) [M-184641-01-1]
Flammability	No flash point up to 111 °C (boiling temp.) (71.4/70.2%)	Francois, 1999 (99-308-SEC) [M-179319-01-1]
Auto-flammability	Self-ignition temperature: 490 °C (70.2%)	Francois, 1999 (99-308-SEC) [M-179319-01-1]
Explosive properties	Not explosive (70.2%)	Francois, 1999 (99-308-SEC) [M-179319-01-1]

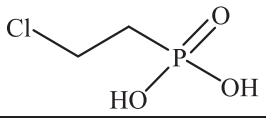
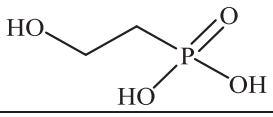
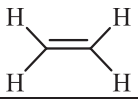
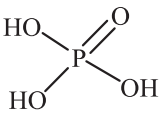
Formulations

Ethephon is mainly formulated as a soluble concentrate (SL). Concentrations are between 120 and 730 g/L. Combinations with chlormequat chloride or cyclanilide are also available for specific uses. Formulations are applied as foliar sprays by either ground or aerial equipment. Available formulations are listed below:

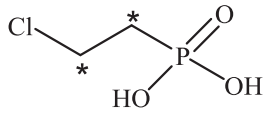
- Soluble liquid (SL) formulations containing either 120 g ai/L, 240 g ai/L, 250 g ai/L, 480 g ai/L, 660 g ai/L or 720 g ai/L
- Soluble liquid (SL) formulations containing a mixture of ethephon + chlormequat-chloride (150 g ai/L + 300 g ai/L or 180 g ai/L + 360 g ai/L ethephon + chlormequat-chloride, respectively)
- Suspension concentrate (SC) formulations containing a mixture of ethephon + cyclanilide (480 g ai/L + 60 g ai/L or 720 g ai/L + 45 g ai/L or 731 g ai/L + 49.5 g ai/L ethephon + cyclanilide, respectively)

METABOLISM AND ENVIRONMENTAL FATE

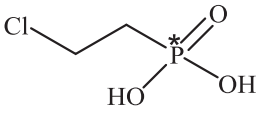
The following links code numbers and structure or description of the compounds appearing in the various metabolism and environmental fate studies.

Name or Code (MW)	IUPAC Name	Structure	Found in:
Ethephon (144.5) Syn: V-1283, S-1283, YI-5301, SCAL-5001	2-Chloroethylphophonic acid		Plants, Animals, Soils
HEPA (126.05)	(2-Hydroxyethyl)-phosphonic acid		Plants, Animals, Soils
Ethylene (28.05)	Ethylene		Plants, Animals
Phosphoric acid (94.97) or Phosphate anion	Phosphoric acid		Plants, Animals

The Meeting received information on plant and animal metabolism for ethephon, its environmental fate in soil and residues in rotational crops. The fate and behaviour of ethephon in plants, animals and soil were investigated using the radio-labelled ethephon with ^{14}C as shown in Figure 1. The radio-labelled ethephon with ^{32}P was also used in the metabolism study in pineapple.



1,2-^{14}C-ethephon ([U-^{14}C]-ethephon, ^{14}C-ethephon)



^{32}P-ethephon

Figure 1 Radio-labelled test materials used in the metabolism and environmental fate studies

In the metabolism and environmental studies, the total radioactive residues were expressed in ethephon equivalents unless otherwise stated.

Plant Metabolism

The Meeting received information on metabolism of ethephon in various plants (mostly fruit and seed crops) in support of supervised trials: pineapple, melon (cantaloupe), tomato, wheat, hazelnut and cotton. Information was also available from the published scientific literature on apple, peach, cherry, grape, squash and cucumber.

Pineapple

The metabolism of ethephon was studied in pineapple using [^{32}P]ethephon and [^{14}C]ethephon (Anonymous, 1968, ETH/M21, [M-188023-01-1]). The technical material used in the study was a mixture of 70% ethephon and 30% monochloroethyl ester. However, the monochloroethyl ester was later removed from all formulations intended for crop use and therefore its metabolism is not relevant for the current uses of ethephon.

In the first experiment, pineapple plants grown in the field were treated with an application to individual leaves of 300 mg of a formulation mixture containing [^{32}P]ethephon and its monochloroethyl ester approximately 5 months before harvesting of fruit. A separate group of pineapple plants was treated with 300 mg of a formulation mixture containing ^{32}P-sodium acid phosphate to investigate the uptake and distribution of phosphate, ethylene and chloride (all expected metabolites of ethephon) under the pH conditions normally found in plant tissues. Plants that were harvested with a longer PHI received a larger amount of ^{32}P-labelled compound due to the short half-life of ^{32}P (14.2 days).

One to 118 days after treatment, the above-ground portions were harvested. Samples were rinsed with water, homogenized and extracted with benzene and then methanol. The post-extraction solids were analysed for radioactivity by combustion. Liquid extracts were analysed by liquid scintillation counting (LSC).

On the day of application and three days after application (DAT), most of the radioactivity was recovered in the water wash. No radioactivity was found in the benzene extract or in the post-extraction solids. More than three days after treatment, little or no radioactivity was recovered in the water wash. On 118 DAT, approximately 40% of the radioactivity remained in the post-extraction solids, and was almost same for plants treated with [^{32}P]ethephon and with [^{32}P]phosphate.

TLC analysis of the water washes and methanol extracts showed complete degradation of ethephon in/on pineapple leaves long before formation of the fruits. No ethephon was found in immature fruits, or in fruits of leaves harvested 1 month before full maturity of the fruits.

In the second experiment, a pineapple leaf was spotted with a solution of [^{14}C]ethephon in methanol, and air-dried. Then the treated area was excised and sliced. The leaf slices were inserted into a sealed two-necked flask. A continuous stream of nitrogen was passed over the slices and led to an absorber tower containing a solution of 0.25 M mercuric perchlorate in perchloric acid to absorb [^{14}C]ethylene. The amount of [^{14}C]ethylene absorbed was determined by LSC for 8 consecutive days, after which time the leaf slices were freeze-dried, and the remaining radioactivity was determined by combustion.

Over the 8-day duration, 40.1% of the applied [^{14}C]ethephon was metabolized to [^{14}C]ethylene, and 36.3% of the applied radioactivity remained in the leaf. The low recovery is attributed to losses during freeze-drying.

In an additional static experiment, a treated pineapple leaf slice was cut into strips and placed in the centre annular ring of a Conway micro diffusion dish. A 0.5 mL aliquot of absorber solution was placed in the inner compartment and the apparatus sealed and left for 72 hours. The absorber solution was analysed by LSC. The leaf strips were extracted with methanol, the extract was diluted with water and then extracted with benzene. The methanol and benzene extracts were analysed by TLC, and the post-extraction solids were analysed by combustion. A portion of the methanol extract was treated with 5 N NaOH to convert the [^{14}C]ethephon to [^{14}C]ethylene. The resulting [^{14}C]ethylene was trapped in the perchlorate absorber and analysed by LSC.

After 72 hours, 25.2% of the applied [^{14}C]ethephon was converted to [^{14}C]ethylene. Of the radioactivity remaining in the leaf, 63.3% of the applied radioactivity (AR) was extracted with methanol, of which 40.1% AR reacted with NaOH to form [^{14}C]ethylene and was therefore characterized as [^{14}C]ethephon. TLC analysis of the methanol extract showed that parent ethephon was the only component of the residue, (Table 1).

Table 1 Recovery of ^{14}C- residues from an excised pineapple leaf slices following application of [^{14}C]ethephon (static experiment)

Fraction	% of Applied Radioactivity
[^{14}C]-ethylene	25.2
Methanol extract	63.3
Radioactivity evolved after treatment of methanol extract with NaOH (presumed to be [^{14}C]ethylene)	40.1
Benzene extract of methanol extract	< 0.1
Post-extraction solids	9.2

In the third experiment, nine pineapple plants were treated shortly (7, 14 or 21 days) before harvest of mature fruit with a spray application of [^{14}C]ethephon at 9 kg ai/ha, and transferred to uncoated cellophane chambers. Cellophane is impervious to ethylene but permeable to air and water vapour. In three of the boxes, glass tubing was inserted and connected to absorber towers filled with mercuric perchlorate-perchloric acid solution to absorb the ethylene evolved. Using a vacuum pump, air was passed through the chamber into the absorber towers at a rate of 1 air change/hour. The absorber solution was changed after 18, 46, 94, 118, 166 and 202 hours, and the radioactivity was determined by LSC. Plants were harvested after 1 hour to 21 days, and sectioned into fruit, top leaves, lower leaves and stump. The fruits were further sub-divided into crown, shell and bottom leaflets ('shell'), shell scrapings, fruit cylinder and core. Samples were frozen in dry ice and ground to a fine powder. The total radioactive residue in each fraction was determined by combustion analysis. Aliquots of each fraction were extracted with benzene and methanol, and the extracts were analysed by LSC. The radioactivity remaining unextracted was determined by combustion.

Very little or no radioactivity was found in the benzene extracts, and therefore these were not analysed further. Selected methanol extracts were analysed for ethephon by TLC. [^{14}C]Ethylene was evolved at an approximately constant rate from the treated plants. Little radioactivity was translocated into the pineapple flesh. TLC analysis showed that the bulk of the radioactivity remained in/on the plants and was found to comprise almost entirely unchanged [^{14}C]ethephon. An additional unidentified minor component of the ^{14}C-residue in pineapple shell and shell scrapings was also found in some stored standard solutions and was therefore postulated to be an impurity in the starting material rather than a metabolite. The distribution of residues in the pineapple fractions is shown in Table 2.

Table 2 Distribution of ^{14}C- residues in pineapple fractions

Application timing (days before normal harvest): Time after treatment	% of Total Radioactivity							
	Top third leaves	Shell	Shell scrapings	Stump	Cylinder	Core	Crown	Lower leaves
21: 45 hours	7.6	16.4	5.9	2.1	0.5	0.1	16.9	50.4
21: 6 days	20.5	23.9	3.7	1.4	0.9	0.1	9.8	39.3
21: 1 hour	50.6	33.6	9.2	2.3	3.4	0.8		
21: 6 hours	66.8	19.6	8.2	4.1	1.0	0.2		
21: 21 hours	42.7	42.1	11.2	2.1	0.2	< 0.1		
21: 45 hours	20.6	50.2	18.1	6.4	1.6	0.2	Not collected	
21: 3 days	41.5	39.8	14.7	1.4	1.7	0.4		
21: 6 days	40.6	47.3	7.3	2.7	1.8	0.2		
21: 9 days	38.7	49.0	9.2	1.4	1.3	0.2		
14: 9 days	26.7	47.0	21.9	2.1	2.1	0.3		
7: 7 days (fully mature)	78.6	8.6	11.8	0.8	0.3	< 0.1		

Melon (Cantaloupe)

Melon plants grown under field conditions were treated with a foliar spray of an SL formulation followed by a localised application of [^{14}C]ethephon to the leaves proximal or distal to the peduncle

(fruit stalk), or directly to the melon rind covering about 40% of the surface area (Palmer, Lewis, Johnson and Smith, 1970, ETH/20, [M-188017-01-1]). The fruits were protected after treatment using a cheesecloth bag and were harvested after 3 days. Surface residues were removed by washing the treated leaves or melon rind with 20% aqueous methanol followed by two water washes. Each melon was separated into rind, flesh and seeds, the samples were cut into thin ribbons and then frozen. The remaining vines were collected and frozen. Samples were freeze-dried and ground into a fine powder, and then extracted with either benzene plus methanol, water and methanol/chloroform (2:1), or water and chloroform.

The methanol extracts from benzene and methanol were combined, acidified and concentrated by rotary evaporation. The concentrated extract was acidified, made up to volume with methanol, and ethyl ether added to precipitate the co-extracted plant material. The combined methanol/water extracts were concentrated by rotary evaporation, acidified, and ethyl ether added to precipitate the ether insoluble residue. This extraction scheme resulted in more complete extraction of radioactivity.

Radioactivity in the methanol, or methanol/water extracts was determined by LSC. Radioactivity in non-aqueous solvents and insoluble plant residues was determined by low beta gas flow counting. Metabolite profiling was performed by radio-TLC using cellulose or silica plates.

Surface washing removed 37.2–47.8% of the AR from the treated melons and 21.4–42.9% of the AR from the treated distal leaves. The treated proximal leaves senesced and desiccated rapidly and therefore two leaves were lost and a low recovery was obtained from the third leaf. Similar but less severe ageing of the proximal leaf was observed on other vines with ripened melons (Table 3).

Table 3 Radioactive residues recovered in surface washes following application of [^{14}C]ethephon to different portions of melon plant

Plant portion to which [^{14}C]ethephon was applied	% of Applied Radioactivity [a]
Melon fruit rind	37.2–47.8
Distal leaf	21.4–42.9
Proximal leaf	12.2 [b]

[a] Range of three replicates

[b] Value for one replicate only. Proximal leaf desiccated and shattered in two replicates.

The total recovered radioactivity from the melon fruits after surface-washing was 6.90% of the AR following application to the melon rind, 1.14% following application to the distal leaf and 1.70% following application to the proximal leaf (Table 4).

Table 4 Radioactive residues in melon sections following application of [^{14}C]ethephon

Plant portion to which [^{14}C]ethephon was applied	% of Applied Radioactivity [a]			
	Rind	Flesh	Seed	Total
Melon fruit rind [b]	6.35	0.06	0.15	6.90
Distal leaf	0.60	0.47	0.07	1.14
Proximal leaf	0.87	0.67	0.14	1.70

[a] Average of three replicates.

[b] After surface washing.

Most (96–98%) of the radioactivity remained in the rind following topical application to the melon rind (Table 5).

Table 5 Distribution of radioactive residues in melon sections following application of [^{14}C]ethephon

Plant portion to which [^{14}C]ethephon was applied	% of Total Radioactivity [a]		
	Rind	Flesh	Seed
Melon fruit rind	96.3–97.8	0.6–1.4	1.5–2.4

Plant portion to which [^{14}C]ethephon was applied	% of Total Radioactivity [a]		
	Rind	Flesh	Seed
Distal leaf	33.1–67.9	30.8–58.8	1.3–15.7
Proximal leaf	29.0–80.7	13.6–61.1	5.7–13.3

[a] Range of three replicates

Ethephon was the only radioactive residue component identified by TLC (Table 6). No other radioactive component was detected.

Table 6 Concentration of [^{14}C]ethephon in melon sections following application of [^{14}C]ethephon

Plant portion to which [^{14}C]ethephon was applied	[^{14}C]Ethephon (µg/kg) [a]		
	Rind	Flesh	Seed
Melon fruit rind	14–34	0.04–0.11	0.60–2.3
Distal leaf	0.82–5.3	0.39–0.76	0.21–0.74
Proximal leaf	1.6–6.2	0.33–1.3	0.83–1.7

[a] Range of three replicates

Tomato

Tomato plants in outdoor plots were treated with a foliar application of [^{14}C]ethephon at 1.46 kg ai/ha and a water volume of 480 L/ha (Smith, 2002, CZ00E500, [M-240722-01-2]). The application timing was at the 'green mature' or 'colour break' stage of development. Tomato fruits were harvested on day 0 and 5 and 12 days after treatment (DAT). The 0 and 5 DAT samples were surface-washed with methanol, and then chopped and extracted with methanol. The 12 DAT samples were ground with dry ice and the total radioactivity was determined by combustion. The 12 DAT samples were subsequently extracted with methanol. Radioactivity in extracts was determined by LSC, and post-extraction solids were analysed by combustion analysis and LSC. Extracts were analysed by HPLC and TLC, and identification of ethephon and HEPA was performed by co-chromatography with reference standards.

The majority of the radioactive residue on 0 DAT was recovered in the surface wash, and most of the remainder was extracted with methanol. At 5 DAT, only 18% of the total radioactive residue (TRR) was recovered in the surface wash and the majority was extracted with methanol. Only 4.6% TRR remained unextracted. At 12 DAT, methanol extraction recovered 98% TRR, leaving only 2.3% TRR unextracted (Table 7).

Table 7 Total radioactive residues in tomato fruit after foliar application of [^{14}C]ethephon at 1.46 kg ai/ha

Fraction	0 DAT		5 DAT		12 DAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
Methanol surface wash	6.5	83.7	0.31	18.4	Not performed	
Methanol extraction	1.3	16.0	1.3	77.1	1.1	97.8
Total extracted	7.8	99.7	1.6	95.5	1.1	97.8
Unextracted residue	0.025	0.4	0.078	4.6	0.026	2.3
TRR by extraction	7.8	100	1.7	100	1.2	106
TRR by combustion	Not performed		Not performed		1.1	100

The main component of the radioactive residue found in tomato fruit was ethephon (96, 70 and 59% TRR on 0, 5 and 12 DAT, respectively). The concentration of ethephon decreased over the time period in the study from 7.5 mg/kg at 0 DAT to 0.68 mg/kg at 12 DAT. The only significant metabolite was HEPA, amounting to 13–15% TRR in fruits of 5 and 12 DAT (Table 8). There were two other discernible metabolites that chromatographed close to HEPA, but both accounted for < 5% TRR and were not identified. The remainder of the unidentified radioactivity was polar in nature and did not exceed 8.5% TRR.

In tomato plants ethephon was metabolised by replacement of the chlorine in the 2-position with a hydroxy group to form HEPA; like in all other plants whose metabolism of ethephon was studied, the majority of the [^{14}C]ethephon applied was decomposed to volatile ethylene and phosphate.

Table 8 Identification of radioactive residues in tomato fruit after foliar application of [^{14}C]ethephon at 1.46 kg ai/ha

Fraction/compound	0 DAT		5 DAT		12 dayDAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
TRR by extraction	7.8	100	1.7	100	1.2	106
Total extracted	7.8	99.7	1.6	95.5	1.1	97.8
Ethephon						
—Methanol surface wash	6.3	81.2	0.3	18.1	–	–
—Methanol extract	1.2	14.9	0.9	51.5	0.71	59.4
—Total	7.5	96.1	1.2	69.6	0.71	59.4
HEPA						
—Methanol surface wash	0.14	1.8	0.01	0.3	–	–
—Methanol extract	0.02	0.2	0.25	14.7	0.16	13.2
—Total	0.16	2.0	0.26	15.0	0.16	13.2
Total identified	7.7	98.1	1.4	84.8	0.87	72.6
Unextracted residue	0.025	0.4	0.078	4.6	0.028	2.3

Wheat

Wheat plants at the forage stage (BBCH 39) in outdoor plots were treated with a foliar application of [^{14}C]ethephon at a normal field rate of 0.36 kg ai/ha and at a 10× rate of 3.6 kg ai/ha in a water volume of approximately 250 L/ha (Smith, 2002, CZ00E501, [M-240723-01-1]). Samples were harvested on 0 (forage), 14 (hay) and 34 (grain and straw) DAT. The 0 and 14 DAT samples were surface-washed with methanol, and then chopped and extracted with methanol. The 34 DAT samples were homogenized and extracted with methanol. The post-extraction solids from the grain (1× and 10× rate) and straw (1× rate) were subjected to acid hydrolysis with 5% HCl, yielding an acid hydrolysate. The residual fibres were extracted with methanol and then acetonitrile, yielding a post-hydrolysis extract and non-extractable residue. Radioactivity in extracts was determined by LSC, and post-extraction solids were analysed by combustion analysis and LSC. The TRR in the 0 and 14 DAT samples were determined by extraction and combustion of the residue. The TRR in the 34 DAT samples was determined by combustion. Extracts were concentrated and analysed by HPLC and TLC, and identification of ethephon and HEPA was performed by co-chromatography with reference standards.

For both application rates at 0 DAT, about half the radioactivity was quickly absorbed into the leaves. On 14 DAT, only a small amount of the applied radioactivity remained on the leaf surface (1.1% TRR) and almost all the radioactivity was recovered in the methanol extract, with about 5% TRR remaining unextracted (Table 9).

On 14 and 34 DAT, the majority of radioactivity was recovered in methanol extracts of plant parts (hay and straw) regardless of the dose used; radioactivity was similarly distributed in methanol surface wash and methanol extract of forage on 0 DAT. Unextracted residues were about 5% in 14 DAT hay but 10% (1×) and 26% (10×) in 34 DAT straw.

Methanol extraction could recover only 28 and 22% TRR from grain (34 DAT) samples after the low and high doses. Acid hydrolysis of remaining solid with 5% HCl released 56 and 71% TRR and extraction of the post-hydrolysis solids with methanol and then acetonitrile further released a total of 9.9% and 4.3% TRR. This indicates the significance of conjugates in grains. Unextracted residues were 1.8–6.0% TRR.

Table 9 Total radioactive residues in wheat fractions after foliar application of [^{14}C]ethephon at 0.36 kg ai/ha (1× rate) or 3.6 kg ai/ha (10× rate)

	Forage, 0 DAT		Hay, 14 DAT		Grain, 34 DAT		Straw, 34 DAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
Application at 0.36 kg ai/ha (1× rate)								
Methanol wash	16.31	44.8	0.06	1.1	Not performed		Not performed	
Methanol extraction	19.94	54.9	4.79	94.1	0.30	27.5	1.38	57.8
Acid hydrolysate	Not performed		Not performed		0.60	56.1	0.47	19.9
Post-hydrolysis extract	Not performed		Not performed		0.11	9.9	0.29	12.4
Total extracted	36.25	99.7	4.85	95.2	1.00	93.5	2.14	90.1
Unextracted residue	0.12	0.4	0.23	4.9	0.06	6.0	0.23	10.1
TRR by extraction	36.37	100	5.09	100	1.07	99.5	2.37	100.2
TRR by combustion	Not performed		Not performed		1.07	100	2.37	100
Application at 3.6 kg ai/ha (10× rate)								
Methanol wash	110.56	45.6	0.22	1.2	Not performed		Not performed	
Methanol extraction	133.32	54.3	17.42	93.7	0.75	22.0	16.52	73.6
Acid hydrolysate	Not performed		Not performed		2.42	71.4	Not performed	
Post-hydrolysis extract	Not performed		Not performed		0.15	4.3	Not performed	
Total extracted	243.88	99.9	17.64	94.9	3.32	97.7	16.52	73.6
Unextracted residue	0.66	0.3	0.96	5.2	0.06	1.8	5.93	26.4
TRR by extraction	244.54	100.2	18.60	100.1	3.38	99.5	22.45	100
TRR by combustion	Not performed		Not performed		3.39	100	22.45	100

At all harvest times, most of TRR was attributed to the sum of ethephon and HEPA, and were the only residues identified. In 0 DAT forage (1× rate), the recovered radioactivity was primarily unchanged ethephon (Table 10).

In the 14 DAT hay, the major radioactive residue was HEPA with 72% TRR and 3.7 mg/kg followed by ethephon with 20% TRR and 1.0 mg/kg in the methanol extract. In the 34 DAT straw, the major radioactive residue was ethephon at 62% TRR (47% TRR in methanol extract, 9.3% in acid hydrolysate and 5.9% TRR in extracts of post acid hydrolysis solid) and 1.5 mg/kg.

In 34 DAT grain, HEPA was found at a similar level as ethephon after the low dose: HEPA, 48% TRR (14% TRR in methanol extract, 29% TRR in acid hydrolysate and 5.5% TRR in extracts post-hydrolysis solid) and 0.51 mg/kg; and ethephon, 44% TRR (13% TRR in methanol extract, 26% TRR in acid hydrolysate and 4.4% TRR in extracts of post-hydrolysis solid) and 0.47 mg/kg. After the higher dose, approximately two times larger amounts of HEPA was found than ethephon (HEPA, total of 60% TRR and 2.0 mg/kg; and ethephon, total of 32% TRR and 1.1 mg/kg). No other metabolites exceeded 3% of TRR.

In total, in 14 and 34 DAT samples, 88–92% of the radioactive residue was identified as ethephon and HEPA, with no other single metabolite comprising more than 2.6% TRR.

Table 10 Identification of radioactive residues in wheat fractions after foliar application of [^{14}C]ethephon at 0.36 kg ai/ha (1× rate) or 3.6 kg ai/ha (10× rate)

	Forage, 0 DAT		Hay, 14 DAT		Grain, 34 DAT		Straw, 34 DAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
Application at 0.36 kg ai/ha (1× rate)								
TRR	36.4	100	5.09	100	1.07	100	2.37	100
Total extracted	36.3	99.7	4.85	95.2	1.00	93.5	2.14	90.1
Ethephon								
—Methanol wash	16.0	43.9	–	–	–	–	–	–
—Methanol extract	18.9	52.0	1.00	19.7	0.14	13.0	1.12	47.1
—Acid hydrolysate	–	–		–	0.28	26.1	0.22	9.3
—Post-hydrolysis ext.	–	–		–	0.05	4.4	0.14	5.9
—Total	34.9	95.9	1.00	19.7	0.47	43.5	1.48	62.3
HEPA								
—Methanol wash	0.15	0.4	–	–	–	–	–	–
—Methanol extract	0.58	1.6	3.67	72.2	0.15	13.6	0.22	9.1

	Forage, 0 DAT		Hay, 14 DAT		Grain, 34 DAT		Straw, 34 DAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
—Acid hydrolysate	–	–	–	–	0.31	28.6	0.25	10.6
—Post-hydrolysis ext.	–	–	–	–	0.06	5.5	0.15	6.4
—Total	0.73	2.0	3.67	72.2	0.51	47.7	0.62	26.1
Total identified	33.6	97.9	4.68	91.9	0.98	91.2	2.09	88.4
Unextracted residue	0.14	0.4	0.23	4.9	0.06	6.0	0.24	10.1

	Grain (34 day)	
	mg/kg	% TRR
Application at 3.6 kg ai/ha kg ai/ha (10× rate)		
TRR	3.39	100
Total extracted	3.32	97.7
Ethephon		
—Methanol extract	0.28	8.3
—Acid hydrolysate	0.74	21.8
—Post-hydrolysis ext.	0.04	1.2
—Total	1.08	31.8
HEPA		
—Methanol extract	0.41	12.1
—Acid hydrolysate	1.53	45.1
—Post-hydrolysis ext.	0.11	3.2
—Total	2.04	60.3
Total identified	3.12	92.1
Unextractable residue	0.06	1.8

In summary, ethephon is metabolised in wheat to form HEPA. The residue in 0 DAT wheat forage comprised mainly ethephon, with low levels of HEPA. In hay, grain and straw, the residue consisted of ethephon and HEPA; no other metabolites were identified.

Hazelnut (Filberts)

Two filbert trees (in the Codex Classification of Foods and Animal Feeds, the entry “Filberts” refers to “Hazelnuts” with the description, “among other *Corylus maxima*, Mill; and the “Hazelnuts”, include *C maxima* and *C. avellana*.) were treated with a foliar spray of non-radio-labelled ethephon at 1000 mg/kg and, six hours later, 2960 kBq [^{14}C]ethephon was applied to two branches of the trees (Anonymous, 1972, [M-188020-01-1]). One branch had 36 leaves and 9 nuts in husks, of which the upper surfaces of 18 leaves and two husks were treated. The other branch had 35 leaves and 11 nuts in husks, of which 15 leaves and three husks were treated.

The treated branches were separately enclosed in a screen cage wrapped in a plastic bag. Small holes in the bags allowed air to enter and flow through the bags. The bags were fitted with tubing which was connected to a gas trapping system consisting of an absorber containing water-saturated n-butanol and a mercuric perchlorate-perchloric acid solution to absorb ethylene. Air was drawn through the gas trapping system at a rate of 475 cm^3/minute. Ethylene absorption was continued for 7 days. [^{14}C]Ethylene in the absorber solution was measured using a liquid scintillation spectrometer.

Filbert nuts were harvested 7 and 14 DAT. Two different types of nut samples were collected: those treated directly on the husk, and those from limbs with treated leaves. Samples were frozen after collection. Nuts were separated into kernels, shells and husks and the samples were ground. TRR were determined by combustion analysis. The 7 DAT nutmeat was extracted by soxhlet extraction for 4 hours with benzene followed by methanol. The benzene extract did not contain any radioactivity and was discarded. The extracted residue was analysed by combustion.

The methanol extract was acidified, concentrated by rotary evaporation and then under nitrogen. The resulting extract was acidified, treated with diethyl ether and centrifuged. The resulting extract was concentrated, diluted with methanol and extracted with isooctane. The isooctane did not contain the radioactive residue and was discarded. The remaining methanol

extract was cleaned-up using a silica gel column and analysed by paper chromatography. The alkaline decomposition of the radioactive residue was investigated by treating an aliquot of the filbert extract with methanol/20% potassium hydroxide solution (1:1 v/v), by refluxing at 60 °C for 8 hours. A sample of control filbert extract was spiked with [^{14}C]ethephon and treated with alkali in the same way.

A significant amount of applied radioactivity was released over the 7 day period after treatment with [^{14}C]ethephon. The greatest amount of ethylene was release on the first day after treatment, gradually declining over the 7 day period (Table 11).

Only a small amount of the applied radioactivity was translocated onto the kernels (nutmeat) 7 DAT: 0.002 mg/kg and 0.87 mg/kg following application to the leaves and husk, respectively. The amount remaining in the kernels was even lower 14 DAT: 0.002 mg/kg and 0.14 mg/kg following application to the leaves and husk, respectively (Tables 12 and 13).

The 7 DAT nutmeat was extracted with benzene to remove the fats/oils. No radioactive residues were detected in the benzene fraction. Extraction with methanol released 98% of the TRR, with a further 1.6% remaining unextracted. After clean-up of the methanol extract, paper chromatography showed that the residue in nutmeat consisted of ethephon. No other radio-labelled component was detected. The presence of ethephon was confirmed by demonstrating that the radioactive residue in the nutmeat extract completely decomposed when treated with a strong base, as the alkaline treatment of [^{14}C]ethephon-spiked control extract confirmed this behaviour (of ethephon having been treated with a strong base).

Table 11 Release of [^{14}C]ethylene after application of [^{14}C]ethephon to filberts

DAT	[^{14}C]Ethylene released	
	dpm	kBq
1	4778000	79.9
2	2378000	87.0
3	2280700	42.2
4–7	1786700	30.4

Table 12 Distribution of [^{14}C]residues in filberts

Plant portion to which [^{14}C]ethephon was applied	DAT	[^{14}C]Ethephon Residue (dpm) [a]		
		Nutmeat	Husks	Shells
Leaves	7	24	566	34
Husks	7	8150	309900	4482
Leaves	14	19	10380	8
Husks	14	1311	257700	1161

[a] Average of three replicates

Table 13 Concentration of [^{14}C]ethephon in filbert kernels

Plant portion to which [^{14}C]ethephon was applied	7 DAT		14 DAT	
	mg/kg	Dpm	mg/kg [a]	dpm [a]
Leaves	0.002	24	0.002	19
Husk	0.87	8150	0.14	1311

[a] Average of three replicates

Cotton

Cotton plants in outdoor plots were treated with a foliar application of [^{14}C]ethephon at a rate of 1.40 kg ai/ha in a water volume of approximately 500 L/ha (Smith, 2003, 601CZ, [M-240888-01-2]). The application timing corresponded to a 7 day PHI. Samples of treated cotton leaves were collected 0 DAT, immediately after the application had dried. The remaining plants were harvested 7 DAT according to normal agricultural practices, and separated into gin trash, lint and seed. The lint was not analysed further. The 0 DAT samples were surface-washed with acetonitrile, and then extracted with

acetonitrile. The mature (7 DAT) samples were frozen, ground and combusted to determine the TRR. The gin trash samples were extracted with methanol:water (9:1). The seed samples were extracted with methanol. The post-extraction solids from the gin trash and seed were hydrolysed with a mixture of concentrated HCl and water (1:7), yielding an acid hydrolysate. Radioactivity in extracts was determined by LSC, and post-extraction solids were analysed by combustion analysis and LSC. The TRR in the 0 DAT leaf samples was determined by extraction and combustion of the residue. The TRR in the 7 DAT samples was determined by combustion. Extracts were concentrated and analysed by HPLC, and identification of ethephon and HEPA was performed by comparison of retention times with radio-labelled reference standards. Identification was confirmed by TLC.

Radioactive residues recovered in leaves at 0 DAT (237 mg/kg) declined rapidly over 7 days after application. Gin trash and seed samples from 7 DAT (final harvest) contained TRR of 31.4 mg/kg and 0.82 mg/kg, respectively (Table). The percentage of residue extracted from leaves harvested 0 DAT by acetonitrile wash and extraction was relatively low (in total 62.5% TRR), but this extraction was used only for the residue levels at 0 DAT and to develop extraction methods for the 7 DAT samples. Methanol extraction of mature gin trash (with the addition of water at a ratio 1:9 of methanol) and seed proved very effective, recovering 89% TRR in gin trash and 82% TRR in seeds respectively. Acid hydrolysis with HCl:water (1:7) further recovered the majority of the remainder of the residue (11% TRR in gin trash and 17% TRR in seeds), leaving only 0.2% TRR remaining unextracted, potentially fibre-bound, in the gin trash and 1.2% in the cotton seed.

Table 14 Total radioactive residues in cotton after foliar application of [^{14}C]ethephon at 1.40 kg ai/ha

Fraction	Leaves, 0 DAT		Gin Trash, 7 DAT		Seeds, 7 DAT	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
Acetonitrile wash	160.15	61.6	Not performed		Not performed	
Solvent extraction	1.35	0.9	27.81	88.6	0.67	82.1
Acid hydrolysate	Not performed		3.52	11.2	0.14	16.8
Total extracted	161.50	62.5	31.33	99.8	0.81	98.9
Unextracted residue	75.77	37.6	0.08	0.2	0.01	1.2
TRR by extraction	237.27	100	31.41	100	0.82	100
TRR by combustion	Not performed		31.41	100	0.82	100

The predominant radioactive residue in gin trash was ethephon at 93% TRR (84% TRR in the methanol:water extract and 9.3% TRR in acid hydrolysate) and 30 mg/kg and 78% TRR (66% TRR in the methanol extract and 12% in acid hydrolysate) and 0.64 mg/kg in seeds. HEPA was low at a total of 1.7% TRR and 0.52 mg/kg in gin trash and 9.6% TRR and 0.08 mg/kg in seeds. A total of 88–95% of the residue in these RACs was identified as ethephon and HEPA, with no other single metabolite comprising more than 1.9% of the residue.

Table 15 Identification of residues in cotton after foliar application of [^{14}C]ethephon at 1.40 kg ai/ha

	Leaves (0 day)		Gin Trash (7 day)		Seeds (7 day)	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
TRR by extraction	237.3	100	31.4	100	0.82	100
Total extracted	160.2 [a]	61.6 [a]	31.3	99.8	0.81	98.9
Ethephon						
—Surface wash	156.3	59.2	–	–	–	–
—Extract (methanol or Methanol + water, 9:1)	–	–	26.3	83.7	0.54	66.1
—Acid hydrolysate	–	–	2.9	9.3	0.10	12.2
—Total	156.3	59.2	29.2	93.0	0.64	78.3
HEPA						
—Surface wash	0.24	0.2	–	–	–	–
—Extract (methanol or Methanol + water, 9:1)	–	–		1.3	0.06	7.7
—Acid hydrolysate	–	–		0.4	0.02	1.9
—Total	0.24	0.2	0.52	1.7	0.08	9.6

	Leaves (0 day)		Gin Trash (7 day)		Seeds (7 day)	
	mg/kg	% TRR	mg/kg	% TRR	mg/kg	% TRR
Total identified	156.5	59.4	30.20	94.7	0.72	87.8
Unextractable residue	75.8	37.6	0.08	0.2	0.01	1.2

[a] For leaves, only the surface wash was profiled

The majority of the ethephon applied to cotton is decomposed to volatile ethylene and phosphates. The metabolic pathway for ethephon in cotton was replacement of the chlorine atom in the 2-position with a hydroxyl function to give HEPA. The main residue found in cotton leaves, gin trash and seed was parent ethephon.

Data from Published Literature

Apple and Cherry (Edgerton and Hatch, 1972)

Radioactive ethephon labelled with ^{14}C was applied (500 ppm with 0.1% of Tween 20) to leaf and fruit surfaces of selected branches of apple and cherry trees 6 to 10 days before normal harvest dates. Samples were collected periodically following application and analysed with appropriate extraction and counting procedures. The level of radioactive ethephon increased in the fruit for about 48 to 72 hr, then decreased to a low level after 6 days. No intermediate metabolites were detected in the fruits. It was found that the majority of the ethephon in the fruits moved there from the application on adjacent leaves; relatively small amounts moved directly into the fruit from surface application. Radioactive ethylene was detected within 12 hr after application of the [^{14}C]ethephon on the leaf surfaces.

Cherry (Gilbert et al., 1975)

The metabolism of [^{14}C]ethephon was investigated after application to the leaves of cherry trees. In extracts from cherry leaves harvested 3 and 11 days after treatment, a metabolite was detected by TLC. The ratio of metabolite to ethephon was greater at 11 days than at 3 days after application. Based on the fact that the metabolite could also be chromatographed on an anion exchange resin column, it was suggested that the metabolite contains an intact phosphonic acid or other anionic group. Characterisation by mass spectrometry was not possible due to matrix interferences.

Peach (Giulivo et al., 1981)

The translocation and metabolism of 1,2-[^{14}C]ethephon was investigated in Andross peach trees at the end of Stage 1 of fruit development. [^{14}C]Ethephon was applied to the fruit surface or to the abaxial surface of the basal leaf of a developing shoot. Translocation did not occur following application to the fruit, but did occur following application to the leaf. TLC analysis indicated that the translocated radioactivity was associated with sugars. However the binding to sugars was not a metabolic reaction.

Grape

The translocation of [^{14}C]ethephon was investigated after spray application to grapevines (Weaver *et al*, 1972). At 7 days after treatment, 62% of the recovered radioactivity remained on the surface of the treated grape berries. In concentrated extracts of methanol-washed grape berries, parent ethephon was detected by TLC, but no radioactive metabolite was found. Application of ethephon to the first leaf above the cluster, or to a berry pedicel or peduncle, failed to result in measurable translocation of ethephon into the berries.

The uptake, translocation and fate of [^{14}C]ethephon in detached grapevine leaves and intact shoots was investigated (Nir and Lavee, 1981). Mature Perlette leaves were treated with [^{14}C]ethephon and the leaves put under constant fluorescent light (9 W/m^2) for 48–120 hours. Recovery of radioactivity from detached leaves was 53–61% after 48 hours, and reduced to 25% after 120 hours. Translocation was found to be mainly basipetal, and this was confirmed by autoradiography.

When young leaves near the apex of young detached cardinal shoots were treated with [^{14}C]ethephon, recovery after 48 hours was 85.5%. 7.5% remained on the leaf surface and 78% was extracted from the shoots. There was almost no translocation to other parts of the shoots.

Application of [^{14}C]ethephon to different sites on the upper parts of young growing shoots (cut surface, shoot apex and mature leaves) showed that translocation was very slight and after 4 hours, recovery was 58–72%. In mature leaves, only 2.4% of the radioactivity had penetrated the tissue, whereas 21–26% had penetrated the apical tissues. Translocation of [^{14}C]ethephon was very slight and most of the applied compound remained at the application site for many hours. No measurement of the loss of ^{14}C as volatiles was made.

Squash, Cucumber and Tomato (Yamaguchi et al, 1971)

The fate of [^{14}C]ethephon was investigated after application to squash, cucumber and tomato plants. At 7 days after application of a [^{14}C]ethephon solution to tomato leaves, about 15% of the radioactivity was recovered from the treated leaves and about 50% had been converted to [^{14}C]ethylene. About 12% of the radioactivity applied was translocated to immature fruits on the same branch. Analysis by paper chromatography showed that the radioactivity recovered from the fruit surface and tissue extracts comprised parent ethephon.

After injection of [^{14}C]ethephon into petioles of summer squash, more than 20% of the applied radioactivity was converted to [^{14}C]ethylene during the first day, followed by slightly less than 15% in the second day. There was a rapid decline in radioactivity in the petioles after the first day which was accompanied by translocation of radioactivity to other parts of the seedlings. One day after application, the radioactive residue comprised mainly ethephon. At 2 days after application the presence of an unknown metabolite was noted and at 6 days after treatment the amount of the unknown metabolite at the site of application was greater than that of ethephon. The translocated radioactivity was all in the form of the unidentified metabolite.

Four days after an application of [^{14}C]ethephon solution to cucumber leaves and fruits, about 40% of the total remaining radioactivity was found to be ethephon. No identification of characterization of the remaining 60% of the radioactive residue was performed.

This paper indicates that the main route of metabolism of ethephon in tomato is conversion to ethylene, and translocation of ethephon occurs. In contrast, in summer squash, besides the formation of ethylene, an unidentified metabolite is formed which is translocated to other parts of the plants whereas translocation of ethephon is not observed. In tomato tissue, the radioactive residue comprised [^{14}C]ethephon, but in squash seedlings much of the radioactivity was present in the form of the unidentified metabolite.

Walnut (Martin et al, 1972)

[^{14}C]Ethephon applied to a walnut leaflet was found to penetrate and translocate rapidly in young plants, but more slowly in older plants. The compound translocated to the kernel at higher levels when applied to a leaflet than when applied to the hull, but levels of radioactivity were low in both cases. Between 5–7 days after application, the amount of radioactivity in the kernel decreased markedly. It was concluded from the decrease in radioactivity that [^{14}C]ethephon in the leaves, hull, shell and kernel was metabolised. TLC analysis revealed the presence of [^{14}C]ethephon in leaf, hull and kernel extracts; however, no metabolites remained in the plant tissue that could be detected by TLC. No measurement of [^{14}C]ethylene was made in this study.

Proposed metabolic pathway of ethephon in plants

The metabolism of ethephon in a wide range of crops were studied. Information taken from published literature was also provided. Recent studies on tomatoes, wheat and cotton (2002–2003) and older studies (1968–1981) on apples, cherries, peaches, grapes, pineapples, cantaloupes, summer squash, cucumbers, tomatoes, filberts and walnuts showed similar metabolism of ethephon.

In the tomato study, the plants were foliarly-treated with 1.44 kg ai/ha of [^{14}C]ethephon. Parent ethephon was found to be the major residue component in tomato fruit harvested 0, 5 and 12 days after treatment. HEPA represented up to 15% of the total radioactive residue.

In the wheat study [^{14}C]ethephon was foliar sprayed at the rate of 0.36 kg ai/ha when the plants had reached the ligule stage (BBCH 39). At mature harvest, grain showed similar levels of parent ethephon and HEPA, whereas straw was found to contain higher levels of ethephon than of HEPA.

In the cotton study, the plants were treated with 1.40 kg ai/ha of [^{14}C]ethephon. The majority of the residue in cotton seed and gin trash harvested 7 days after treatment was parent ethephon. HEPA represented 1.7% of the total radioactive residue in gin trash and 9.6% in seed.

Overall, the main degradation route of ethephon was shown to involve decomposition of ethephon to ethylene and phosphates. The ethylene is rapidly released into the atmosphere while the phosphates are taken up in the natural phosphate cycle of the plant. However, part of the applied ethephon is metabolized according to a different metabolic pathway that results in the formation of the metabolite HEPA. HEPA is further metabolized by incorporation of the two carbon atoms in natural bio-molecules. The proposed metabolic pathway of ethephon in plants is presented below.

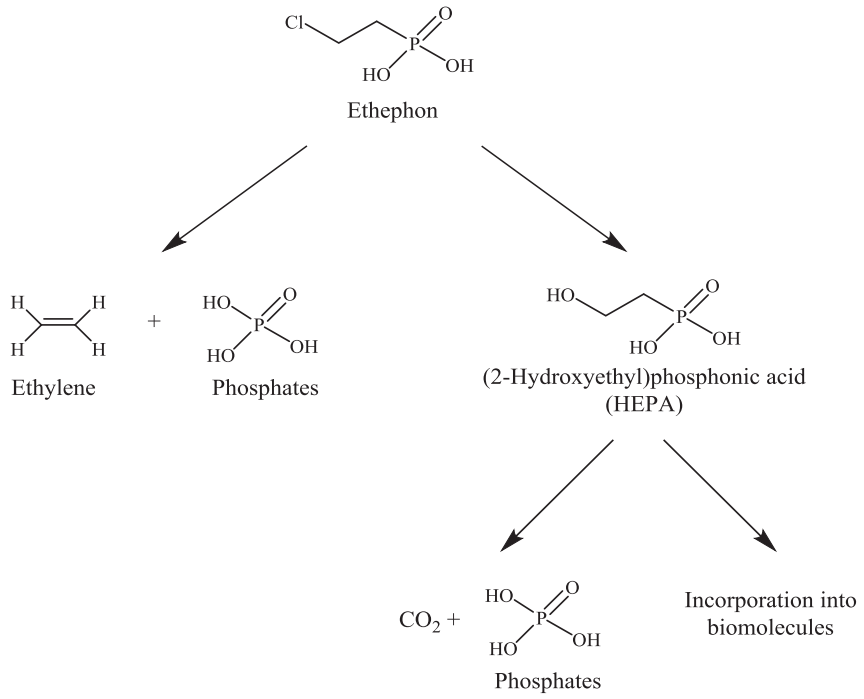


Figure 2 Proposed Metabolic Pathway of Ethephon in Plants

Animal Metabolism

The Meeting received information on the results of studies on lactating goats and laying hens which were fed [^{14}C]ethephon.

Metabolism studies on laboratory animals including rats were reviewed in the framework of toxicological evaluation by the current JMPR and the relevant information is summarized below.

Rat

After oral administration of ethephon to rats, absorption was rapid with a Tmax of 1.0–1.3 hours and 1.9–2.5 hours after a single oral dose of 50 or 1000 mg/kg bw, respectively. Six days after a single dose, tissue and carcass contained only 0.08% or less of administered radioactivity. Highest concentrations were found in liver and kidney. Radioactivity was excreted in urine (47–60%), expired air (18–21%, mainly ethylene) and faeces (4–6.5%), indicating that at least 65% of the administered dose was absorbed. Ethephon was mainly metabolized to ethylene and to a small extent to HEPA.

Lactating goats

The metabolism of ethephon in the lactating goat (Nubian and Alpine/Nubian cross) has been studied using [^{14}C]ethephon (Huhtanen *et al.*, 1984, ETH/M3, [M-187423-01-1]; Fisher, 2005, C046890, [M-223288-02-1]). The [^{14}C]ethephon was administered twice daily orally in capsules to two lactating goats for seven consecutive days. One dose followed the morning milking, and the other followed the afternoon milking. The goats received mean daily doses of 0.37 and 0.46 mg/kg bodyweight/day, respectively, equivalent to a dose level of approximately 10 ppm in the diet. A third goat served as a control animal.

Urine, faeces, milk and blood samples were collected daily. Milk samples were collected twice daily, in the morning and in the afternoon, approximately ten hours later, immediately prior to dosing. Selected milk sub-samples were separated into skimmed milk and milk fat by centrifugation. Whole blood samples were collected from each animal immediately prior to the afternoon dose. On Day 6, blood was collected from each goat at intervals of 0.25, 0.5, 1, 2, 4, 6, 8 and 10 hours after the morning dose. Volatile compounds were collected for 24 hours on the seventh day of the study. Carbon dioxide was trapped using 10% aqueous potassium hydroxide and ethylene was trapped using mercuric perchlorate solution. The animals were sacrificed approximately 16 hours after the final dose, and the following tissues were collected: liver, kidney, heart, composite fat, skeletal muscle, blood, and contents of the stomach and small and large intestine.

Radioactivity was quantified by LSC. Liquid samples (milk and urine) were analysed directly by LSC. Solid samples (tissues and intestinal contents) were analysed by oxidative combustion followed by LSC.

Freeze-dried sub-samples of liver were extracted with ether and then methanol. Extracts were radio-assayed and the remaining solids were analysed by combustion. Proteins and glycogen from the liver were isolated and analysed by combustion. Levels of ethephon in tissues, urine and milk were determined by base hydrolysis to ethylene which was trapped in a mercuric perchlorate solution.

A major proportion of the administered dose was released as volatiles in the form of ethylene (29% of administered dose) and CO_2 (2% of administered dose). Urinary excretion accounted for 19% and faecal excretion about 7% of the administered dose. Only 3.3% was excreted in milk and 3% remained in tissues on Day 7 (Table). The low total recovery (64%) was attributed to the difficulties in trapping large amounts of volatile compounds and the fact that volatile compounds were only collected over a 24 hour period.

Table 16 Distribution of radioactivity in tissues, milk and excreta from goats following oral administration of [^{14}C]ethephon at a nominal dietary concentration of 10 ppm for 7 days

Fraction	% of Administered dose
[^{14}C]ethylene [a]	29 [a]
$^{14}CO_2$ [a]	2.0 [a]
Urine	19
Faeces	6.7
Milk	3.3
Tissues	3.0
Gut contents	0.84
Total Recovery	64

[a] [^{14}C]ethylene and $^{14}CO_2$ were collected only over a 24-hour period on Day 7

Kidney and liver contained the highest total radioactive residue, at 1.2 and 1.0 mg/kg, respectively. TRRs in heart and muscle were low at 0.16 and 0.10 mg/kg, respectively, whilst fat contained a TRR of 0.50 mg/kg (Table).

Table 17 Average concentration of radioactive residues in tissues of goats sacrificed 16 hours after oral administration of [^{14}C]ethephon at a nominal 10 ppm for 7 days

Tissue	TRR, mg/kg
Kidney	1.2
Liver	1.0
Fat	0.50
Heart	0.16
Muscle	0.10

Average radioactive residue levels in whole milk were 0.28 mg/kg on Day 1, 0.36 mg/kg on Day 2 and 0.37 mg/kg on Day 3. Radioactive residue levels in milk increased until the afternoon milking on Day 3, where a plateau level of about 0.42 mg/kg was reached (Table). The milk fat fraction contained 45% of the radioactivity in milk. Radioactive residue concentrations in skimmed milk were 0.15–0.20 mg/kg, whilst those in milk fat were 3.03–4.18 mg/kg. As ethephon is hydrophilic and not expected to partition into fat, the residue in milk fat was attributed to incorporation of ^{14}C via [^{14}C]acetate into milk fats.

Table 18 Average concentration of radioactive residues in milk from goats during oral administration of [^{14}C]ethephon at a nominal 10 ppm for 7 days

Time, days	Average concentration, mg/kg
0.5	0.081
1.0	0.279
1.5	0.318
2.0	0.357
2.5	0.366
3.0	0.371
3.5	0.420
4.0	0.380
4.5	0.394
5.0	0.427
5.5	0.423
6.0	0.405
6.5	0.422
7.0	0.419

For the determination of ethephon, base degradation method was used to convert parent ethephon to ethylene. The analytical results indicate that no ethephon were present in fat, muscle, liver and milk. Kidney was the only tissue which yielded measurable levels of ethylene after base hydrolysis, equivalent to ethephon levels of 0.0085 mg/kg. Extraction of liver with ether released 5.3% TRR, extraction with methanol released a further 63.7% TRR, and 27.2% TRR remained in the post-extraction solids. Precipitation with trichloroacetic acid showed that 12.4% TRR in liver was associated with proteins. Radioactivity was also found to be associated with liver glycogen.

The incorporation of radiocarbon into liver protein, glycogen and fats as well as the elimination of $^{14}CO_2$ demonstrated that ethephon was incorporated into natural products possibly through an acetate-like intermediate. It was observed that radioactive carbon was present in milk fat and fat tissue, which indicates metabolic degradation of ethephon to a less hydrophilic compound.

The results show that significant amounts of the parent ethephon are degraded to ethylene and respired. The absence of parent ethephon in tissues demonstrated the complete metabolic degradation of ethephon, probably through an acetate-like intermediate. The study indicated that

there is low potential for transfer of residues of ethephon and/or its metabolites to milk, meat or meat by-products in ruminants after dietary exposure to ethephon.

Laying Hens

In the first study (Byrd, 1992, 9015C, [M-179283-01-1]), eight hens received daily oral capsule doses of [^{14}C]ethephon for five consecutive days at a rate equivalent to 53 ppm diet. Three hens in Group I were individually housed in metabolism cages designed to collect expired ethylene in a 2 M mercuric perchlorate trap solution and CO_2 in a 2 M sodium hydroxide solution. Five hens in Group II were individually housed in layer cages. Five other hens in Group III served as controls, and were individually housed in layer cages. Eggs were collected twice daily and excreta were collected once daily. Blood was collected prior to termination. Hens were terminated 22–23 hours after the final dose, and the following tissues collected: liver, kidney, muscle, fat, gastrointestinal tract and contents. A cage wash sample was collected after termination.

Liver, kidney, muscle, fat, yolk (Day 4) and excreta (Day 5) were freeze-dried and sequentially extracted with hexane and methanol using soxhlet extraction. The hexane and methanol extracts were pooled and the unextracted residues were subjected to enzyme hydrolysis (glucuronidase and sulphatase), and acid and base hydrolysis. The hydrolysates were extracted with dichloromethane but no radioactivity in any of hydrolysates partitioned into the organic layer. Radioactivity in extracts and hydrolysates was determined by LSC. Solid samples were analysed by combustion and LSC. Radioactivity in extracts was characterised by radio TLC.

The majority of the radioactivity (58% of the administered dose) was recovered as ethylene in the mercuric perchlorate trap solution. The identity of ethylene was confirmed by GC/MS headspace analysis. The amount of radioactivity trapped as $^{14}CO_2$ was negligible. A significant amount (26–30%) of the administered dose was recovered in the excreta. Radioactive residues in the CO_2 trap, eggs and tissues accounted for less than 1% of the total radioactivity administered (Table).

Table 19 Distribution of radioactivity in tissues, eggs and excreta from hens following oral administration of [^{14}C]ethephon at a nominal dietary concentration of 53 ppm for 5 days

Sample	% of Administered dose
[^{14}C]ethylene	58
$^{14}CO_2$	< 1
Excreta	26, 30[a]
Eggs (whole)	< 0.1
White	0.00
Yolk	0.05
Liver	0.05
Kidneys	0.01
Muscle	0.03
Fat	0.01
Plasma	0.01
Erythrocytes	0.01

[a] Group in the metabolism cages (Group I) and layer cages (Group II), respectively

The highest TRR among tissues was found in liver (0.31 mg/kg), followed by kidneys (0.23 mg/kg) and fat (0.15 mg/kg) (Table). The TRR in eggs increased to a plateau level of about 0.18 mg/kg (mean of Groups II and III) after 4 days (Table).

Table 20 Concentration of radioactive residues in tissues of hens following oral administration of [^{14}C]ethephon at a nominal 53 ppm for 5 days

Tissue	TRR, mg/kg
Eggs	0.18 [a]
White	0.042[a]
Yolk	0.45 [b]
Liver	0.31

Tissue	TRR, mg/kg
Kidneys	0.20
Muscle	0.023
Fat	0.15
Plasma	0.078
Erythrocytes	0.063

[a] Highest residue concentration (found on Day 4)

[b] Highest residue concentration (found on Day 5)

Table 21 Mean concentration of radioactive residues in eggs from hens following oral administration of [^{14}C]ethephon at a nominal 53 ppm for 5 days

Study day	Average concentration, mg/kg					
	Group I (expired air cage)			Group II (layer cage)		
	White	Yolk	Whole egg	White	Yolk	Whole egg
1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
2	0.014	0.028	0.019	0.016	0.043	0.025
3	0.028	0.180	0.078	0.028	0.199	0.086
4	0.041	0.205	0.149	0.043	0.541	0.216
5	0.033	0.408	0.154	0.034	0.509	0.203

Soxhlet extraction released the largest amount of radioactivity from all samples, except excreta. In excreta, the majority of the radioactivity was released by enzyme and acid hydrolysis. For all tissues, more than 75% of the residue was characterized. In liver and kidney, the radioactive residue was less readily extracted by solvent and 27% TRR in liver and 41% TRR in kidney remained unextracted. The extracted residue from liver and egg yolk could not be characterized by TLC due to the low amount of radioactivity in the extracts and interference from co-extractives.

Table 22 Characterisation of residues in tissues, egg yolk (Day 4) and excreta (Day 5)

Fraction	Liver		Kidney		Muscle		Fat		Egg yolk (Day 4)		Excreta (Day 5)	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Soxhlet extraction	0.16	52	0.083	41	0.012	53	0.15	101	0.27	72	1.0	8.1
Enzyme hydrolysis	< 0.01	2.3	< 0.01	2.5	< 0.01	2.5	< 0.01	0.0	0.025	6.7	5.8	45
Acid hydrolysis	< 0.01	0.5	< 0.01	0.2	< 0.01	0.9	< 0.01	0.9	< 0.01	2.4	2.2	17
Base hydrolysis	< 0.01	2.3	< 0.01	1.8	< 0.01	0.0	< 0.01	3.6	< 0.01	2.1	1.1	8.9
Bound residues	0.084	27	0.083	41	< 0.01	0.4	< 0.01	0.5	0.041	11	2.9	22
Total recovery		84		87		83		106		95		101

The results indicate that the metabolism of ethephon proceeds almost exclusively by hydrolysis and dechlorination to ethylene, which is then expired. It appears that incorporation of the two carbon moiety into cellular components may result as no other radioactive metabolite could be isolated in tissue extracts.

In the second study (Schocken, 1995, 94-10-5526, [M-188154-01-1]), two groups (Groups II and III) of five hens received daily gavage doses of [^{14}C]ethephon for five consecutive days at a rate equivalent to 59 ppm diet (Group II) or 67 ppm diet (Group III). Five hens in Group II were individually housed in metabolism cages designed to collect expired ethylene in a 2 M mercuric perchlorate trap solution and CO_2 in a 2 M sodium hydroxide solution. Five hens in Group III were individually housed in layer cages. Three hens in Group I served as controls

and were individually housed in layer cages. Eggs were collected twice daily, and excreta were collected once daily. Blood was collected prior to termination. Hens were terminated 9–10 hours after the final dose, and the following tissues collected: liver, kidney, muscle, fat, gastrointestinal tract and contents.

Radioactivity in liquid samples was determined by LSC. Solid samples were analysed by combustion and LSC. [^{14}C]ethylene was confirmed by GC/MS headspace analysis of the mercuric perchlorate trap. $^{14}CO_2$ in the sodium hydroxide trap was determined by barium carbonate precipitation.

Fat and egg yolk samples were extracted with hexane/tetrahydrofuran. Other tissue samples were extracted with methanol/water. Fat and egg yolk were saponified with methanolic potassium hydroxide and analysed by LC/MS and/or HPLC to identify radio-labelled fatty acids, cholesterol and glycerol. The post-extraction solids from muscle, kidney, liver, egg white and egg yolk samples from Group III were digested with protease. Aliquots of hydrolysates were further hydrolysed with 6 N HCl. The protease and acid hydrolysates were profiled by HPLC to detect the presence of radio-labelled amino acids. The remaining solids were analysed by combustion.

The majority of the radioactivity was recovered in excreta, accounting for about one third of the administered dose. Radioactive residues in tissues accounted for 0.12–0.14% of the dose, with the highest concentrations in kidney (0.71–1.1 mg/kg) and liver (0.63–0.90 mg/kg) and lowest concentrations in fat (0.051–0.091 mg/kg) and muscle (0.051–0.058 mg/kg). Radioactive residues in egg white and egg yolk accounted for 0.03% and 0.07–0.10% of the dose, respectively. Due to leakage in the gas collection system, a total of only 2.7% of the administered dose was recovered in the expired volatiles trap (Table).

Table 23 Distribution of radioactivity in tissues, eggs and excreta from hens following oral administration of [14C]ethephon for 5 days

Fraction	% of Administered dose	
	59 ppm Diet (Group II) (expired air cage)	67 ppm Diet (Group III) (layer cage)
[^{14}C]ethylene	2.66 [a]	Not collected
$^{14}CO_2$	0.03	Not collected
Excreta	26	36
Egg white	0.03	0.03
Egg yolk	0.07	0.10
Tissues	0.12	0.14

[a] Recovery of expired [^{14}C]ethylene is not representative due to leakage in the gas collecting system

The highest TRR among tissues was found in kidneys (1.1 and 0.71 mg/kg), followed by liver (0.90 and 0.63 mg/kg) (Table). The TRR in eggs increased to a level of about 0.40 mg/kg (mean of Groups II and III) after 5 days (Table).

Table 24 Mean concentration of radioactive residues in tissues of hens following oral administration of [^{14}C]ethephon for 5 days

Tissue	TRR, mg/kg	
	59 ppm Diet (Group II) (expired air cage)	67 ppm Diet (Group III) (layer cage)
Egg white	0.10	0.10
Egg yolk	1.0	1.0
Liver	0.90	0.63
Kidneys	1.1	0.71
Muscle	0.058	0.051
Fat	0.091	0.051

Table 25 Mean concentration of radioactive residues in eggs from hens following oral administration of [^{14}C]ethephon for 5 days

Study day	Average concentration, mg/kg						Mean whole egg [a], mg/kg
	59 ppm Diet (Group II) (expired air cage)			67 ppm Diet (Group III) (layer cage)			
	White	Yolk	Whole egg	White	Yolk	Whole egg	
1	0.001	0.001	0.001	0.002	0.000	0.001	0.001
2	0.029	0.003	0.020	0.046	0.006	0.033	0.027
3	0.095	0.248	0.148	0.069	0.265	0.134	0.141
4	0.098	0.579	0.299	0.100	0.657	0.283	0.291
5	0.098	1.035	0.420	0.086	1.014	0.384	0.402

[a] Average concentration in whole eggs from Group II and Group III

Ethephon and HEPA were both identified in muscle, liver and kidney. Radioactivity in egg white and yolk was mainly incorporated into amino acids (57% TRR) and fatty acids/cholesterol (74–77% TRR), respectively. In organs, radioactivity was also incorporated into amino acids (up to 35% TRR in muscle). In fat, the only characterised fraction was fatty acids/cholesterol (39–44% TRR). The unknown fractions in Group III liver included a metabolite at 0.039 mg/kg, a multi-component peak (with no individual component exceeding 0.033 mg/kg) and a region of unidentified radioactivity (0.023 mg/kg) which could represent polypeptides. The unknowns in Group III kidney included two metabolites at levels of 0.015 and 0.045 mg/kg, as well as a multi-component peak (with no individual component exceeding 0.050 mg/kg) and a region of unidentified radioactivity (0.059 mg/kg) which could represent polypeptides. Unidentified residues in other Group III matrices were below 0.05 mg/kg. Bound residues from Group III samples, which had been subjected to protease hydrolysis in addition to solvent extraction, were all below 0.035 mg/kg (Table).

Table 26 Characterisation and identification of residues in tissues and eggs (Day 4) of laying hens following oral administration of [^{14}C]ethephon for 5 days

	Liver		Kidney		Muscle		Fat		Egg white		Egg yolk	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
59 ppm diet (Group II—expired air cage)												
Extracted	0.64	71	0.69	64	0.045	79	0.087	96	0.094	94	0.96	95
Unextracted residue	0.16	18	0.13	12	0.026	45	0.012	13	0.001	0.5	0.17	16
Total recovered	0.80	89	0.82	75	0.071	124	0.099	108	0.095	95	1.12	111
Ethephon	0.15	17	0.42	38	0.017	29	nd	nd	nd	nd	nd	nd
HEPA	0.11	12	0.10	9	0.013	22	nd	nd	nd	nd	nd	nd
Polypeptides	–	–	–	–	–	–	–	–	0.093	93	–	–
Amino acids	0.17	19	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
Fatty acids/ cholesterol	Nd	nd	nd	nd	nd	nd	0.040	44	nd	nd	0.78	77
Glycerol	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.022	2
Total identified	0.43	48	0.52	48	0.030	52	0.040	44	0.093	93	0.80	79
Unidentified	0.20	23	0.17	16	0.015	26	0.038	42	0.001	1	0.16	16
67 ppm diet (Group III—layer cage)												
Extracted	0.40	64	0.55	78	0.024	47	0.048	93	0.065	65	0.83	82
Protease hydrolysis	0.11	17	0.078	11	0.018	35	nd	nd	0.003	3	0.12	12
Unextracted residue	0.034	5	0.015	2	0.006	12	0.005	10	0.007	7	0.013	1
Total recovered	0.54	86	0.65	91	0.049	96	0.054	105	0.075	75	0.97	96

	Liver		Kidney		Muscle		Fat		Egg white		Egg yolk	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Ethephon	0.11	17	0.30	42	0.006	12	nd	nd	nd	nd	nd	nd
HEPA	0.10	16	0.096	14	0.009	18	nd	nd	nd	nd	nd	nd
Amino acids	0.084	13	0.019	3	0.018	35	nd	nd	0.057	57	0.091	9
Fatty acids/ cholesterol	Nd	nd	nd	nd	nd	nd	0.020	39	nd	nd	0.75	74
Glycerol	Nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.033	3
Total identified	0.29	46	0.42	59	0.033	65	0.020	39	0.057	57	0.84	83
Unidentified	0.22	40	0.22	30	0.009	18	0.036	71	0.008	8	0.031	3

nd = Not determined

The radioactivity present in excreta was almost completely extracted with methanol. For the Group III samples which were treated with protease, a further 2.3% TRR was released by protease and 0.6% TRR remained bound. The major radioactive residue in excreta was ethephon, accounting for 83% TRR for the Group II hens and 88% TRR for the Group III hens, and represents the unabsorbed dose. The metabolite (2-hydroxyethyl)phosphonic acid (HEPA) accounted for 4.4–6.5% TRR. In the Group III excreta, an unknown metabolite was detected at 4.6% TRR. No radioactive amino acids, fatty acids/cholesterol or glycerol were detected.

Table 27 Characterisation and identification of residues in excreta

	% TRR in Excreta	
	59 ppm Diet (Group II) (expired air cage)	67 ppm Diet (Group III) (layer cage)
Extractable	92.4	100.5
Protease hydrolysis	Not performed	2.3
Unextracted residue	2.5	0.6
Total recovered	94.9	103.4
Ethephon	83.4	87.8
HEPA	6.5	4.4
Total identified	89.9	92.2
Unidentified	–	4.6

nd = Not determined

The results indicate that ethephon metabolism in laying hens is postulated to involve the direct release of ethylene from parent ethephon, as well as the competitive removal of chlorine to form HEPA, which is further metabolised to release CO_2, and intermediates which can enter biochemical pathways, leading to the biosynthesis of proteins and lipids. The highest residue levels were found in liver, kidney and egg. Ethephon and HEPA were the major components of the residue in liver and kidney, whereas in egg yolk, most of the radioactivity was incorporated into fatty acids and cholesterol.

Proposed metabolic pathway of ethephon in animals

The metabolism of [^{14}C]ethephon was studied in lactating goats and laying hens. Orally administered [^{14}C]ethephon is rapidly eliminated either in the excreta or as [^{14}C]ethylene in expired air. The main route of metabolism is degradation/metabolism to [^{14}C]ethylene, and to a much lesser degree to $^{14}CO_2$.

A similar route of metabolism of ethephon to ethylene is seen in rats, goats and hens. In livestock, radioactivity was found in fat (fatty acids/cholesterol and glycerol), proteins (polypeptides and amino acids) and glycogen, demonstrating that metabolic degradation of ethephon through an acetate-like intermediate in the tricarboxylic acid cycle was occurring. Ethephon and the metabolite HEPA were found only at low levels in tissues. The proposed metabolic pathway of ethephon in animals is presented below.

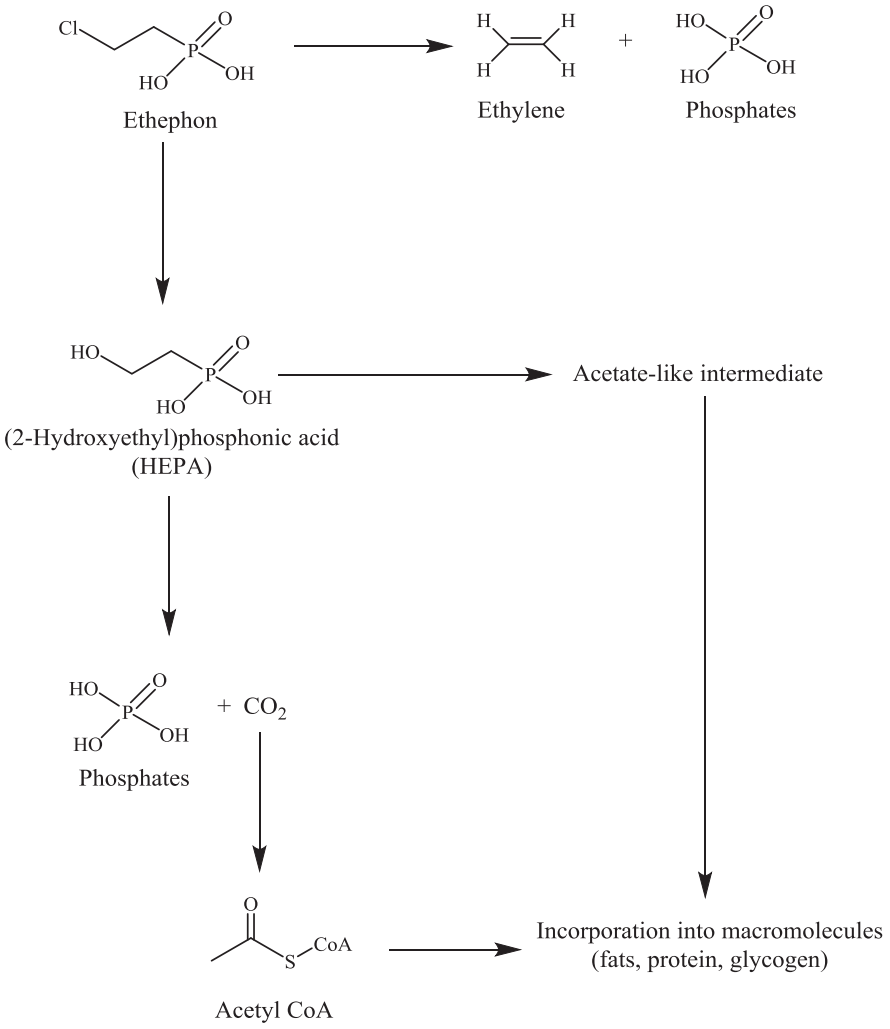


Figure 3 Proposed metabolic pathway for ethephon in animals

Environmental Fate in Soil

The Meeting received information on hydrolysis, photochemical degradation, aerobic and anaerobic degradation of ethephon in soil, photolysis of ethephon on soil, ethephon field dissipation, and residues in rotational crops.

Hydrolysis

The results of the hydrolysis study are summarized in the Physical and Chemical Properties section.

Photochemical degradation

The photolysis of ethephon in water was investigated under artificial sunlight in acetate buffer at pH 5 (Das, 1990, ISSI 89151, Bayer Ref: M-187634-01-1). [^{14}C]Ethephon was mixed with non-radio-labelled ethephon and dissolved in sterile acetate buffer and irradiated continuously using a xenon arc

simulated sunlight source (> 290 nm, 510.5 W/m^2) for up to 360 hours at 25 ± 1 °C; for control, ethephon in the acetate buffer was kept in darkness. Samples were taken at 0, 12, 36, 84, 168, 252 and 360 hours during irradiation. The samples were acidified immediately with HCl solution to prevent breakdown of ethephon during analysis. [^{14}C]ethylene was quantified by flushing the headspace with oxygen, and analysing the gas mixture by sample oxidation/LSC. The identity of ethylene was confirmed by GC-MS analysis of the headspace gases. The test solutions were evaporated to dryness and methylated with diazomethane for GC-MS analysis.

The mean recovery of radioactivity was 96.6% from the irradiated samples and 96.5% from the non-irradiated samples. The pH was confirmed in both the irradiated and non-irradiated samples. Microscopic analysis at 0 and 360 hours confirmed the sterility of the test solutions. GC-MS analysis confirmed the identity of [^{14}C]ethephon and [^{14}C]ethylene as the only major degradate in the test solution. [^{14}C]Ethylene was the only ethephon-related compound in the headspace.

The quantities of radioactive components in irradiated and non-irradiated test solutions of pH 5 buffer treated with [^{14}C]ethephon are presented in Table. In both irradiated and non-irradiated samples, [^{14}C]ethylene was the only major degradate. The calculated DT_{50} was 29.4 days for irradiated samples, and 51.4 days for non-irradiated samples.

Table 28 Recovery of radioactivity as [^{14}C]ethephon and [^{14}C]ethylene in an aqueous photolysis study

Time (hours)	Mean % recovery of total applied radioactivity			
	Irradiated samples (n=2)		Non-irradiated samples (n=2)	
	[^{14}C]ethephon	[^{14}C]ethylene	[^{14}C]ethephon	[^{14}C]ethylene
0	99.9	0.1	99.9	0.1
12	96.2	1.2	96.0	0.5
36	93.4	1.2	94.6	0.5
84	92.7	2.5	91.3	2.4
168	81.4	17.0	85.7	11.0
252	76.0	20.2	84.8	12.0
360	71.2	23.1	81.7	15.2

Aerobic degradation

In the first study, the aerobic degradation of ethephon was investigated in four soils for 180 days (Burr, 2001, C016772, [M-203033-01-1]). [^{14}C]Ethephon was applied to each soil at a rate equivalent to 2.24 kg ai/ha. The soils were incubated aerobically in the dark with 45% maximum water holding capacity at 10 °C or 20 °C under continuous air flow. Three traps containing a saturated solution of pyridinium hydrogen bromide per bromide (PHBPB) were used to collect [^{14}C]ethylene, and a 2 M KOH trap to collect $^{14}CO_2$. Soil samples were taken at 0, 1, 3, 7, 14, 27–28, 56–60, 77–80, 100–102, 120–123, 150–152 and 180 days after treatment. The soil was extracted with phosphoric acid followed by methanol.

The total recovered radioactivity decreased over time during the test (below 70% in the sandy loam, sandy silt loam and clay loam after approximately 102 days). This is probably due to problems with trapping [^{14}C]ethylene, caused by loss of dibromoethane (which is volatile) between trap removal and sampling.

Significant quantities of a volatile metabolite (ethylene) were found in the PHBPB traps, at up to approximately 60% applied radioactivity. Small amounts of (2-hydroxyethyl) phosphonic acid (HEPA) were detected in the soil samples (< 10% applied radioactivity), which is therefore regarded as a minor metabolite (Table 29).

Table 29 Recovery of radioactivity in soil after application of [^{14}C]ethephon

Days after appl.	% of Applied radioactivity						
	Extract 1 Phosphoric acid	% Ethephon in Extract 1	Extract 2 Methanol	Volatiles in PHBPB traps (ethylene)	Volatiles in KOH trap (CO_2)	Unextracted Residue	Total

Days after appl.	% of Applied radioactivity						
	Extract 1 Phosphoric acid	% Ethephon in Extract 1	Extract 2 Methanol	Volatiles in PHBPB traps (ethylene)	Volatiles in KOH trap (CO_2)	Unextracted Residue	Total
	Clay loam soil (00/18), 20 °C. Soil pH 6.9.						
0.02	80.76	80.76	n.a.	n.a.	n.a.	28.93	109.69
1	66.94	66.41	n.a.	0.00	0.00	24.99	92.07
3	66.34	65.15	n.a.	0.00	0.00	33.88	100.54
7	54.51	47.07	2.85	–	–	33.08	90.44
14	49.58	47.17	n.a.	1.61	0.00	46.88	98.06
28	44.34	41.61	n.a.	2.24	0.40	46.18	93.16
56	35.01	30.85	2.09	6.12	0.23	48.74	92.20
80	29.16	24.82	2.50	7.53	0.44	43.77	83.39
100	28.23	23.35	2.88	6.42	0.18	53.40	91.12
123	27.16	21.50	2.30	5.19	0.16	46.77	81.58
152	18.04	14.68	2.05	6.81	0.04	50.64	77.57
180	9.76	4.33	1.87	8.17	0.10	49.71	69.61
	Clay loam soil (00/18), 10 °C. Soil pH 6.9.						
0.02	85.98	83.71	2.34	n.a.	n.a.	11.68	100.0
1	74.77	74.42	0.00	0.02	0.00	19.42	94.21
3	72.38	72.39	0.00	0.00	0.00	27.89	100.72
7	71.25	68.31	2.86	0.00	0.00	26.74	100.85
14	61.78	60.37	0.00	0.13	0.00	26.68	88.59
28	61.31	59.00	0.00	0.18	0.00	34.08	95.57
56	52.99	50.29	2.59	0.61	0.00	40.11	96.30
80	48.96	45.55	3.06	0.86	0.01	51.72	104.60
100	35.08	29.95	4.07	1.44	0.00	60.44	101.03
123	63.33	58.70	4.37	1.32	0.01	23.97	93.00
152	32.01	29.38	3.97	4.35	0.03	43.62	83.98
180	19.12	17.38	4.07	12.59	0.04	34.86	70.68
	Sandy loam soil (00/14), 20 °C. Soil pH 6.8.						
0.02	90.25	90.25	2.15	n.a.	n.a.	8.66	101.06
1	78.06	78.06	3.23	0.27	0.00	18.85	100.41
3	69.26	69.26	3.68	0.71	0.00	21.62	95.27
7	59.86	59.86	3.68	0.60	0.00	29.14	93.28
14	47.50	47.50	3.05	1.51	0.00	32.81	84.87
27	34.50	34.50	2.64	24.80	0.00	28.54	90.48
60	15.00	15.00	1.97	55.98	0.00	13.02	85.97
77	7.14	7.14	1.26	58.09	0.29	11.87	78.65
102	4.87	3.10	0.97	51.27	0.58	11.02	68.70
120	5.31	1.00	1.74	17.33	0.85	13.54	38.76
150	2.48	1.26	0.85	36.44	0.02	12.06	51.85
180	2.21	1.36	0.64	31.90	0.41	10.57	45.73
	Sandy silt loam soil (00/15), 20 °C. Soil pH 5.9.						
0.02	73.06	73.06	1.24	n.a.	n.a.	26.01	100.31
1	65.80	65.80	1.51	0.00	0.00	38.51	105.85
3	63.23	63.23	2.18	0.07	0.00	33.19	98.67
7	54.88	54.88	2.56	0.10	0.00	38.42	95.96
14	50.81	50.45	1.84	2.16	0.00	43.60	98.41
27	44.17	44.17	2.27	8.89	0.00	42.88	98.21
60	42.05	41.27	4.57	15.73	0.68	19.21	82.24
77	38.74	38.15	4.50	11.26	0.12	20.60	75.22
102	33.05	33.05	3.24	22.23	0.41	18.95	77.88
120	20.70	20.70	2.23	13.89	0.30	18.55	55.67
150	19.49	17.22	2.22	8.25	0.36	18.62	48.94
180	14.06	12.42	1.77	22.58	0.30	17.08	55.78
	Clay loam soil (00/16), 20 °C. Soil pH 7.6.						
0.02	82.03	81.32	2.40	n.a.	n.a.	11.10	95.53
1	62.56	61.62	2.30	4.65	0.00	18.08	87.59
3	48.21	47.62	4.63	10.57	0.00	20.02	83.43
7	25.50	24.85	2.52	14.36	0.00	28.79	71.17
14	10.82	10.39	1.16	35.94	0.00	30.09	78.01

Days after appl.	% of Applied radioactivity						
	Extract 1 Phosphoric acid	% Ethephon in Extract 1	Extract 2 Methanol	Volatiles in PHBPB traps (ethylene)	Volatiles in KOH trap (CO_2)	Unextracted Residue	Total
27	1.89	1.18	0.84	51.12	0.00	27.60	81.45
60	0.74	0.50	0.67	53.37	0.00	19.17	73.95
77	0.59	0.36	0.63	43.69	0.00	20.73	65.64
102	0.52		0.54	52.67	0.09	20.14	73.96
120	0.40		0.60	39.74	0.25	23.19	64.18
150	0.33		0.39	62.06	0.32	17.45	80.54
180	0.28		0.46	24.82	0.21	20.35	46.11

n.a. = Not applicable

– = Data not available (traps not aliquotted in error)

The rate of degradation of ethephon under aerobic conditions was also determined. Degradation of ethephon in soil under aerobic conditions depended on the pH of the soil and the temperature, being more rapid at higher pH values and at higher temperatures. The DT_{50} values at 20 °C ranged from 2.7 to 37.6 days. The DT_{50} value at 10 °C (for a clay loam soil) was slower (51.4 days) than the DT_{50} for the same soil at 20 °C (22.2 days). The DT_{50} and DT_{90} values for ethephon in aerobic soils are presented below in Table 30.

Table 30 DT_{50} and DT_{90} values of [^{14}C]ethephon in aerobic soils

Temp.	Clay loam (00/18) Soil pH 7.6.		Sandy loam (00/14) Soil pH 5.9.		Sandy silt loam (00/15) Soil pH 6.8.		Clay loam (00/16) Soil pH 6.9.	
	DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)	DT_{50} (days)	DT_{90} (days)
20 °C	22.2	160	14.2	60.7	37.6	173	2.7	12.5
10 °C	51.4	254						

In the second study, the aerobic degradation of ethephon was investigated in a sandy loam soil for 30 days (Das, 1991, ISSI 90031, [M-187639-01-1]). [^{14}C]Ethephon was applied to the soil at a rate of 10.2 µg/g dry weight of soil. The soil was incubated aerobically in the dark with 75% maximum water holding capacity at 25 ± 1 °C under the airtight conditions. Soil samples were taken at 0, 1, 3, 7, 14, 21 and 30 days after treatment.

[^{14}C]Ethylene was quantified by flushing the headspace with oxygen (Headspace 1). The resulting gas mixture was fed through a NaOH solution (to capture $^{14}CO_2$) and then into a biological sample oxidiser. During oxidization, the [^{14}C]ethylene was quantitatively converted to $^{14}CO_2$ which was trapped in a scintillation cocktail. The soil was extracted with methanol and then with 1.0 N NaOH solution to hydrolyse the ethephon to ethylene. Immediately after addition of the NaOH solution, the vessels were sealed and the headspace contents sampled as described previously (Headspace 2). The headspace gases were analysed by GC-MS to confirm the identity of ethylene. Methanol soil extracts were methylated with diazomethane for GC-MS analysis. Alkaline soil extracts were neutralized and cleaned-up and then analysed in the same way as the methanol extracts.

The mean recovery was 97.3% of applied radioactivity. The oxygen content was 8.9 mg/L at the beginning and 8.7 mg/L at the end of the study, confirming aerobic incubation conditions. The results are summarized in Table 31.

Table 31 Recovery of radioactivity in sandy loam soil after application of [^{14}C]ethephon

Days after appl.	% of Applied radioactivity						
	Extract 1 Methanol	Headspace 1	Extract 2 NaOH solution	Headspace 2	Unextracted Residue	Extract 1 + Headspace 2 (sub-total)	Total
	Sandy loam soil, 25 °C. Soil pH 6.1.						
0	97.2	1.2	< 0.1	2.4	0.9	99.6	101.7
1	75.8	1.1	1.4	16.4	2.2	92.2	96.8
3	63.3	3.8	6.5	16.3	8.0	79.6	97.8
7	47.0	11.6	23.2	10.6	6.7	57.6	99.0
14	29.2	11.6	43.6	5.1	8.6	34.3	98.0
21	21.4	15.0	46.0	3.4	10.8	24.8	96.6
30	0.3	8.5	63.5	4.4	14.6	4.7	91.4

GC-MS analysis showed that ethylene was the only compound in all the headspace fractions (Headspace 1 and 2). Ethephon and phosphoric acid were identified in the methanol extract of soil. HEPA was found in large quantities in the alkaline soil extract, but this may be an artefact caused by the alkaline extraction procedure.

The formation and detection of HEPA was investigated in more detail in a separate study (Lowden and Oddy, 2000, 202534, [M-198831-01-1]). Significant loss of radioactivity was found for [^{14}C]ethephon in 0.1 M or 1.0 M NaOH solutions after incubation at room temperature for 2 hours or 2 days. No loss of radioactivity was found in acidic solutions (0.1 M phosphoric acid or 0.1 M acetic acid). In tests to determine the best extraction solvent to use for soil, phosphoric acid gave the highest recoveries. Freeze-drying of the phosphoric acid extract gives a quantitative recovery of applied radioactivity. Methanol gives a poor recovery of radioactivity from soil samples. Extraction of soil with NaOH solution causes ethephon to transform to HEPA.

In the third aerobic degradation study, the degradation of ethephon was investigated in a soil different from those used by Burr for 44 days (Fitzmaurice, 2003, CX/02/32, [M-232779-01-1]). [^{14}C]Ethephon was applied to a clay loam soil at a rate of 2.24 µg/kg. The soil was incubated aerobically in the dark with 45% maximum water holding capacity at 20 °C under continuous air flow. $^{14}CO_2$ was trapped in an individual trap per flask and a merged trap prior to the air passing over a bed of cuprous oxide at 800 °C to convert volatile hydrocarbons to CO_2, which was trapped in two more CO_2 traps. Soil samples were taken at 0, 1, 3, 7, 14, 21, 38 and 44 days after treatment. The soil was extracted with acetonitrile/water (80:20 v/v) followed by 0.1 M phosphoric acid, and then washed with acetone.

Extracts were analysed by LSC, and post-extraction solids by combustion/LSC. The acetonitrile/water and acetone extracts were concentrated by evaporation and analysed by HPLC. Phosphoric acid extracts were concentrated by freeze-drying. Identification was by co-chromatography with ethephon and HEPA reference standards. Phosphoric acid extracts were analysed by LC-MS/MS for confirmation. The unextracted radioactivity was further characterized by fractionation of the soil organic matter. Volatile traps were treated with sodium carbonate chloride and barium chloride to characterize the radioactivity present.

The recovery of radioactivity ranged from 90.1–107.7% of applied radioactivity. Procedural recoveries ranged from 90.2 to 106.8%. The amount of extracted radioactivity decreased over time from an initial 98.8% to 16.3% on Day 44. Unextracted residues gradually increased to a maximum of 34% at Day 21 and were 27% at 44 days. The largest proportion of non-extracted radioactivity (12.6–19%) was associated with the fulvic acid soil fraction. The amount of radioactivity recovered as volatiles increased to 46.9% at Day 44. CO_2 evolution reached a maximum of 22.8% at Day 38. Ethylene accounted for 24.6% at Day 44.

Ethephon degraded from 98.7 to 10.8% of the applied radioactivity after 44 days. Minor amounts of HEPA (up to 1.6%) were detected. The presence of ethephon and HEPA was confirmed in the phosphoric acid extracts of Day 0 and Day 44. Ethylene was found at up to 25.6% of applied radioactivity. CO_2 and unextracted residues accounted for 22 and 27% of the

applied radioactivity after 44 days. Three unidentified polar degradates were found as minor metabolites (< 5%), (Table 32).

Table 32 Recovery of radioactivity in soil after application of [^{14}C]ethephon

Days after appl.	% of Applied radioactivity						
	Extracted residue	Ethylene trap	Unextracted Residue	CO_2	Total (mass balance)	Ethephon	HEPA
	Clay loam soil, 20 °C. Soil pH 7.9.						
0	98.8	n.d.	8.8	0.0	107.7	98.7	n.d.
1	90.3	3.6	13.2	0.01	107.2	90.2	0.10
3	70.6	10.5	19.4	0.7	101.2	69.9	0.11
7	54.6	12.2	25.9	3.2	95.8	52.4	0.98
14	38.8	15.2	32.1	12.4	98.6	36.2	0.05
21	30.4	18.0	34	15.7	98.0	28.2	0.04
38	18.6	22.8	27.1	22.8	91.4	15.0	0.43
44	16.3	25.6	27.0	22.3	90.2	10.8	1.56

The DT_{50} and DT_{90} were 6 days and 63 days, respectively. For the five soils for which the DT_{50} and DT_{90} were calculated above, the mean DT_{50} and DT_{90} values were 16.5 days and 93.8 days, respectively.

Anaerobic Degradation

The anaerobic degradation of ethephon was studied in a flooded clay loamy soil for 30 days (Oddy, 2001, C013378, [M-204496-01-1]). [^{14}C]Ethephon was applied to the soil at a rate equivalent to 2.24 kg ai/ha. The soil was incubated anaerobically in the dark at 20 ± 2 °C. Soil samples were taken at 0, 6 and 12 hours and 1, 2, 4, 7, 14 and 30 days after treatment. Four traps containing saturated solution of pyridinium hydrogen bromide per bromide (PHBPB) were used to collect [^{14}C]ethylene, and the fifth trap contained 2 M KOH to collect $^{14}CO_2$.

The extraction and recovery of radioactivity from anaerobic soil after application of [^{14}C]ethephon is summarized in Table 33. Recoveries were in the range 90–110% of applied radioactivity at all time-points, except at 2 days where the mean recovery was 86%. At the end of the incubation period, 94% of the applied radioactivity was found in the PHBPB traps. This was identified by GC-MS as dibromoethane from the reaction of ethylene with bromine. At 30 days, < 5% of the applied radioactivity was recovered in the water phase, the remaining radioactivity was found in the soil. Small amounts of HEPA (max 3.7% of applied radioactivity after 12 hours) were detected in the water phase. Ethylene was found in the water phase at up to 18.5% of applied radioactivity at 6 days. The amount of ethylene in the water phase declined to 0.4% after 14 days. Two minor metabolites were also detected.

Table 33 Extraction and recovery of radioactivity from an anaerobic soil after application of [^{14}C]ethephon

Time after application	% of Applied radioactivity							
	Water phase	% ethephon in water phase	Soil extract	% ethephon in soil extract	KOH trap (CO_2)	PHBPB trap (ethylene)	Unextracted residue	Total
0 hours	103.88	90.46	0.00	0.00	0.00	0.00	0.00	103.88
6 hours	89.00	66.05	8.14	7.90	0.00	3.09	1.11	101.33
12 hours	85.97	70.13	7.03	6.90	0.00	1.80	1.01	95.81
1 day	66.63	54.01	10.12	9.96	0.01	12.75	1.62	91.13
2 days	48.17	40.02	10.98	10.46	0.03	25.49	1.70	86.36
4 days	21.14	18.56	15.27	13.93	0.04	68.18	3.17	107.76
7 days	13.60	8.94	10.38	8.99	0.05	71.02	2.88	97.88
14 days	5.85	2.24	7.00	6.28	0.00	80.54	2.34	95.72
30 days	2.65	n.a.	2.67	n.a.	0.03	94.06	2.05	101.43

The major compound identified in soil was [^{14}C]ethephon. Five minor metabolites were detected in the soil at levels below 5% applied radioactivity.

The rate of degradation of ethephon under anaerobic conditions was determined. The DT_{50} and DT_{90} values for ethephon in an anaerobic soil system are presented below in Table 34.

Table 34 DT_{50} and DT_{90} values of [^{14}C]ethephon in an anaerobic soil system

Parameter	DT_{50} (days)	DT_{90} (days)
Anaerobic soil system	2.2	8.8

Soil Photolysis

The photolytic degradation of ethephon was studied on a clay loamy soil (Hatcher and Oddy, 2001, 202650, [M-199517-01-1]). [^{14}C]ethephon was applied to 1 cm thick layers of soil at a concentration equivalent to an application rate of 2.24 kg ai/ha. The soil layers was maintained at 45% of maximum water holding capacity under artificial sunlight from a xenon lamp at 20 ± 2 °C. A non-irradiated group was maintained in the dark at 20 ± 2 °C. Moistened CO_2-free air was supplied at a continuous rate, and the effluent air led through a series of four traps. Three traps containing saturated solution of PHBPB were used to collect [^{14}C]ethylene, and the last trap contained 2 M KOH to collect $^{14}CO_2$. Traps were replaced at 6, 12, 16 and 23 days after application. Duplicate soil samples were taken at 0, 1, 2, 5, 10, 21 and 30 days after treatment. Soil was extracted with 0.2 M phosphoric acid solution, the extracts neutralised and analysed directly by HPLC. Quantification of extracts and trapping solutions was done by LSC. Unextracted radioactivity in soil was analysed by combustion LSC.

Total recoveries of radioactivity for irradiated soils were in the range 76–106% of applied radioactivity. After 21 days, the mean recovery decrease to below 90%, probably due to incomplete trapping of ethylene by the PHBPB traps. The extraction and recovery of radioactivity from irradiated soil following application of [^{14}C]ethephon are presented in Table 35. For comparison, the extraction and recovery of radioactivity from non-irradiated soil following application of [^{14}C]ethephon are also presented.

In the irradiated experiment, after 30 days, 45.1% of the applied radioactivity was recovered in the phosphoric acid extract and 20.7% remained unextractable. 12.3% was found in the PHBPB traps and is attributed to ethylene. Small amounts of HEPA were detected in the soil extract, reaching a maximum of 10.6% applied radioactivity after 10 days, and decreasing to 8.7% after 30 days. The main component in soil was [^{14}C]ethephon. Four minor metabolites were detected in soil extracts at levels below 3% applied radioactivity.

At the end of the non-irradiated experiment, 49.4% applied radioactivity was recovered in the phosphoric acid extract and 19.6% remained unextractable. 7.8% was found in the PHBPB traps (ethylene). A further 5.7% was recovered in the KOH trap and characterised by precipitation as $^{14}CO_2$. The main component in soil was [^{14}C]ethephon, and small amounts of HEPA were detected in the extract (5.7% after 30 days). Three minor metabolites were detected in soil extracts at levels below 3% of the applied radioactivity

Table 35 Extraction and recovery of radioactivity from soil following application of [^{14}C]ethephon

Sampling time, days	% of applied radioactivity					
	H_3PO_4 extract	% ethephon in soil extract	KOH trap (CO_2)	PHBPB trap (ethylene)	Unextracted residue	Total
Irradiated						
0	100.52	99.11	0.00	0.00	0.80	101.32
1	96.80	90.62	0.00	0.27	2.85	99.92
2	96.03	87.95	0.00	0.80	3.42	100.25
5	89.91	76.76	0.02	2.85	8.79	101.57
10	72.96	59.08	0.05	4.52	15.12	92.64
21	54.74	43.51	0.99	7.29	18.34	81.35
30	45.14	32.55	0.50	12.25	20.68	78.56
Non-irradiated						

Sampling time, days	% of applied radioactivity					
	H_3PO_4 extract	% ethephon in soil extract	KOH trap (CO_2)	PHBPB trap (ethylene)	Unextracted residue	Total
0	100.52	99.11	0.00	0.00	0.80	101.32
1	95.84	89.90	0.08	1.13	3.22	100.26
2	92.42	86.44	0.00	0.51	4.32	97.26
5	83.29	77.74	1.08	2.91	8.67	95.95
10	71.08	62.99	2.21	4.30	14.87	92.46
21	59.90	51.96	4.97	5.69	16.96	87.51
30	49.40	40.47	5.67	7.78	19.60	82.45

The result indicates that the degradation pathway did not differ between the irradiated and non-irradiated soils. The rate of degradation of ethephon was slightly enhanced by irradiation. The DT_{50} and DT_{90} of [^{14}C]ethephon in non-irradiated and irradiated soil are shown below.

Table 36 DT_{50} and DT_{90} values of [^{14}C]ethephon in irradiated and non-irradiated soil

Parameter	DT_{50} (days)	DT_{90} (days)
Irradiated soil	16.5	57.8
Non-irradiated soil	20.7	74.4

Field Dissipation

The dissipation of ethephon was studied in three soils under field conditions in the USA (Norris, 1991, 41011, [M-187653-01-1]). The study was carried out over a period of four months under the growing conditions of tomatoes, cotton and spring wheat. Sites in the USA (California, North Carolina and Washington) were selected with plot areas of 960–1600 m^2. The field were tilled, the crops were planted and ethephon was applied at each location as follows:

Table 37 Dissipation of ethephon in soils

Trial location	Crop	Formulation	Application rate	Soil characterization (0–15 cm depth)
California	Tomato	SL, 22% ethephon	1.85 kg ai/ha	Loam, pH 7.8, 1.5% OM
North Carolina	Cotton	SL. 55% ethephon	2.25 kg ai/ha	Sand, pH 6.6, 0.7% OM
Washington	Spring wheat	SL, 40% ethephon	1.86 kg ai/ha [a]	Loamy sand, pH 7.1, 1.2% OM

[a] For the Washington site, the actual application rate was 3.3× the nominal rate of 0.56 kg ai/ha due to a calculation error

Crops were grown according to local standard agronomic practices. At the California and Washington trials sites, crops were irrigated in order to maintain a viable crop. Directly after application, 0–15 cm depth soil cores were collected. Soil cores collected at later intervals were segmented into 0–15, 15–30, 30–45, 45–60, 60–75 and 75–90 cm depth increments. After air-drying and sieving (2 mm), endogenous ethylene was removed from the soil samples. The soil was then subjected to alkaline hydrolysis to convert any ethephon present to ethylene, which was measured by GC analysis of the headspace.

The procedural recoveries for ethephon were in the range 63–104% (RSD 13%, n=78). The procedural recoveries were similar for soil from the three sites. In addition to the soil samples, filter paper strips placed in the field during application were analysed for evaluation of the application rate achieved.

Following application, residues of ethephon declined with time. Residues found in soil after application were 0.73–1.2 mg/kg, and assuming a soil density of 1.6 g/cm, fairly well matched the application rate as determined in the field (except for the Washington site). Residues declined to 0.01–0.03 mg/kg within 60–120 days. The majority of the residues were found in the top soil (0–15 cm), except for the Washington trial, which was attributed to excessive irrigation shortly after application, causing ethephon to penetrate into the soil as deep as 45–60 cm.

Dissipation seems to be temperature dependent, i.e. fastest in the south (North Carolina) and slowest in the north (Washington). Dissipation of ethephon in soil follows first order kinetics. The DT_{50} and DT_{90} values for dissipation of ethephon in soil under local field conditions are 6.8–20 days and 22–66 days, respectively (Table 38).

Table 38 DT_{50} and DT_{90} values for three USA soils

Location	Crop	Application rate, kg ai/ha	DT_{50}, days	DT_{90}, days	Function	Regression coefficient
California	Tomato	1.85	12 20	66	1st order linear 1st order non-linear	–0.986
North Carolina	Cotton	2.25	6.8 6.8	22	1st order linear 1st order non-linear	–0.964
Washington	Spring wheat	1.86	25 15	65	1st order linear 1st order non-linear	–0.986

Proposed degradation pathway in soil

Under aerobic, anaerobic and photolytic conditions, the route of degradation was similar with ethylene being formed as the major metabolite. Small amounts of HEPA and CO_2 are formed. The proposed degradation pathway of ethephon in soil is shown below.

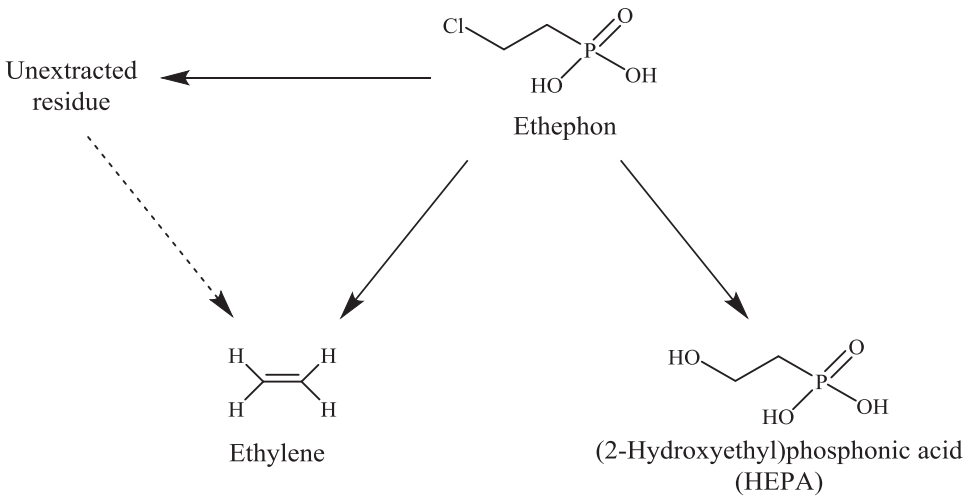


Figure 4 Proposed degradation pathway of ethephon in soil

Residues in Succeeding or Rotational Crops

A confined accumulation study on rotational crops was conducted with [^{14}C]ethephon using wheat, collards and radish (Miller, 1994, EC-91-158, [M-187425-01-1]). The test material was applied to bare plots in plastic containers containing a sandy loam soil, at an application rate of 2.36 kg ai/ha. Crops were planted into the treated soil at plant-back intervals (PBI) of 30, 120 and 379 days after treatment (DAT) after thorough manual mixing of soil (ca. 10 cm). Mature crops were harvested 54–62 days after planting (radishes), 68–91 days after planting (collards) and 110–158 days after planting (wheat). Immature wheat foliage was harvested 47–68 days after planting. Soil samples were collected at each planting and harvest interval. Total radioactive residues (TRR) in crops and soil were determined by combustion LSC.

Crop matrices were homogenized and subsequently extracted with hexane, ethyl acetate and methanol, and then by soxhlet extraction using acidified methanol. The extracts were combined and analysed using HPLC with UV and radiochemical detection. Radioactive components were co-chromatographed with ethephon and HEPA.

The unextracted residue was subjected to a sequential extraction procedure to give water-soluble polysaccharide (potassium phosphate extraction), starch (alpha-amylase digestion), protein (Pronase E digestion), pectin (sodium acetate/ EDTA extraction at pH 4.5), lignin (sodium chlorite digestion at 70 °C), hemi-cellulose (24% potassium hydroxide digestion) and cellulose (72% sulphuric acid digestion at 100 °C) fractions. These fractions were derivatized with phenyl hydrazine and oxidized to $^{14}CO_2$ in order to investigate the incorporation of [^{14}C]ethephon into biomolecules.

TRR in soil at a depth of 0–10 cm following application of [^{14}C]ethephon are summarized in Table 39. At 525 DAT, no detectable radioactive residue was observed in soil at a depth of 20–40 cm, and not more than 0.04 mg/kg was found at 10–20 cm depth.

Table 39 Total radioactive residues in soil at 0–10 cm depth after treatment with [^{14}C]ethephon

DAT	0	30	97	118	120	167	188	230	379	440	470	525
TRR in soil, mg/kg	2.0	1.5	1.2	0.71	0.69	0.73	0.86	0.94	0.33	0.20	0.23	0.22

TRRs in radishes, collards and wheat following application of [^{14}C]ethephon are summarized in Table 40. The highest TRRs were found in the 30 day PBI wheat straw (0.49 mg/kg) and grain (0.35 mg/kg), but in the 379 day PBI samples, 0.03 and 0.02 mg/kg, respectively. Extracted radioactive residues were low (< 50% of TRR) at all time points. Most of the extracted radioactivity from the crop matrices was released by extraction with methanol and the soxhlet extraction with acidified methanol, whereas hardly any radioactivity was extracted with hexane and ethyl acetate. The total extracted residue did not exceed 0.07 mg/kg in any sample analysed. Only the extracts containing residues above 0.01 mg/kg were subjected to HPLC analysis. Low levels of ethephon and HEPA were present in some extracts analysed (30 day PBI radish root and foliage, collard, wheat forage and straw, 120 day PBI radish root and wheat forage, and 379 day PBI wheat grain), and no unidentified metabolites were detected at significant concentrations.

Table 40 Total radioactive residues in rotational crops planted 30, 120 and 379 days after soil application of [^{14}C]ethephon

Crop matrices	Harvest time	TRR	Solvent-extracted radioactive residue [a]	
	DAT	mg/kg	mg/kg	% TRR
30 day PBI				
Radish foliage	98	0.07	0.03	33
Radish roots	98	0.07	0.02	38
Collards	117	0.11	0.03	35
Immature wheat forage	98	0.14	0.05	43
Wheat grain	188	0.35	0.02	8.1
Wheat straw	188	0.49	0.07	15
120 day PBI				
Radish foliage	174	0.07	0.02	29
Radish roots	174	0.06	0.03	49
Collards	188	0.05	0.02	42
Immature wheat forage	167	0.12	0.04	40
Wheat grain	230	0.13	0.02	18
Wheat straw	230	0.19	0.05	24
379 day PBI				
Radish foliage	441	0.01	< 0.01	11
Radish roots	441	0.00	< 0.01	21
Collards	470	0.01	< 0.01	1.4
Immature wheat forage	441	0.01	< 0.01	0.6
Wheat grain	523	0.02	0.01	23
Wheat straw	523	0.03	< 0.01	21

[a] Sum of extractions with hexane, ethyl acetate, methanol and acidified methanol

All crop samples contained radioactive residues in the post-extraction solids. In general, 30 day PBI wheat contained the highest unextracted residues. In these samples, the cellulose fractions from wheat grain and straw were 0.07 mg/kg (20% TRR) and 0.12 mg/kg (25% TRR), respectively. Radioactivity in other biomolecule fractions was found to be lower, (Table 41).

Table 41 Characterization of the unextracted residue by solvents in 30 day and 120 day PBI crop samples

Fraction	30 day PBI Collards		30 day PBI Wheat grain		30 day PBI Wheat straw		30 day PBI Wheat foliage	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Buffer fraction	0.01	6.4	0.02	5.1	0.01	1.5	0.00	3.3
Starch fraction	0.01	11.1	0.03	9.0	0.01	2.5	0.00	3.1
Protein fraction	0.03	27.6	0.05	14.0	0.01	2.0	0.04	30.3
Pectin fraction	0.00	2.8	0.01	2.2	0.01	1.0	0.01	5.9
Lignin fraction	0.00	1.6	0.01	4.2	0.01	1.6	0.01	4.3
Hemi-cellulose fraction	0.01	8.3	0.05	13.9	0.06	12.6	0.02	11.2
Cellulose fraction	0.01	9.5	0.07	20.1	0.12	24.8	0.02	14.7
Filters + ash	0.00	3.9	0.01	4.7	0.15	31.3	0.01	11.1
Solvent extracts	0.03	36.1	0.02	7.3	0.07	13.7	0.05	37.3
Total recovery	0.10	107.2	0.27	80.5	0.45	91.0	0.16	121.1
TRR	0.11		0.35		0.49		0.14	
Fraction	120 day PBI Radish tops		120 day PBI Wheat grain		120 day PBI Wheat straw		120 day PBI Wheat foliage	
	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR
Buffer fraction	0.01	18.9	0.00	2.5	0.00	2.2	0.00	3.6
Starch fraction	0.00	6.2	0.01	10.5	0.00	1.1	0.00	3.3
Protein fraction	0.03	34.2	0.02	16.0	0.01	2.8	0.02	15.6
Pectin fraction	0.01	14.0	0.01	4.1	0.00	2.2	0.00	4.0
Lignin fraction	0.01	7.9	0.01	4.2	0.00	1.4	0.00	3.1
Hemi-cellulose fraction	0.01	8.2	0.01	8.9	0.02	12.7	0.01	10.3
Cellulose fraction	0.01	15.7	0.02	17.4	0.04	22.7	0.01	9.7
Filters + ash	0.01	11.6	0.00	3.8	0.04	21.4	0.01	6.0
Solvent extracts	0.02	36.0	0.02	15.3	0.05	23.8	0.04	34.5
Total recovery	0.11	152.8	0.10	82.6	0.16	90.4	0.09	90.2
TRR	0.07		0.13		0.19		0.12	

Overall, [^{14}C]ethephon residues declined steadily in soil. Radioactivity in mature plant samples paralleled or decreased at an even faster rate compared to the soil levels. In plant extracts, no radioactive peaks greater than 0.01 mg/kg were detected. Very low levels of ethephon and HEPA were detected in radishes, collards and wheat. Most of the radioactivity in the crop samples was attributable to incorporation into natural plant constituents.

The metabolism in rotational crops is similar to that seen in primary crops, with degradation to HEPA and natural incorporation into biomolecules.

Residue analytical methods

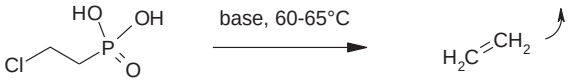
The Meeting received information on analytical methods together with validation data for residues of ethephon in plant, and animal matrices.

The analytical methods presented in this section are based on three different principles:

Ethylene-release method

This method was widely used in studies performed in the USA, and involves base hydrolysis of the residue to ethylene, with measurement of the released ethylene by GC-FID. The samples are first heated in a solution of tartaric acid in order to remove the endogenous ethylene. Thereafter the solution is made basic and heated again in capped bottles which allow headspace samples to be collected. By this procedure the ethephon present in the samples decomposes to ethylene, which is

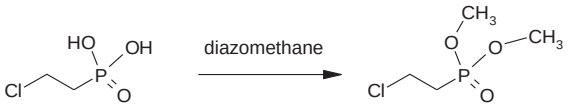
determined by headspace GC/FID. The released ethylene allows the ethephon residues in the sample to be quantified. The LOQ is typically 0.02–0.10 mg/kg.



ethephon **ethylene**

Derivatisation to methyl ester method

This method was used in the earlier studies performed in Europe and involves extraction with methanol and derivatisation of the ethephon residue with diazomethane to give the methyl ester, with measurement by GC-NPD or GC-FPD in phosphorus mode. The LOQ is typically 0.05–0.20 mg/kg.



ethephon **ethephon dimethyl ester**

LC-MS/MS method

This is a highly specific method which has been used in the more recent studies and involves extraction of the ethephon residue, sample clean-up and measurement by LC-MS/MS. The LOQ is typically 0.05 mg/kg.

Detailed descriptions of all these analytical methods are presented below. Validation data for methods on plant and animal matrices are summarized in Table 42.

Analytical Methods for Determination of Ethephon Residues

Analytical methods for plant matrices

Method: 11-94 (Ethylene release method) (Nygren, 1994, 11-94, [M-188198-01-1])

Analyte:	Ethephon	GC-FID	
LOQ:	0.10 mg/kg in fig, 0.02 in pineapple, 0.07 mg/kg in cotton seed,		
Description:	The ground sample is placed in a 250 mL pressure bottle with a crown cap that has a provision for withdrawing a headspace sample with a syringe. An aqueous tartaric acid-surfactant solution is added. The bottle is then capped, heated to about 60 °C and periodically agitated to drive any endogenous ethylene from the sample. After one hour heating, the cap is removed and the bottle is flushed with a gentle stream of nitrogen to remove any released ethylene. The sample is allowed to cool to room temperature. Trisodium phosphate, sufficient to make the sample basic, is added. The bottle is immediately capped and heated for one hour with periodic agitation to convert any ethephon residues into ethylene. The ethylene accumulates in the headspace and is quantified by gas chromatography with flame ionisation detection.		

Method: Union Carbide, 1981 (Diazomethane method) (Conn, 1992, SARS-89-24, [M-187553-01-1])

Method title “Detailed Method of Analysis for Residues of (2-Chloroethyl)Phosphonic Acid (Ethephon) in Wheat and Barley Grain, Straw and Milling Fractions”			
Analyte:	Ethephon	GC-FPD	
LOQ:	0.05 mg/kg in wheat grain and straw		

Description:	This method is the predecessor of SOP 90074 Samples are hard-frozen, ground and freeze-dried. Grain samples are soxhlet extracted with methanol for 4 hours. Straw samples are soxhlet extracted with 1% citric acid in methanol for 4 hours. The pH is adjusted by the addition of 10% methanolic hydrochloric acid. An aliquot of the extract is concentrated, 10% methanolic HCl added and solid materials precipitated by the addition of diethyl ether. After centrifugation and concentration of the liquid extract to ca. 1 mL, the ethephon residues are methylated with diazomethane. Straw samples are subjected to an additional clean-up step using a florisil column. The thus formed ethephon dimethyl ester is measured by means of gas chromatography with flame photometric detection.

Method: SOP–90070 (Diazomethane method) (Nygren, 1990, SOP–90070, [M-163159-01-1])

Analyte:	Ethephon	GC-FPD or GC-NPD	
LOQ:	0.05 mg/kg in wheat grain and straw, 0.02 in tomato		
Description:	This method is essentially the same as Method SOP 90074. Samples are hard-frozen, ground (in case of solid matrices) and freeze-dried. Samples are soxhlet extracted with methanol for 4 hours. The pH is adjusted by the addition of 10% methanolic hydrochloric acid. An aliquot of the extract is concentrated, 10% methanolic HCl added and solid materials precipitated by the addition of diethyl ether. After centrifugation and concentration of the liquid extract to ca. 1 mL, the ethephon residues are methylated with diazomethane. The thus formed ethephon dimethyl ester is measured by means of gas chromatography with either flame photometric detection in the phosphorous mode or with nitrogen phosphorus detection. Minor adjustments of the general procedure may be necessary to adapt for individual crops.		

Method: SOP 90069 (Diazomethane method) (Nygren, 1991, 89-REN-WA-S, [M-187529-01-1])

Analyte:	Ethephon	GC-NPD	
LOQ:	0.01 mg/kg in macadamia nuts		
Description:	Samples are hard-frozen, ground and freeze-dried. Samples are soxhlet extracted with methanol for 4 hours. The pH of the extract is adjusted by the addition of 10% methanolic hydrochloric acid. The acidified extract is frozen overnight to solidify the extracted lipid material. The methanolic solution is separated from the lipid material, concentrated and the solid materials in the extract precipitated by the addition of diethyl ether and separated by centrifugation. The resulting extract is concentrated and residues of ethephon methylated with diazomethane. The ethephon dimethyl ester is analysed by gas chromatography with nitrogen phosphorus detection.		

Method: SOP 90074 (Diazomethane method) (Eckert, 1992, Report: RP-01-89I, [M-187521-01-1])

Analyte:	Ethephon	GC-FPD	
LOQ:	0.05 mg/kg in wheat grain and straw		
Description:	Samples are hard-frozen, ground and freeze-dried. Grain samples are soxhlet extracted with methanol for 4 hours. Straw samples are soxhlet extracted with 1% citric acid in methanol for 4 hours. The pH is adjusted by the addition of 10% methanolic hydrochloric acid. An aliquot of the extract is concentrated, 10% methanolic HCl added and solid materials precipitated by the addition of diethyl ether. After centrifugation and concentration of the liquid extract to ca. 1 mL, the ethephon residues are methylated with diazomethane. Straw samples are subjected to an additional clean-up step using a florisil column. The thus formed ethephon dimethyl ester is measured by means of gas chromatography with flame photometric detection in phosphorus mode.		

Method: SOP 90075 (Diazomethane method) (Eckert, 1992, RP-01-89J, [M-187525-01-1])

Analyte:	Ethephon	GC-FPD	
LOQ:	0.05 mg/kg in cotton seed		

Description:	Cotton seed, hulls and meal: Samples are hard-frozen, ground and freeze-dried. Samples are soxhlet extracted with methanol for 4 hours. The pH of the extract is adjusted by the addition of 10% methanolic hydrochloric acid. An aliquot of the extract is concentrated, 10% methanolic HCl added and solid materials precipitated by the addition of diethyl ether. After centrifugation and concentration of the liquid extract to ca. 1 mL, the ethephon residues are methylated with diazomethane. The resulting ethephon dimethyl ester is analysed by gas chromatography with flame photometric detection in phosphorus mode or alkali flame thermionic detection. Cottonseed oil and soapstock: Samples are extracted by vortex mixing with 1% methanolic citric acid for 1 minute. After centrifugation, the upper methanol phase is removed and reserved, and the extraction procedure repeated a further two times. The combined methanol extracts are concentrated and solid materials precipitated by the addition of diethyl ether. After centrifugation and concentration of the liquid extract to ca. 1 mL, the ethephon residues are methylated with diazomethane. The resulting ethephon dimethyl ester is analysed by gas chromatography with flame photometric detection in phosphorus mode or alkali flame thermionic detection.

Method: Analytical methods for pesticide residues in foodstuffs, Sixth edition, June 1996: Ethephon (Diazomethane method) [M-208923-01-1])

Analyte:	Ethephon	GC-FPD	
LOQ:	0.1 mg/kg		
Description:	This is an official method for determination of ethephon in foodstuffs of plant origin, which has been published by the Dutch General Inspectorate for Health Protection. This method is similar to method SOP 90070 except that ethyl acetate is used as an extraction solvent instead of methanol. The ground samples (50 g) are extracted with ethyl acetate (400 mL) in presence of sulphuric acid, magnesium sulphate and sodium sulphate. An aliquot of the extract (100 mL) is methylated with diazomethane and then concentrated on a rotary evaporator. The ethephon dimethyl ester present in the final extract is measured by means of gas chromatography with flame photometric detection in the phosphorus mode. If necessary the final extract can first be cleaned up by treatment with charcoal.		

Method: HVA 12/89 (Diazomethane method) (Maestracci, 1998, R&D/CRLD/AN/msa/9816152, [M-165702-02-1])

Analyte:	Ethephon	GC-FPD	
LOQ:	0.10 mg/kg in pineapple (skin and flesh), cotton (seed and lint)		
Description:	Samples are extracted by homogenization with methanol, filtered, and the extraction repeated. The combined extract is concentrated and made up to a known volume with methanol. An aliquot of the extract is diluted with diethyl ether and acidified with acetic acid. The ethephon is methylated with diazomethane and residues determined by gas chromatography with flame photometric detection in the phosphorus mode. Quantification is done by external standardisation.		

Method: HVA SOP 10071 (Diazomethane method) (Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1])

Analyte:	Ethephon and HEPA	GC-FPD	
LOQ:	0.05 mg/kg		
Description:	Samples are extracted by homogenization with methanol, filtered, concentrated and made up to a known volume with methanol. An aliquot of the extract is liquid/liquid partitioned into diethyl ether, the diethyl ether dried with sodium sulphate and evaporated to 1–2 ml. Ethephon and HEPA are methylated with diazomethane and residues determined by gas chromatography with flame photometric detection in the phosphorus mode. Quantification is done by external standardisation. For sweet pepper, an additional clean up on silica gel is necessary prior to GC-determination.		

Method: V5229/01 (LC-MS/MS method) (Kerkdijk, 1994, V5229/01, [M-226290-01-1])

Analyte:	Ethephon and HEPA	LC-MS/MS	
LOQ:	0.05 mg/kg in apple, cherry and sweet pepper		
Description:	Samples are extracted by high speed blending with demineralized water. The extract is centrifuged and filtered to give a clear supernatant. The pH of the supernatant is adjusted to pH 4–5 using 1 N formic acid solution. A further clean-up is performed by solid phase extraction (SPE) using SDB1 columns. The resulting eluate is analysed by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) in the negative electrospray mode. Ethephon is monitored by means of the MS/MS transition at m/z 142.9 → 107.0 (^{35}Cl isotope) and HEPA at m/z 124.9 → 94.9.		

Method: 00902 (LC-MS/MS method) (Oel & Bardel, 2005, MR-128/04, [M-247578-01-1])(Independent-laboratory-validated)

Analyte:	Ethephon	LC-MS/MS	
LOQ:	0.05 mg/kg in tomato, wheat grain, orange, olive		
Description:	Residues of ethephon are extracted from plant material by high speed blending with methanol/water/formic acid (90/10/0.1, v/v/v). For dry matrices (e. g. cereal grain) the sample must be soaked prior to blending and some cysteine hydrochloride is added to extraction solvent. For dry matrices it is also possible to use microwave extraction instead of high speed blending. After concentration to dryness the extract is reconstituted in water/methanol/formic acid (80/20/0.5, v/v/v). The reconstituted extract is analysed by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) using a triple-quadrupole apparatus that is operated in the negative electrospray mode. Ethephon is monitored by means of the MS/MS transitions m/z 143 → 107 (^{35}Cl isotope) and/or m/z 145 → 107 (^{37}Cl isotope). Satisfactory chromatographic separation is achieved on a C_{18} column with polar embedding (Synergi Fusion-RP 80Å, 150×4.6 mm, 4 µm). Elution is performed using water/methanol (80/20, v/v) acidified with 0.5% formic acid as the mobile phase.		

Method: 00918 (LC-MS/MS method) (Oel & Bardel, 2005, MR-173/04, [M-248933-01-1])

Analyte:	Ethephon and HEPA	LC-MS/MS	
LOQ:	0.05 mg/kg in cereal green material, grain and straw		
Description:	The residues of ethephon and HEPA are extracted from cereal green material, straw, and grain by high speed blending with methanol/water/formic acid (50/50/0.1, v/v/v). Samples of straw and grain must be soaked prior to blending. Alternately it is possible to extract residues from cereal grain by microwave extraction using the same solvent mixture. The raw extracts are cleaned-up on an SPE Bond Elut ENV cartridge. For determination of ethephon and HEPA an aliquot of the eluate is concentrated to dryness and reconstituted in 0.01% formic acid. The final extracts are measured by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) using a triple-quadrupole apparatus that is operated in the negative electrospray mode. Satisfactory chromatographic separation is achieved an ion chromatography column (Metrosep A Supp 4) with an aqueous solution of ammonium carbonate (15 mmol/L) as mobile phase. Ethephon is monitored by means of the MS/MS transition m/z 143 → 107, while HEPA is monitored by means of the MS/MS transition m/z 125 → 95.		

Method: 00903 and 00903/E001 (LC-MS/MS method) (Oel & Bardel, 2005, MR-131/04, [M-254165-01-1])

Analyte:	Ethephon and HEPA	LC-MS/MS	
LOQ:	0.05 mg/kg in grapes, apple, tomato, olives and processed fractions		
Description:	Apple and grape samples are extracted by soaking and then high speed blending with 0.01% formic acid. The extract is filtered under vacuum to give a clear supernatant. Tomato matrices are extracted by soaking and then high speed blending with 0.01% formic acid. Celite is added to the extract, which is then filtered under vacuum to give a clear supernatant. The filtered extract is cleaned-up by solid phase extraction (SPE) using Bond Elut ENV columns. The resulting eluate is filtered and analysed by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) in the negative ion mode. Ethephon is monitored by means of the MS/MS transition at m/z 143 → 107 (^{35}Cl isotope) and HEPA at m/z 125 → 95. The method can be performed using either internal or external standards.		

Method: 01429 (LC-MS/MS method)(Schulte and Sruskus, 2015, MR-14/100)

Analyte	Ethephon and HEPA	LC-MS/MS	
LOQ:	For both compounds: 0.01 mg/kg in cereal grains and 0.05 mg/kg in cereal green material and straw		
Description:	The residues were extracted from cereal green material by blending two times with methanol. For cereal straw and grain the residues were extracted by blending three times with methanol followed by hydrolysis/extraction with a mixture of hydrochloric acid (32%)/water (1/7, v/v) at 50 °C overnight. After addition of isotopically labeled internal standards the extracts were analysed by HPLC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 × 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. The mass spectrometer was operated in the negative ionization mode using the mass transitions m/z 142.9 → 106.8 for the quantitation of ethephon and m/z 125.0 → 94.8 for the quantitation of the metabolite HEPA.		

Method Validation

Validation data of the methods used for determining ethephon in plant and animal commodities from related studies are summarized below.

Table 42 Summary of Method Validation

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Plant commodities—ethylene release method								
Barley grain	Ethephon	0.16 0.8 2	4 4 4	88–97 92–100 95–102	94 96 98	4.8 3.5 3.4	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Wheat grain	Ethephon	0.16 0.8 2	8 8 8	86–98 97–102 97–104	92 99 101	4.6 1.9 2.2	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Barley straw	Ethephon	0.82 4.1 10	8 8 8	87–106 83–105 93–105	94 98 97	6.5 7.2 3.8	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Wheat straw	Ethephon	0.82 4.1 10	4 4 4	113–130 99–106 94–101	122 102 98	6.0 2.9 3.6	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Apples	Ethephon	0.02-1 0.05 5	4 4 4	94–102 93–102 94–105	97 97 99	3.6 4.4 5.2	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Tomatoes	Ethephon	0.02 0.1 2	4 4 4	101–107 98–102 98–100	104 100 100	2.4 1.7 1.0	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Grapes	Ethephon	0.02 0.1 2	8 8 8	89–95 99–106 92–104	91 102 99	2.0 2.5 3.5	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Cherries	Ethephon	0.02 0.1 10	8 8 8	74–92 80–103 85–101	82 94 96	8.3 7.2 6.5	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Pineapple	Ethephon	0.02 0.1 2	8 8 8	89–108 89–112 100–120	99 105 105	6.4 3.5 6.3	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Cotton seed	Ethephon	0.07 0.35 2	4 4 4	82–92 94–97 87–95	87 95 90	5.1 1.6 3.8	11-94 (EC-92-228)	Nygren, 1993, EC-92-228, [M-179285-01-1]
Plant commodities—diazomethane method								
Wheat grain (6% FFAP column packing)	Ethephon	0.05 0.25 0.5	2 2 2	85–120 86–98 98–110	103 92 104		Union Carbide, 1981	Conn, 1992, SARS-90-24P, [M-187550-01-1]
Wheat straw (6% FFAP column packing)	Ethephon	0.05 0.25 0.5	2 2 2	100 79–94 100–108	100 87 104		Union Carbide, 1981	Conn, 1992, SARS-90-24P, [M-187550-01-1]
Wheat grain (20% OV-11 column packing)	Ethephon	0.05	1	78			Union Carbide, 1981	Conn, 1992, SARS-90-24P, [M-187550-01-1]
Wheat straw (20% OV-11 column packing)	Ethephon	0.05 0.1	1 1	108 79			Union Carbide, 1981	Conn, 1992, SARS-90-24P, [M-187550-01-1]
Wheat grain	Ethephon	0.05 0.2 0.5	6 6 6	72–97 70–92 81–01	86 83 87	9.7 10.5 8.6	SOP 90074	Eckert, 1992, RP-01-89I, [M-187521-01-1]
Wheat straw	Ethephon	0.05 0.2 2	6 6 6	87–111 71–112 85–106	96 96 96	9.2 15.1 9.0	SOP 90074	Eckert, 1992, RP-01-89H, [M-187519-01-1]
Apple	Ethephon	0.05 0.2 1	6 6 6	76–94 69–106 84–108	86 84 91	8.4 15.6 9.9	SOP–90070	Eckert, 1992, RP-01-89C, [M-187515-01-1]

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Tomato	Ethephon	0.05 0.2 0.5	6 6 6	75–89 72–93 83–100	82 83 88	6.6 8.8 6.8	SOP–90070	Eckert, 1992, RP-01-89A, [M-187533-01-1]
Grapes	Ethephon	0.05 0.2 0.5	6 6 6	69–79 81–96 79–101	72 87 87	7.3 6.2 9.1	SOP–90070	Eckert, 1992, RP-01-89D, [M-187544-01-1]
Blackberry	Ethephon	0.05 0.2 1	6 6 6	85–112 78–105 82–92	94 88 88	10.8 11.0 4.4	SOP–90070	Eckert, 1992, RP-01-89B, [M-187511-01-1]
Pineapple fruit	Ethephon	0.05 0.2 0.5	6 6 6	77–118 88–96 77–94	93 92 88	15.8 3.8 7.0	SOP–90070	Eckert, 1992, RP-01-89E, [M-187540-01-1]
Pineapple forage	Ethephon	0.05 0.2 0.5	6 6 6	70–85 79–86 79–92	77 82 85	7.7 3.2 5.2	SOP–90070	Eckert, 1992, RP-01-89F, [M-187538-01-1]
Tomato dry pomace	Ethephon	0.02 0.2 2	3 3 3	86–104 90–104 70–120	96 96 93	9.5 7.7 27.1	SOP–90070	Nygren, 1991, USA89E30, [M-187599-01-1]
Tomato canned fresh juice	Ethephon	0.02 0.2 2	3 2 3	88–122 88–94 70–91	109 91 81	16.7 4.7 13.0	SOP–90070	Nygren, 1991, USA89E30, [M-187599-01-1]
Tomatoes	Ethephon	0.02 0.2 2	3 3 3	72–88 76–90 77–100	77 82 90	11.9 8.8 13.2	SOP–90070	Nygren, 1991, USA89E16, [M-187596-01-1]
Tomatoes	Ethephon	0.01 0.2 2	3 3 3	72–76 80–85 100–105	74 82 102	2 3 3	SOP–90070	Dorschner, 2008, 00250, [M-301374-01-1]
Apples	Ethephon	0.05 0.2 2	3 3 3	82–110 82–105 99–108	95 97 104	14.7 13.6 4.4	SOP–90070	Nygren, 1990, USA89E32, [M-187583-01-1]
Apple dry pomace	Ethephon	0.05 0.2 2	3 3 3	80–97 84–98 92–108	86 91 103	10.8 7.7 9.0	SOP–90070	Nygren, 1990, USA89E32, [M-187583-01-1]
Apple juice	Ethephon	0.05 0.2 2	3 3 3	79–98 102–108 88–104	91 105 95	11.5 2.9 8.6	SOP–90070	Nygren, 1990, USA89E32, [M-187583-01-1]
Grapes	Ethephon	0.1 0.2 0.4 0.5 2	3 1 1 1 1	73–93 75 70 78 85	83 75 70 78 85	12.1 – – – –	Similar to SOP – 90070 Based on ‘Analytical methods for pesticide residues in foodstuffs’, 5th edition, 1988	Grolleau, 1997, EA950185, [M-188232-01-1]
Barley plant	Ethephon	0.05 0.5 10	8 8 7	71–93 74–108 75–104	86 89 88	9.1 12.2 9.8	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Barley grain	Ethephon	0.05 0.5	7 7	69–97 69–98	85 84	11.1 11.9	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Barley straw	Ethephon	0.05 0.5	8 9	67–104 81–104	89 89	15.4 10.4	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Wheat plant	Ethephon	0.05 0.5 10	3 3 3	80–96 86–91 70–104	88 89 88	7.4 2.6 15.9	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Wheat grain	Ethephon	0.05 0.5	4 4	77–93 78–110	83 90	7.7 13.6	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Wheat straw	Ethephon	0.05 0.5	5 4	78–92 82–93	82 87	6.9 4.6	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Apple	Ethephon	0.05 0.5 1	10 9 2	74–112 81–108 95–99	92 94 97	12.6 8.0 –	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Cherry	Ethephon	0.05 0.5 1 3	9 9 1 5	69–95 70–104 94 80–94	84 90 94 89	11.8 12.1 – 5.5	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Tomato	Ethephon	0.05 0.5 1 2	12 11 1 1	73–112 76–104 88 108	85 89 88 108	12.5 8.8 – –	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Sweet peppers	Ethephon	0.05 0.5 1 3	6 6 1 1	85–98 83–104 82 96	92 94 82 96	5.7 8.7 – –	HVA SOP 10071	Fuchsbichler, 2002, HVA SOP 10071, [M-210331-01-1]
Pineapple skin	Ethephon	0.1 0.2 0.5	1 1 1	82 114 76	82 114 76	– – –	HVA 12/89	Maestracci, 1998, R&D/CRLD/AN/msa/9816152, [M-165702-02-1
Pineapple flesh	Ethephon	0.1 0.2 0.5	1 1 1	89 76 82	89 76 82	– – –	HVA 12/89	Maestracci, 1998, R&D/CRLD/AN/msa/9816152, [M-165702-02-1
Cotton seed	Ethephon	0.1	3	80–82	81	1.2	HVA 12/89	Richard & Muller, 1995, R&D/CRLD/AN/bd/9515891, [M-163122-01-1]
Cotton lint	Ethephon	0.1 2 20	2 1 1	78–93 88 70	86 88 70	– – –	HVA 12/89	Richard & Muller, 1995, R&D/CRLD/AN/bd/9515911, [M-163133-01-1]
Cotton seed	Ethephon	0.1 0.5	2 1	111–115 69	113 69	– –	HVA 12/89	Richard & Muller, 1995, R&D/CRLD/AN/bd/9515911, [M-163133-01-1]
Cotton lint	Ethephon	0.1 0.5 2	1 1 1	86 89 74	86 89 74	– – –	HVA 12/89	Muller, 1996, R&D/CRLD/AN/bd/9516706, [M-163236-01-1]
Cotton seed	Ethephon	0.1 0.5	1 1	115 75	75 115	– –	HVA 12/89	Muller, 1996, R&D/CRLD/AN/bd/9516706, [M-163236-01-1]
Cotton seed	Ethephon	0.1 0.5 3	1 1 1	98 85 73	98 85 73	– – –	HVA 12/89	Muller, 1996, R&D/CRLD/AN/vg/9516705, [M-163240-01-1]
Walnut nutmeat	Ethephon	0.2	11	67–112	80	17.0	SOP 90069	Nygren, 1991, 89-REN-WA-S, [M-187529-01-1]
Cotton seed	Ethephon	0.05 0.2 2	6 6 6	63–138 77–98 74–87	93 90 80	28.5 8.4 6.5	SOP 90075	Eckert, 1992, RP-01-89J, [M-187525-01-1]
Plant commodities—LC/MS/MS method								

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Apple	Ethephon	0.05 0.5	5 5	92–108 86–93	99 90	6.4 3.1	V5229/01	Kerkdijk, 1994, V5229/01, [M-226290-01-1]
Cherry	Ethephon	0.05 0.5	5 5	92–98 92–102	95 97	2.5 4.3	V5229/01	Kerkdijk, 1994, V5229/01, [M-226290-01-1]
Sweet peppers	Ethephon	0.05 0.5	5 5	103–109 75–91	107 88	2.5 8.6	V5229/01	Kerkdijk, 1994, V5229/01, [M-226290-01-1]
Tomato	Ethephon m/z 143 → 107	0.05 0.5	5 5	98–103 99–103	101 102	1.9 1.8	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Tomato	Ethephon m/z 145 → 107	0.05 0.5	5 5	98–103 97–101	100 99	1.9 1.5	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Wheat grain (conventional extraction)	Ethephon m/z 143 → 107	0.05 0.5	5 5	86–94 90–96	89 92	3.8 2.5	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Wheat grain (conventional extraction)	Ethephon m/z 145 → 107	0.05 0.5	5 5	85–90 84–91	87 86	2.4 3.6	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Wheat grain (microwave extraction)	Ethephon m/z 143 → 107	0.05 0.5	5 5	93–99 92–100	96 95	2.5 3.1	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Wheat grain (microwave extraction)	Ethephon m/z 145 → 107	0.05 0.5	5 5	94–99 92–100	97 95	2.1 3.8	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Orange	Ethephon m/z 143 → 107	0.05 0.5	5 5	95–103 96–107	98 101	3.2 4.4	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Orange	Ethephon m/z 145 → 107	0.05 0.5	5 5	96–99 95–104	97 99	1.3 3.8	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Olive	Ethephon m/z 143 → 107	0.05 0.5	5 5	95–104 98–101	101 100	3.7 1.1	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Olive	Ethephon m/z 145 → 107	0.05 0.5	5 5	97–104 101–104	100 103	2.6 1.1	00902	Oel & Bardel, 2005, MR-128/04, [M-247578-01-1]
Tomato	Ethephon m/z 143 → 107	0.05 0.5	5 5	95–100 105–110	97 108	2.0 2.0	00902	Ballesteros, 2005, MR-029/05, [M-247677-01-1]
Wheat grain (conventional extraction)	Ethephon m/z 143 → 107	0.05 0.5	5 5	77–89 91–98	85 93	5.7 3.1	00902	Ballesteros, 2005, MR-029/05, [M-247677-01-1]
Olive	Ethephon m/z 143 → 107	0.05 0.5	5 5	98–99 95–102	98 99	0.5 2.9	00902	Ballesteros, 2005, MR-029/05, [M-247677-01-1]
Wheat green material	Ethephon	0.05 0.5	5 5	77–89 79–82	84 80	5.2 1.4	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Wheat straw	Ethephon	0.05 0.5	5 5	77–88 81–87	81 84	6.1 3.3	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Wheat grain	Ethephon	0.05 0.5	5 5	66, 70–77 65–69	71 67	4.5 3.4	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Wheat grain (microwave extraction)	Ethephon	0.05 0.5	5 5	77–86 76–83	82 79	5.7 2.4	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Barley green material	Ethephon	0.05 0.5	3 3	100–103 99–102	102 101	1.5 1.7	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Barley straw	Ethephon	0.05 0.5	3 3	70–75 76–77	72 76	3.7 0.8	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Barley grain (microwave extraction)	Ethephon	0.05 0.5	3 3	93–98 93–96	95 95	2.6 1.6	00918	Oel & Bardel, 2005, MR-173/04, [M-248933-01-1]
Olive	Ethephon	0.05 0.5	5 5	77–81 100–106	79 104	1.9 2.3	00918	Schulte, 2014, MR 13/083, [M-463954-01-1]
Olive oil	Ethephon	0.05 0.5	3 3	83–86 101–108	84 104	2.1 3.7	00918	Schulte, 2014, MR 13/083, [M-463954-01-1]
Olive	Ethephon	0.05 0.5	5 5	84–102 93–107	91 99	8.6 5.4	00903/E001	Schulte, 2014, MR 13/083, [M-463954-01-1]
Grape berry	Ethephon	0.05 0.5	3 3	93–98 94–97	96 96	2.6 1.8	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Grape juice	Ethephon	0.05 0.5	3 3	105–118 116–117	112 116	5.9 0.5	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Grape must	Ethephon	0.05 0.5	3 3	99–106 74–107	102 89	3.4 18.8	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Wine	Ethephon	0.05 0.5	3 3	95–104 104–105	100 105	4.5 0.6	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Grape pomace	Ethephon	0.05 0.5	3 3	74–81 84–86	77 85	4.5 1.4	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Apple fruit	Ethephon	0.05 0.5	3 3	105–109 102–110	107 106	2.0 3.8	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Apple juice	Ethephon	0.05 0.5	3 3	101–105 103–107	103 104	1.9 2.2	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Apple washing water	Ethephon	0.05 0.5	3 3	96–104 100–101	100 100	4.1 0.6	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Apple sauce	Ethephon	0.05 0.5	3 3	92–119 87–104	101 96	15.1 8.9	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Apple pomace	Ethephon	0.05 0.5	3 3	89–90 93–97	90 95	0.6 2.1	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Tomato fruit	Ethephon	0.05 0.5	3 3	98–105 101–103	102 12	3.5 1.0	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Tomato juice	Ethephon	0.05 0.5	3 3	98–104 101–108	101 105	3.0 3.4	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Tomato pomace	Ethephon	0.05 0.5	3 3	86–91 88–92	89 90	3.0 2.3	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Tomato puree	Ethephon	0.05 0.5	3 3	95–101 92–101	98 98	3.1 5.3	00903/E001	Oel & Bardel, 2005, MR-131/04, [M-254165-01-1]
Wheat grain	Ethephon	0.01 0.1	5 5	93–107 64, 93–98	100 89	5.2 15.8	01429	Schulte & Druskus, 2015, MR-14/100
Wheat straw	Ethephon	0.05 0.5	5 5	84–95 87–89	88 88	4.6 1.1	01429	Schulte & Druskus, 2015, MR-14/100
Wheat green material	Ethephon	0.05 0.5	5 5	98–109 87–104	102 95	4.2 7.5	01429	Schulte & Druskus, 2015, MR-14/100
Wheat grain	HEPA	0.01 0.1	5 5	88–98 76–103	94 96	4.4 11.7	01429	Schulte & Druskus, 2015, MR-14/100
Wheat straw	HEPA	0.05 0.5	5 5	85–98 86–95	91 90	5.4 4.1	01429	Schulte & Druskus, 2015, MR-14/100
What green material	HEPA	0.05 0.5	5 5	94–108 97–115	99 108	6.0 6.6	01429	Schulte & Druskus, 2015, MR-14/100

Analytical methods for animal matrices

Method: 18980A 9-REN-74-76 (Ethylene release method) (Leonard, 1993, EC-92-198, [M-187997-01-1])

Analyte:	Ethephon	GC-FID	
LOQ:	0.01 mg/kg in meat, milk and egg		
Description:	This is the same as method 11-94, with some minor modifications for analysing animal tissues. The sample is placed in a pressure bottle with a crown cap that has a provision for withdrawing a headspace sample with a syringe. Water and an aqueous tartaric acid-surfactant solution are added. The bottle is then capped, heated to 60–65 °C and periodically agitated to drive any endogenous ethylene from the sample. After one hour heating, the headspace gases are released, the sample shaken for 5 minutes and then incubated at 60–65 °C with periodic agitation for a further 30 minutes. After shaking for a further 5 minutes, the cap is removed and the bottle is flushed with a gentle stream of nitrogen to remove any released ethylene. The sample is allowed to cool to room temperature. Trisodium phosphate, sufficient to make the sample basic, is added. The bottle is immediately capped and heated for one hour at 60–65 °C with periodic agitation to convert any ethephon residues into ethylene. The ethylene accumulates in the headspace and is quantified by gas chromatography with flame ionisation detection.		

Method: 11-94 (Ethylene release method) (Nygren, 1994, 11-94, [M-188198-01-1])

Analyte:	Ethephon	GC-FID
LOQ:	0.002 mg/kg in milk and eggs, 0.01 mg/kg in tissues	
Description:	The sample is placed in a pressure bottle with a crown cap that has a provision for withdrawing a headspace sample with a syringe. Water and an aqueous tartaric acid-surfactant solution are added. The bottle is then capped, heated to 60–65 °C and periodically agitated to drive any endogenous ethylene from the sample. After one hour heating, the headspace gases are released, the sample shaken for 5 minutes and then incubated at 60–65 °C with periodic agitation for a further 30 minutes. After shaking for a further 5 minutes, the cap is removed and the bottle is flushed with a gentle stream of nitrogen to remove any released ethylene. The sample is allowed to cool to room temperature. Trisodium phosphate, sufficient to make the sample basic, is added. The bottle is immediately capped and heated for one hour at 60–65 °C with periodic agitation to convert any ethephon residues into ethylene. The ethylene accumulates in the headspace and is quantified by gas chromatography with flame ionisation detection. A radiovalidation performed using poultry liver containing incurred residues of [^{14}C]ethephon. The sample was analysed twice using the ethylene-release method. Both analyses indicated a residue level of 0.048 mg/kg. The same sample was analysed using a radiometric technique, which yielded an ethephon concentration of 0.041 mg/kg. The two values therefore are in good agreement, indicating that the ethylene-release method adequately determines the concentration of ethephon residues in animal tissues.	

Method: 00995 (LC-MS/MS method) (Bardel, 2006, MR-054/06 and Amendment 1, [M-274047-02-1])

Analyte:	Ethephon	LC-MS/MS	
LOQ:	0.01 mg/kg in milk, 0.05 mg/kg in meat (muscle), fat, kidney and egg		

Description:	Residues of ethephon are extracted from milk, fat, meat, and kidney by high speed blending with methanol/water/formic acid (90/10/0.1, v/v/v). Residue extraction from egg samples is performed according to a similar procedure, except that some cysteine hydrochloride is added to the extraction solvent. In all cases the extract is cleaned-up on a styrene divinyl benzene SPE column (Varian Bond Elut ENV), concentrated to dryness and reconstituted in water/methanol/formic acid (80/20/0.5, v/v/v). The reconstituted extract is analysed by liquid chromatography with tandem mass spectrometric detection (LC/MS/MS) using a triple-quadrupole apparatus that is operated in the negative electrospray mode. Ethephon is monitored by means of the MS/MS transitions m/z 143 → 107 (^{35}Cl isotope) and/or m/z 145 → 107 (^{37}Cl isotope). Satisfactory chromatographic separation is achieved on a C_{18} column with polar embedding (Synergi Fusion-RP 80Å, 150×4.6 mm, 4 µm). Elution is performed using water/methanol (74/26, v/v) acidified with 0.5% formic acid as the mobile phase.

Table 43 Method Validation

Matrix	Analyte	Fortification, mg/kg	n	Recovery (%)		% RSD	Method	Reference
				Range	Mean			
Animal commodities—ethylene release method								
Milk	Ethephon	0.002 0.004 0.01 0.02 0.04 0.1	1 1 6 1 4 4	88 96 92–104 115 97–102 98–100	88 96 99 115 99 100	– – 4.5 – 2.6 1.0	11-94	Wells-Knecht, 1996, 96E08334, [M-188195-01-1]
Bovine fat	Ethephon	0.01 0.4	1 1	68 72	68 72	– –	11-94	Wells-Knecht, 1996, 96E08334, [M-188195-01-1]
Bovine kidney	Ethephon	0.01 0.1 1 10 12	1 1 1 1 1	71 101 99 102 96	71 101 99 102 96	– – – – –	11-94	Wells-Knecht, 1996, 96E08334, [M-188195-01-1]
Bovine liver	Ethephon	0.01 0.4 2	1 1 1	113 99 102	113 99 102	– – –	11-94	Wells-Knecht, 1996, 96E08334, [M-188195-01-1]
Bovine muscle	Ethephon	0.01 0.4	1 1	94 101	94 101	– –	11-94	Wells-Knecht, 1996, 96E08334, [M-188195-01-1]
Eggs	Ethephon	0.002 0.004 0.005 0.01 0.02 0.1	3 3 1 4 3 3	90–102 93–102 96 100–105 99–102 98–101	95 98 96 102 101 100	6.4 4.7 – 2.3 1.7 1.7	11-94	Wells-Knecht, 1996, 96E08335, [M-188192-01-1]
Poultry liver	Ethephon	0.01 0.1 0.5	1 2 1	115 106–107 90	115 107 90	– – –	11-94	Wells-Knecht, 1996, 96E08335, [M-188192-01-1]
Poultry muscle	Ethephon	0.004 0.01 0.1	2 2 1	84–98 101–107 102	91 104 102	– – –	11-94	Wells-Knecht, 1996, 96E08335, [M-188192-01-1]
Poultry skin + fat	Ethephon	0.004 0.01 0.2	2 2 1	81–89 89–93 93	85 91 93	– – –	11-94	Wells-Knecht, 1996, 96E08335, [M-188192-01-1]
Milk	Ethephon	0.01 0.05 0.1	4 4 4	96–106 95–109 94–103	100 101 99	4.8 5.9 4.9	18980A 9-REN-74-76	Leonard, 1993, EC-92-198, [M-187997-01-1]
Egg	Ethephon	0.01 0.05 0.1	4 4 4	79–93 92–98 93–98	86 96 95	6.4 2.6 2.2	18980A 9-REN-74-76	Leonard, 1993, EC-92-198, [M-187997-01-1]
Meat	Ethephon	0.01 0.05 0.1	4 4 4	73–105 80–107 77–84	93 93 81	15.4 11.8 3.1	18980A 9-REN-74-76	Leonard, 1993, EC-92-198, [M-187997-01-1]
Egg	Ethephon m/z 143 → 107	0.05 0.5	5 5	68–74 95–107	72 101	3.5 4.4	00995	Cavaillé, 2007, MR-06/164, [M-283314-01-1]

Multi-residue Methods

DFG S 19

The applicability of multi-methods has been investigated (Fuchsbichler, 2000, HVA 24/00, [M-184660-01-1]). Multi-residue methods for products of plant origin typically involve extraction with acetone or ethyl acetate. Ethephon is known to be a very hydrophilic compound but it is also readily soluble in acetone and ethyl acetate (solubility > 600 g/L).

Wheat grain was chosen as crop material for the experimental assessment. The samples were fortified with ethephon at 2 or 10 mg/kg. Two variants of the German multi-residue method DFG S19 were investigated. Extraction was performed with acetone/water (2:1, v:v). The extract was cleaned-up by liquid/liquid partition. Depending on the variant of the method, this was done either with dichloromethane or with a mixture of cyclohexane and ethyl acetate. At this stage, the organic phase was dried with sodium sulphate and reacted with (trimethylsilyl) diazomethane in order to methylate any ethephon residues. The methylated extracts were analysed by gas chromatography with flame photometric detection (GC/FPD). There was no ethephon dimethyl ester, indicating that the extraction procedure was not appropriate to ethephon. The same result was found when blank reagents were fortified at the beginning of the procedure. Therefore, the problem was not due to any effect of the crop matrix. In order to demonstrate the accuracy of the derivatisation reaction, control samples and reagent blanks were fortified with ethephon after the extraction step. In this case the concentrations determined by GC/FPD were between 84% and 105% of the theoretical value, therefore validating the derivatisation procedure.

An alternate extraction procedure was investigated similarly. The samples were homogenised with ethyl acetate and sodium sulphate. The extracts were filtered and reacted with (trimethylsilyl) diazomethane. The amounts of ethephon dimethyl ester determined by GC/FPD were less than 30% of the theoretical value. This was a better result than with the DFG S19 extraction procedure, but still insufficient to develop a reliable method.

The study shows that instead of using diazomethane it is possible to perform the methylation with (dimethylsilyl) diazomethane, which is a less hazardous reagent. However, acetone and ethyl acetate are not suitable extraction solvents for ethephon. The extraction procedures used in the classical multi-residue enforcement methods therefore do not work for ethephon.

Storage Stability under Frozen Conditions

Plant commodities

The stability of ethephon residues in commodities has been investigated in high water content commodities (apples, cherries, melons, peppers and tomatoes), high acid content commodities (grapes, blackberries and pineapples), high starch content commodity (wheat) and high oil content commodities (walnuts and cotton) stored under frozen conditions. In all studies on raw agriculture commodities except on wheat and cotton seed, 20 g homogenized control samples were fortified with ethephon. In studies on wheat and cotton seed, 10 g, 5 g and 10 or 5 g of homogenized wheat grain, wheat straw and cotton seed, respectively, were fortified. In studies on apple juice and cottonseed oil, 25 g and 10 g of control samples were fortified.

The stability of ethephon residues has also been investigated in freeze-dried commodities stored at room temperature (apples, cherries, grapes, blackberries, pineapples, melons, peppers, tomatoes and walnuts) because freeze-drying is part of analytical methods. All stored samples were spiked prior to freeze-drying but, for procedural recovery, samples were spiked after freeze-drying.

Conditions and results of storage stability studies are summarized in Table 44 (under frozen conditions) and Table 45 (freeze-dried samples at room temperature). Percent of ethephon remaining was not corrected for procedural recoveries.

Plant matrices

Table 44 Storage stability ethephon in various matrices under frozen conditions

Fortification, mg/kg	Storage temp., °C	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
Apple						
0.5	–20	0	91, 85	89	SOP 90070	Eckert, 1992, RP-01-89C, [M-187515-01-1]
		1	92, 87	90		
		2	102, 100	99		
		4	101, 92	102		
		6	81, 90	94		
		9	67, 70	79		
		12	70, 69	89		
		18	93, 90	102		
		24	83, 84	88		
Sweet cherry						
1.0	–15	0	91, 95	84	SOP 90070	Nygren, 1992,89-REN-CH-S, [M-187505-01-1]
		1	112, 110	116		
		2	105, 91	112		
		6	91, 93	103		
		9	93, 70	77		
		12	86, 85	99		
		18	97, 80	104		
		24	102, 90	98		
Grape						
0.5	–20	0	78, 91	89	SOP 90070	Eckert, 1992, RP-01-89D, [M-187544-01-1]
		1	70, 78	83		
		2	84, 81	84		
		4	110, 104	93		
		6	99, 76	93		
		9	78, 93	103		
		12	125, 110	112		
		18	73, 75	83		
		24	88, 71	83		
Blackberry						
1.0	–20	0	102, 82	88	SOP 90070	Eckert, 1992, RP-01-89B, [M-187511-01-1]
		1	98, 99	89		
		2	95, 96	91		
		4	100, 108	93		
		6	95, 87	91		
		9	75, 73	86		
		12	114, 92	91		
		18	75, 110	91		
		24	83, 96	95		
Pineapple fruit						
0.5	–20	0	86, 86	83	SOP 90070	Eckert, 1992, RP-01-89E, [M-187540-01-1]
		1	88, 93	79		
		2	95, 95	93		
		4	97, 117	94		
		6	108, 106	98		
		9	90, 90	102		
		12	87, 89	99		
		18	117, 112	110		
		24	77, 98	86		
Pineapple forage						
0.5	–20	0	82, 79	76	SOP 90070	Eckert, 1992, RP-01-89F, [M-187538-01-1]
		1	95, 85	79		

Fortification, mg/kg	Storage temp., °C	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
		2	91, 86	90		
		4	106, 82	100		
		6	81, 72	92		
		9	85, 88	85		
		12	82, 89	89		
		18	84, 95	93		
		24	85, 98	83		
Cantaloup						
0.5	–20	0	79, 89	104	SOP 90070	Eckert, 1993, RP-01-89G, [M-187507-01-1]
		1	79, 90	76		
		2	96, 86	83		
		4	96, 96	105		
		6	107, 99	99		
		9	102, 92	90		
		12	84, 84	93		
		18	75, 80	80		
		24	82, 82	77		
		30	113, 111	105		
		36	98, 98	104		
Sweet pepper						
1.0	–15	0	120, 110	130	SOP 90070	Nygren, 1992, 89-REN-P-S, [M-187542-01-1]
		2	120, 110	110		
		4	100, 100	98		
		6	100, 87	110		
		9	92, 78	100		
		12	88, 96	85		
		18	110, 120	110		
		24	120, 130	130		
Tomato						
0.5	–20	0	96, 84	91	SOP 90070	Eckert, 1992, RP-01-89A, [M-187533-01-1]
		1	76, 78	93		
		2	118, 84	102		
		4	84, 100	81		
		6	74, 72	75		
		9	61, 82	71		
		12	104, 89	104		
		18	97, 75	78		
		24	99, 107	97		
Wheat grain						
0.5	–20	0	86, 89	75	SOP 90074	Eckert, 1992, RP-01-89I, [M-187521-01-1]
		1	88, 74	90		
		2	118, 98	98		
		4	72, 76	88		
		6	104, 111	111		
		9	100, 78	89		
		12	94, 79	90		
		18	103, 82	89		
		24	90, 79	92		
Wheat straw						
1.0	–20	0	98, 94	85	SOP 90074	Eckert, 1992, RP-01-89H, [M-187519-01-1]
		1	92, 83	80		
		2	88, 75	82		
		4	86, 66	82		
		6	109, 121	93		
		9	87, 87	76		
		12	72, 66	78		
		18	101, 76	91		
		24	90, 108	90		
Walnut nutmeat (English walnut) [e]						
0.2	< –15	0	31, 40	112	SOP 90069	Nygren, 1991, 89-REN-

Fortification, mg/kg	Storage temp., °C	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
		0 [a]	107, 84 126, 87	72 70		WA-S, [M-187529-01-1]
		1	84, 93	81		
		3	108, 105	64		
		5	69, 74	87		
		5 [b]	66, 83	89		
Cottonseed (10 g homogenized sample) [e]						
1.0	–20	0	76, 86	93	SOP 90075	Eckert, 1992, RP-01-89J, [M-187525-01-1]
		1	89, 98	103		
		2	84, 81	102		
		4	98, 79	108		
		6	89, 72	108		
		9	66, 72	92		
		12	77, 83	79		
		18	57, 65 (46, 65) [c]	94 (77) [c]		
		24 (25) [d]	76, 92 (90, 96) [d]	74 (91) [d]		
Cottonseed (5 g homogenized sample), stored at room temperature in the dark						
0.5	Room temp.	0 day	91, 91, 100, 97, 97 (mean: 95)	96, 91 (mean: 94)	00918	Schmeer and Reineke, 2010, MR-09/053, [M-384885-01-1]
	In the dark	28 days	16, 6, 10 (mean: 11)	100, 94 (mean: 97)		
		35 days	9, 5, 9 (mean: 7.7)	93, 93 (mean: 93)		
Apple juice						
0.20	–20	0	102, 102	103	EC-92-228	Nygren, 1995, EC-94-253, [M-188009-01-1]
		1	99, 100	105		
		2	103, 100	102		
		3	104, 105	104		
		6	104, 104	101		
		9	108, 97	100		
		12	106, 105	100.5		
Cottonseed oil						
0.20	–20	0	94, 95	91	EC-92-228	Nygren, 1995, EC-94-253, [M-188009-01-1]
		1	92, 95	96		
		2	92, 90	93		
		3	80, 82	90		
		6	88, 89	90		
		9	104, 107	102.5		
		12	96.5, 97	94		

[a] Additional set of “Day 0” samples

[b] Additional set of “Day 5” samples

[c] For reanalysis of the samples after 18 months in parentheses

[d] For reanalysis of the samples after 25 months in parentheses

[e] No indication in the study report about whether data were adjusted for procedural recovery

Table 45 Storage stability of ethephon in various freeze-dried matrices at room temperature

Fortification, mg/kg	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
Apple					
0.5	0	91, 85	89	SOP 90070	Eckert, 1992, RP-01-89C, [M-187515-01-1]
	1	83, 75	81		
	2	97, 101	95		
	4	86, 112	98		
	6	96, 100	93		
	9	77, 83	86		

Fortification, mg/kg	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
	12	87, 85	87		
	18	95, 89	95		
	24	77, 89	87		
Sweet cherry					
1.0	0	91, 95	84	SOP 90070	Nygren, 1992,89-REN-CH-S, [M-187505-01-1]
	1	111, 97	108		
	2	105, 95	80		
	6	94, 110	105		
	9	104, 89	104		
	12	89, 89	82		
	18	81, 70	96		
	24	83, 85	101		
Grape					
0.5	0	78, 91	89	SOP 90070	Eckert, 1992, RP-01-89D, [M-187544-01-1]
	1	71, 65	77		
	2	81, 87	75		
	4	121, 117	110		
	6	74, 80	82		
	9	64, 70	78		
	12	86, 108	100		
	18	88, 76	98		
	24	79, 92	82		
Blackberry					
1.0	0	102, 82	88	SOP 90070	Eckert, 1992, RP-01-89B, [M-187511-01-1]
	1	82, 86	93		
	2	98, 105	101		
	4	108, 71	104		
	6	101, 90	92		
	9	85, 76	85		
	12	97, 99	87		
	18	99, 64	95		
	24	71, 68	82		
Pineapple fruit					
1.0	0	86, 86	83	SOP 90070	Eckert, 1992, RP-01-89E, [M-187540-01-1]
	1	89, 86	73		
	2	100, 93	89		
	4	90, 90	90		
	6	92, 102	82		
	9	103, 91	89		
	12	98, 94	104		
	18	106, 86	102		
	24	75, 84	87		
Pineapple forage					
0.5	0	82, 79	76	SOP 90070	Eckert, 1992, RP-01-89F, [M-187538-01-1]
	1	73, 86	74		
	2	92, 99	85		
	4	92, 90	90		
	6	87, 88	85		
	9	76, 74	90		
	12	49, 70 (51, 53)	81 (85) [a]		
	18	77, 77	96		
	24	52, 59 (56, 63)	89 (83) [b]		
Cantaloup					
0.5	0	79, 89	104	SOP 90070	Eckert, 1993, RP-01-89G, [M-187507-01-1]
	1	80,76	83		
	2	76, 64	73		
	4	102, 93	88		
	6	59, 37 (47, 38) [c]	89 (106) [c]		
	18	12, 12	81		

Fortification, mg/kg	Storage time, month	Ethephon, % Remaining	Procedural recovery, %	Analytical method	Reference
Sweet pepper					
1.0	0	120, 110	130	SOP 90070	Nygren, 1992, 89-REN-P-S, [M-187542-01-1]
	2	110, 100	130		
	4	92, 93	82		
	6	62, 83 (97, 85) [c]	120 (110) [c]		
	9	47, 57 (70, 60) [c]	96 (98) [c]		
	12	42, 46	87		
	18	37, 36	130		
Tomato					
0.5	0	96, 84	91	SOP 90070	Eckert, 1992, RP-01-89A, [M-187533-01-1]
	1	90, 77	88		
	2	103, 100	83		
	4	82, 87	103		
	6	61, 70	71		
	9	61, 78	80		
	12	97, 97	97		
	18	68, 58	81		
	24	102, 84	98		
Walnut nutmeat (English walnut) [f]					
0.2	0	31, 40	112	SOP 90069	Nygren, 1991, 89-REN-WA-S, [M-187529-01-1]
	0 [d]	107, 84 126, 87	72 70		
	1	91, 74	88		
	5	64, 51	67		
	5 [e]	42, 77	79		
	6	73, 83	73		

[a] Value in parentheses: for reanalysis of the samples after 12 months

[b] Value in parentheses: for reanalysis of the samples after 24 months

[c] Value in parentheses: for reanalysis of the samples

[d] Additional set of “day 0” samples

[e] Additional set of “day 5” samples

[f] No indication in the study report about whether data were adjusted for procedural recovery.

1.

The results showed that ethephon was stable for at least the following periods under frozen conditions:

Table 46 Summary of storage stability of ethephon in various plant matrices under frozen conditions

Matrix	Storage temp., °C	Stable period (at least)	Note
Apple	–20 (–18 to –26)	24 months	Longest period tested
Sweet cherry	–15	24 months	Longest period tested
Grape	–20 (–18 to –26)	24 months	Longest period tested
Blackberry	–20 (–18 to –26)	24 months	Longest period tested
Pineapple fruit	–20 (–18 to –26)	24 months	Longest period tested
Pineapple forage	–20 (–18 to –26)	24 months	Longest period tested
Cantaloupe	–20 (–18 to –26)	36 months	Longest period tested
Sweet pepper	–15	24 months	Longest period tested
Tomato	–20 (–18 to –26)	24 months	Longest period tested
Wheat grain	–20 (–18 to –26)	24 months	Longest period tested
Wheat straw	–20 (–18 to –26)	24 months	Longest period tested
Walnut	–15	3 months	Not conclusive due to analytical uncertainty
Cottonseed	–20 (–18 to –26)	25 months	Longest period tested (some uncertainty)
Apple juice	–20	12 months	Longest period tested
Cottonseed oil	–20	12 months	Longest period tested

Ethephon was shown to be stable during storage at room temperature after freeze-drying for the longest period tested (24 months) in apples, sweet cherries, grapes, blackberries, pineapple fruit, and tomato samples.

However, ethephon was stable up to only 9 months in pineapple forage, 4 months in cantaloupe, and 6 months in sweet pepper samples during storage at room temperature after freeze-drying. Due to significant analytical uncertainty, it was also not possible to determine storage stability of freeze-dried walnut samples at room temperature.

Animal Commodities

A storage stability study was conducted on meat, milk and eggs in 1992–1993 (Leonard, 1993, EC-92-198, [M-187997-01-1]).

Bovine meat was trimmed, and ground to homogeneity. Eggs were removed from their shells and beaten to a homogenous mixture. Milk was used as received. The prepared control samples (40 g) were fortified with ethephon at a concentration of 0.10 mg/kg and then stored frozen at about –20 °C. Samples were analysed using the ethylene release method 18980A 9-REN-74-76

The results showed that ethephon was stable when stored frozen (actual temperature: –10 to –23 °C) for the longest periods tested: in milk for 4 months, in meat 12 months and in eggs 15 months.

Table 47 Storage stability of ethephon in animal matrices at a fortification level of 0.1 mg/kg and at -20 ºC

Time, month	Ethephon, % Remaining	Procedural recovery, %
Bovine milk		
0	95, 99	97
1	99, 98	100
2	98, 89	93
3	93, 94	99
4	96, 97	96
Bovine meat		
0	93, 106	97
1	91, 93	97
2	96, 91	99
3	96, 94	94
4	97, 86	97
6	95, 94	95
9	92, 92	95
12	91, 89	85
Poultry eggs		
0	95, 90	93
1	96, 102	95
2	101, 88	99
3	94, 93	91
4	97, 96	102
6	96, 92	88
9	92, 89	92
12	94, 90	94
15	93, 92	94

USE PATTERN

Ethephon is registered in many countries for use on cereals (wheat, barley, rye and rice) to increase resistance to lodging through straw shortening and strengthening; fruits and vegetables to promote

fruit maturity (early and uniform ripening and colouring of mature fruits); and on cotton to promote uniform boll opening and enhance defoliation.

Ethephon is mainly formulated as a soluble concentrate (SL). Combinations with chlormequat chloride are also used for cereals, and combinations with cyclanilide are used for cotton. Formulations are applied as foliar sprays by either ground or aerial equipment, except for applications to figs in Brazil where ethephon is applied directly to fruits using brushes or other equipment for even distribution.

For the purposes of estimating maximum residue levels, only the registered uses in countries relevant for the submitted supervised trials are recorded in Table 48.

For cereals, where there is a long interval between application and harvest, PHIs are often not given on the label. The PHI is described by the vegetative growth between applications; the labels give the growth stage at application. Therefore for cereals in the table below, both the PHI (where available) and the application timing (growth stage at application) are given.

Table 48 Registered Uses of Ethephon

Crop	Country	Form. Ethephon conc Type	Application				PHI (days)/Application timing Notes
			Max rate, g ai/ha	Max. Spray conc., g ai/hL	Water volume (L/ha)	No. (max g ai/ha/ season)	
Pome fruits							
Apple	Austria	660 g/L SL	198		500 L/ha/m crown height	2 (396 g ai/ha)	91/ BBCH 59–31
Apple (cider varieties)	France	120 g/L SL		48		1–2	10/ Pre-bloom or post-bloom
Apple (other varieties)	France	120 g/L SL		36		1–2	10/ 15–20 days before expected harvest date
Apple	Italy	480 g/L SL		48	1500–2000	– (768 g ai/ha)	14/ 14–20 days before harvest
Stone fruits							
Cherry	Austria	660 g/L SL	357		500 L/ha/m crown height	1	7/ BBCH 79–89
Cherry	France	120 g/L SL		36		1	10
Cherry, sour	Netherlands	480 g/L SL	360			1	7/ 7–10 days before harvest
Berries and other small fruits							
Grape	France	180 g/L SL	450		100–200	1	28/ 15–30% berries ripe
Assorted tropical fruits and sub-tropical fruits—edible peel							
Fig	Brazil	720 g/L SL		936		1	5 fruit in bloom stage with pink ostioles. Apply directly to fruit using brushes with sponge tip or any other equipment that evenly distribute the mixture over the fruit.
Olive for oil and table olive	Italy	480 g/L SL	1st 450 2nd 600	1st 36 2nd 48	1250	2	11 (1st appl. 18 days before harvest)
Assorted tropical fruits and sub-tropical fruits—inedible peel							

Crop	Country	Form. Ethephon conc Type	Application				PHI (days)/Application timing Notes
			Max rate, g ai/ha	Max. Spray conc., g ai/hL	Water volume (L/ha)	No. (max g ai/ha/ season)	
Pineapple	Belize, El Salvador, Honduras, Domenican Rep.	480 g/L SL	1920		2000–3000	1 or 2 (1920 g ai/ha)	7–14/ Apply 1–2 weeks before first round of harvesting (common label)
Pineapple	Brazil	720 g/L SL	936 (Dec, Jan, Feb)		200–500 30 (aerial)	1	14
Pineapple	Costa Rica, Panama, Guatemala	720 g/L SL	936		2000–3000	1	7–14 (common label)
Pineapple	Costa Rica, Panama, Guatemala	720 g/L SL	1152		1000	1 or 2 (1152 g ai/ha)	7–14/ Apply 1–2 weeks before first round of harvesting (common label)
Pineapple	Costa Rica	480 g/L SL	1200		2800–3800	2 (2400 g ai/ha)	1
Pineapple	Costa Rica	480 g/L SL	1200		2800–3800	2 (2400 g ai/ha)	1
Pineapple	Costa Rica	480 g/L SL	1200		2000–3000	2 (1920 g ai/ha)	1
Pineapple	Kenya	480 g/L SL	480		3000	1	–/ Apply when plants are ready to be forced to flower
Pineapple	Kenya	480 g/L SL	1920		500–1000	1	7
Fruiting vegetables, other than cucurbits							
Tomato (except cherry tomato)	Austria	660 g/L SL	594		1200	1	7/ BBCH 81–85
Tomato	Bolivia	240 g/L SL	1920		100–400	1	21
Tomato	Canada	240 g/L SL	1536		30–500	1	14–21/ Apply when 5–30% of fruits partly red or red
Tomato (for fresh consumption)	France	120 g/L SL		192		1	7/ Apply after harvest of first fruits, when max fruits on 1st to 3rd trusses. 10–15 days before last harvest
Tomato (for processing)	France	120 g/L SL	1680		800–1000	1	7/ Apply when 20–25% of fruits are red
Tomato (for fresh consumption)	Italy	480 g/L SL		120		1	7/ Apply when 40–60% of fruits are ripe and remaining fruits are at mature green stage. Can be divided into two applications
Tomato (for processing)	Italy	480 g/L SL	1920		1000 (for determined variety)	2 (1920 g ai/ha)	
Tomato	Netherlands	480 g/L SL		48		1	–/ senescent crops
Cereal grains							
Barley, winter	Austria	660 g/L SL	462		100–300	1	– / BBCH 32–49
Barley, spring	Austria	660 g/L SL	330		100–300	1	– / BBCH 37–51

Crop	Country	Form. Ethephon conc Type	Application				PHI (days)/Application timing Notes
			Max rate, g ai/ha	Max. Spray conc., g ai/hL	Water volume (L/ha)	No. (max g ai/ha/ season)	
Barley, winter	Belgium	480 g/L SL	600		200–400	1	– / BBCH 37–39
Barley, spring	Belgium	480 g/L SL	384		200–400	1	– / BBCH 37–39
Barley, spring	France	480 g/L SL	360		100–200	1	56 / BBCH 32–39
Barley, winter	France	480 g/L SL	480		100–200	1	56 / BBCH 32–39
Barley, spring	France	150 g/L SL	225			1	– / BBCH 31–37 (+ chlormequat-chloride 300 g/L)
Barley, winter	France	150 g/L SL	375			1	– / BBCH 31–39 (+ chlormequat-chloride 300 g/L)
Barley, winter	Germany	660 g/L SL	462		100–300	1	– / BBCH 32–49
Barley, spring	Germany	660 g/L SL	330		100–300	1	– / BBCH 37–49
Barley, winter	Poland	480 g/L SL	720		150–300	1	– / BBCH 32–39
Barley, spring	Poland	480 g/L SL	360		150–300	1	– / BBCH 32–49
Barley, winter	UK	480 g/L SL	480		100–400	– (480 g ai/ha)	– / BBCH 32–49
Barley, spring	UK	480 g/L SL	240		100–400	– (240 g ai/ha)	– / BBCH 32–49
Rye, winter	Austria	660 g/L SL	726		100–300	1	– / BBCH 37–49
Rye	Belgium	480 g/L SL	720		200–400	1	– / BBCH 39–45
Rye, winter	Germany	660 g/L SL	726		100–300	1	– / BBCH 37–49
Rye, winter	UK	480 g/L SL	480		100–400	– (480 g ai/ha)	– BBCH 37–49
Triticale, winter	Austria	660 g/L SL	495		100–300	1	– / BBCH 37–39
Triticale	Belgium	480 g/L SL	600		200–400	1	– / BBCH 37–45
Triticale	France	480 g/L SL	480		100–200	1	70 / BBCH 32–39
Triticale	France	150 g/L SL (+ chlormequat-chloride 300 g/L)	375			1	– / BBCH 31–37
Triticale, winter	Germany	660 g/L SL	495		100–300	1	– / BBCH 37–49
Triticale	Poland	480 g/L SL	480		150–300	1	– / BBCH 32–37
Triticale, winter	UK	480 g/L SL	480		100–400	– (480 g ai/ha)	– / BBCH 37–47
Wheat	Austria	660 g/L SL	462		100–300	1	– / BBCH 37–51
Wheat, winter	Belgium	480 g/L SL	600		200–400	1	– / BBCH 37–45
Wheat, winter	Canada	240 g/L SL	600		30–300	1	35 / BBCH 37–49
Wheat, spring	Canada	240 g/L SL	360		30–300	1	35 / BBCH 37–49

Crop	Country	Form. Ethephon conc Type	Application				PHI (days)/Application timing Notes
			Max rate, g ai/ha	Max. Spray conc., g ai/hL	Water volume (L/ha)	No. (max g ai/ha/ season)	
Wheat, hard, winter	France	480 g/L SL	480		100–200	1	70 / BBCH 39
Wheat, soft, winter	France	480 g/L SL	288		100–200	1	56 / BBCH 39
Wheat, hard, winter	France	150 g/L SL	375			1	– / BBCH 31–37 (+ chlormequat-chloride 300 g/L)
Wheat, soft, winter	France	150 g/L SL	300			1	– / BBCH 31–37 (+ chlormequat-chloride 300 g/L)
Wheat	Germany	660 g/L SL	462		100–300	1	– / BBCH 37–51
Wheat, winter Wheat, spring	Poland	480 g/L SL	360		150–300	1	– / BBCH 31–37
Wheat, winter	UK	480 g/L SL	360		100–400	– (360 g ai/ha)	– / BBCH 37–47
Oilseeds							
Cotton	Greece	480 g/L SL	1440		500–600	1	7/ BBCH 82–84
Cotton	Brazil	480 g/L SC	1200		200–500	1	7/ Apply at 90% boll maturity (+ cyclanilide 60 g/L)
Cotton	USA	720 g/L SC	2240		28–47 aerial 94–234 ground	1	7 (+ cyclanilide 45 g/L)
Cotton	USA	720 g/L SL	2240		19–94	1	7

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised trials have been conducted on the following crops: apples, cherries, grapes, figs, olives, pineapples, tomatoes, cereal grains (wheat, barley and rye) and cotton. The results of these supervised trials are summarized in the following tables:

Crop Group	Commodity	Country/Region, year of trials	Table No.
Pome fruit	Apple	Europe, 2000, 2002, 2006, 2007	49
Stone fruit	Cherries	Europe, 2000, 2002, 2009	50
Berries and other small fruits	Grapes	Europe, 1995, 2006, 2009	51
Assorted tropical and sub-tropical fruits—edible peel	Fig	Brazil, 2004, 2005	52
	Olive	Europe, 2007, 2008	53
Assorted tropical and sub-tropical fruits—inedible peel	Pineapple	Brazil, 1994, 1997, 2005 Costa Rica, 1998 Côte d'Ivoire, 1997, 1999 USA, 1989	54
Fruiting vegetables, other than cucurbits	Tomatoes	Europe, 1999, 2000, 2001, 2004 USA, 1989, 1990, 1991, 2005	55

Crop Group	Commodity	Country/Region, year of trials	Table No.
Cereal grains	Barley	Europe, 2000, 2001, 2004, 2006, 2007, 2008	56
			57
	Rye	Europe, 2013, 2014	58
	Wheat	Europe, 2006, 2007	59
		Europe, 2000, 2001, 2004, 2006, 2007	60
		Europe, 2013, 2014	61
		USA, 1981, 1989	
Oilseeds	Cotton	Europe, 1993, 1994, 1995, 2008	62
		USA, 1989, 1993, 1994	
		Brazil, 1996, 2006	
Primary animal feed	Barley	(See above)	63, 64
	Rye		65
	Wheat		66, 67, 68

In addition to the description and details of the field trials and analytical methods, each study report includes procedural recoveries and in some cases a summary of the method validation.

In the trials where multiple analyses are conducted on a single sample, the mean value is reported. Where multiple samples were taken from a single plot, the mean residue value is reported. Where results from separate plots with distinguishing characteristics such as different formulations, varieties or treatment schedules were reported, results are listed for each plot.

Results have not been corrected for concurrent method recoveries. Residues and application rates have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from the trials conducted according to the maximum GAP were used for the estimation of maximum residue levels. Those results included in the tables are underlined. Where a higher residue value was obtained at a later PHI, the higher value has been used.

Apple

A total of eighteen supervised trials were conducted on apples in France, Germany, the UK, Italy, Spain, Portugal and Greece. A 480 g/L SL formulation was applied as a foliar spray at BBCH 78–89 at a rate of 0.35–0.42 kg ai/ha. In studies 00-551 and 00-550, residues of ethephon were determined using method HVA SOP 10071. In study 02R792, residues of ethephon were determined using method V5229/01. In studies RA-2514/06 and RA-2576/07, residues of ethephon were determined using method 00903, supplement E001. The maximum period of storage of frozen samples was 406 days at < –18 ºC.

Table 49 Ethephon residues in apples resulting from supervised trials in Europe

APPLE Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, France	120 g/L SL		0.036		1	10		
GAP, Italy	480 g/L SL		0.048	1500–2000	1	14		
00551AM1 Saulty, France, 2000 (Canada Grise)	480 g/L SL	0.35	0.035	1000	1	10	0.40	Ballesteros, 2002, R&D/CRLD/AN/0215010 (M-209123-01-1)

APPLE Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
00551RS1 Damard, France, 2000 (Idared)	480 g/L SL	0.35	0.035	1000	1	11	0.27	Ballesteros, 2002, R&D/CRLD/AN/0215010 (M-209123-01-1)
00550RN1 Bellevue, France, 2000 (Judeline)	480 g/L SL	0.36	0.035	1029	1	0 3 7 10	0.62 0.54 0.62 0.26	Ballesteros, 2002, R&D/CRLD/AN/0215012 (M-210409-01-1)
00550RS1 Monthurel, France, 2000 (Judeline)	480 g/L SL	0.42	0.035	1201	1	0 3 7 10	0.39 0.15 0.22 0.075	Ballesteros, 2002, R&D/CRLD/AN/0215012 (M-210409-01-1)
02R792-1 Soucelles, France, 2002 (Golden Delicious)	480 g/L SL	0.36	0.072	500	1	0 3 7 10 14 21	0.47 0.84 0.68 0.31 0.40 0.28	Sonder, 2004, 02 R 792 (M-220915-01-1)
02R792-2 Cheille, France, 2002 (Gala)	480 g/L SL	0.36	0.067	550	1	0 3 7 10 14 21	0.29 0.30 0.34 0.13 0.13 0.12	Sonder, 2004, 02 R 792 (M-220915-01-1)
02R792-3 Geisenheim, Germany, 2002 (Jonagold)	480 g/L SL	0.36	0.045	800	1	0 3 7 10 14 21	0.13 0.19 0.20 0.14 0.11 0.14	Sonder, 2004, 02 R 792 (M-220915-01-1)
02R792-4 Wurzen-Roitzsch, Germany, 2002 (Rubin)	480 g/L SL	0.36	0.036	1000	1	0 3 7 10 14 21	0.11 0.11 0.15 0.059 0.051 < 0.05	Sonder, 2004, 02 R 792 (M-220915-01-1)
02R792-5 Royston, UK, 2002 (Bramley)	480 g/L SL	0.36	0.072	500	1	0 3 7 10 14 22	0.18 0.13 < 0.05 0.081 < 0.05 < 0.05	Sonder, 2004, 02 R 792 (M-220915-01-1)
R 2006 0116/6 Pernes les Fontaines, France, 2006 (Galaxy)	480 g/L SL	0.36	0.036	1000	1	0 7 10 14 21	0.25 0.17 < 0.05 < 0.05 < 0.05	Billian, 2007, RA-2514/06 (M-292470-01-1)
R 2006 0245/6 Bologna, Italy, 2006 (Golden)	480 g/L SL	0.36	0.036	1000	1	0 7 10 14 21	0.17 0.21 0.15 0.12 0.08	Billian, 2007, RA-2514/06 (M-292470-01-1)
R 2006 0246/4 Torrelavit, Spain, 2006 (Golden)	480 g/L SL	0.39	0.045	856	1	0 7 10 14 21	0.48 0.64 0.49 0.31 0.09	Billian, 2007, RA-2514/06 (M-292470-01-1)

APPLE Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
R 2006 0247/2 Peral-Cadaval, Portugal, 2006 (Fuji)	480 g/L SL	0.36	0.045	800	1	0 7 10 14 21	0.41 0.20 0.07 0.09 0.06	Billian, 2007, RA-2514/06 (M-292470-01-1)
R 2006 0248/0 Tripotamos, Greece, 2006 (Jonagold Red)	480 g/L SL	0.36	0.048	750	1	0 7 10 14 21	0.14 0.16 0.13 0.15 0.09	Billian, 2007, RA-2514/06 (M-292470-01-1)
R 2007 0176/4 Eyragues, France, 2007 (Brock field)	480 g/L SL	0.36	0.036	1000	1	0 7 10 14 21	0.18 0.25 0.24 0.18 0.16	Billian, Erler & Wolters, 2008, RA-2576/07 (M-311032-01-1)
R 2007 0188/8 Zevio, Italy, 2007 (Golden Rainders)	480 g/L SL	0.36	0.036	1000	1	0 7 10 14 21	0.19 0.08 0.07 < 0.05 < 0.05	Billian, Erler & Wolters, 2008, RA-2576/07 (M-311032-01-1)
R 2007 0189/6 Caldes de Malavella-Girona, Spain, 2007 (Golden Smoothy)	480 g/L SL	0.36	0.036	1000	1	0 7 9 14 21	0.19 0.25 0.15 0.14 0.07	Billian, Erler & Wolters, 2008, RA-2576/07 (M-311032-01-1)
R 2007 0191/8 Tripotamos, Greece, 2007 (Jonagold Red)	480 g/L SL	0.36	0.036	1000	1	0 7 10 14 21	0.09 0.07 0.08 0.05 < 0.05	Billian, Erler & Wolters, 2008, RA-2576/07 (M-311032-01-1)

Cherries

A total of fifteen supervised trials were conducted on cherries in France, Italy, Spain, Greece, Belgium and the Netherlands. A 480 g/L SL formulation was applied as a foliar spray to cherry trees at BBCH 76–89 at a rate of 0.35–0.36 kg ai/ha. In general, residues were determined in the whole fruit at earlier time points, and in the pitted fruit at the last time point, and the residue in the whole fruit was calculated. Whether whole fruit or pitted fruit was analysed is specified in the following Table. In the trials conducted in 2000, residues of ethephon were determined using method HVA SOP 10071. In the trials conducted in 2002, residues of ethephon were determined using method V5229/01. In the trials conducted in 2009, residues of ethephon were determined using method 00903, supplement E001. The maximum period of storage of frozen samples at < –18 ºC was 483 days.

Table 50 Ethephon residues in cherries resulting from supervised trials in Europe

CHERRY Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Austria	660 g/L SL	0.36		500 L/h a/m crown height	1	7			

CHERRY Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Netherlands	480 g/L SL	0.36			1	7			
00552AV1 Malaucene, France, 2000 (Napoleon)	480 g/L SL	0.35	0.036	962	1	0 3 7 11 11	Whole fruit Whole fruit Whole fruit Pitted fruit Whole fruit (calculated)	0.55 0.65 0.65 0.53 0.48	Ballesteros, 2002, R&D/CRLD/AN/mr/ 0115439 (M-208089-01-1)
00552TL1 Belcastel, France, 2000 (Stark)	480 g/L SL	0.35	0.035	1000	1	0 2 7 10 10	Whole fruit Whole fruit Whole fruit Pitted fruit Whole fruit (calculated)	0.54 0.66 1.40 0.64 0.59	Ballesteros, 2002, R&D/CRLD/AN/mr/ 0115439 (M-208089-01-1)
00553AV1 L'Isle s/la Sorge, France, 2000 (Napoleon)	480 g/L SL	0.35	0.035	1000	1	10 10	Pitted fruit Whole fruit (calculated)	0.17 0.15	Ballesteros, 2002, R&D/CRLD/AN/01154 58 (M-208961-01-1)
00553TL1 Adge, France, 2000 (Van)	480 g/L SL	0.35	0.035	1000	1	9 9	Pitted fruit Whole fruit (calculated)	2.9 2.7	Ballesteros, 2002, R&D/CRLD/AN/01154 58 (M-208961-01-1)
00554BKA1 Fougerolles, France, 2000 (Bechat thermo)	480 g/L SL	0.35	0.035	997	1	0 3 7 10 10	Whole fruit Whole fruit Whole fruit Pitted fruit Whole fruit (calculated)	0.65 1.2 0.91 0.50 0.42	Ballesteros, 2002, R&D/CRLD/AN/02150 09 (M-210351-01-1)
00554BKA2 Saxon Sion, France, 2000 (Montmorency)	480 g/L SL	0.35	0.035	1000	1	0 3 7 10 10	Whole fruit Whole fruit Whole fruit Pitted fruit Whole fruit (calculated)	2.1 2.6 0.30 0.15 0.14	Ballesteros, 2002, R&D/CRLD/AN/02150 09 (M-210351-01-1)
00555BKA1 Fourgerolles, France, 2000 (Marie-Jean Diaude)	480 g/L SL	0.35	0.035	993	1	9 9	Pitted fruit Whole fruit (calculated)	0.61 0.52	Ballesteros, 2002, R&D/CRLD/AN/02150 13 (M-210352-01-1)
00555BKA2 Saint Maurice s/les Cotes, France, 2000 (Griotte à jus clair)	480 g/L SL	0.36	0.035	1008	1	9 9	Pitted fruit Whole fruit (calculated)	0.36 0.33	Ballesteros, 2002, R&D/CRLD/AN/02150 13 (M-210352-01-1)
02R795-1 Boe, France, 2002 (Coralise)	480 g/L SL	0.36	0.036	1000	1	0 4 7 11 11	Whole fruit Whole fruit Whole fruit Pitted fruit Whole fruit (calculated)	2.7 2.3 2.3 1.8 1.6	Sonder, 2004, 02 R 795 (M-220921-01-1)
02R795-2 Malaucene, France, 2002 (Bigareau Napolélon)	480 g/L SL	0.36	0.037	972	1	0 9 0 9	Pitted fruit Whole fruit (calculated)	0.77 0.93 0.66 0.67	Sonder, 2004, 02 R 795 (M-220921-01-1)

CHERRY Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
02R795-3 Andria, Italy, 2002 (Ferrovia)	480 g/L SL	0.36	0.043	834	1	0 4 7 10 0 4 7 10	Pitted fruit Whole fruit (calculated)	1.5 1.8 1.7 2.3 1.0 1.6 1.5 2.0	Sonder, 2004, 02 R 795 (M-220921-01-1)
02R795-4 Segorbe, Spain, 2002 (Precoz De Bernat)	480 g/L SL	0.36	0.023	1550	1	0 10 10	Whole fruit Pitted fruit Whole fruit (calculated)	0.30 0.76 0.64	Sonder, 2004, 02 R 795 (M-220921-01-1)
02R795-5 Lokindros, Greece, 2002 (Bourla)	480 g/L SL	0.36	0.024	1500	1	0 9 9	Whole fruit Pitted fruit Whole fruit (calculated)	0.57 0.40 0.37	Sonder, 2004, 02 R 795 (M-220921-01-1)
09-2147-01 Rosoux, Belgium, 2009 (Regina)	480 g/L SL	0.36	0.030	1200	1	0 4 7 10 14	Whole fruit	0.25 0.42 0.44 0.31 0.31	Uceda and Meilland-Berthier, 2011, 09-2147 (M-403958-01-1)
09-2147-02 ND Wognum, Netherlands, 2009 (Regina)	480 g/L SL	0.36	0.024	1500	1	0 4 7 10 14	Whole fruit	0.16 0.21 0.28 0.23 0.21	Uceda and Meilland-Berthier, 2011, 09-2147 (M-403958-01-1)

Grapes

Ten supervised trials were conducted on grapes in France. A 180 g/L SL formulation was applied once as a foliar spray to grape vines at BBCH 83–85 at a rate of 0.45–0.47 kg ai/ha. In the trials conducted in 1995, residues of ethephon were determined using the analytical method referenced in "Analytical Method for Residues of Pesticides" Part II-89, 5th Edition, SDU Publishers, The Netherlands (1988). This method is similar to SOP 90070 and was validated on grapes prior to use. The LOQ was 0.10 mg/kg. In the trials conducted in 2006 and 2009, residues of ethephon were determined using method 00903, supplement E001. The maximum period of storage of frozen samples at < –18 ºC was 447 days.

Table 51 Ethephon residues in grapes resulting from supervised trials in Europe

GRAPES Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, France	180 g/L SL	0.45		100–200	1	28		
EA950185-FR01 Mercurol, France, 1995 (Syrah)	180 g/L SL	0.45	0.45	99	1	0 25 35	0.80 0.35 0.37	Grolleau, 1997, EA950185 (M-188232-01-1)
EA950185-FR02 Pouzillac, France, 1995 (Grenache)	180 g/L SL	0.47	0.45	105	1	0 25 35	1.02 0.17 0.25	Grolleau, 1997, EA950185 (M-188232-01-1)

GRAPES Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
R 2006 0333/9 Blere, France, 2006 (Cabernet franc)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.58 1.5 0.74 0.52 0.39	Billian, Lorenz, Telscher, 2005, RA-2562/06 (M-294217-01-1)
R 2006 0411/4 Saint Nicolas de Bourgueil, France, 2006 (Cabernet franc)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.53 0.58 0.45 0.21 0.21	Billian, Lorenz, Telscher, 2005, RA-2562/06 (M-294217-01-1)
R 2006 0334/7 Fronton, France, 2006 (Négrette)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.81 0.68 0.24 0.18 0.13	Billian, Telscher, 2005, RA-2563/06 (M-294366-01-1)
R 2006 0412/2 Laudun, France, 2006 (Merlot)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.63 0.09 0.07 0.05 < 0.05	Billian, Telscher, 2005, RA-2563/06 (M-294366-01-1)
09-2176-01 La Chapelle de Guinchay, France, 2009 (Gamay)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.42 0.30 0.09 0.05 0.07	Uceda, Meilland, Berthier, 2011, 09-2176 (M-403873-01-1)
09-2176-02 Athee sur Cher, France, 2009 (Gamay)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.34 0.25 0.28 0.20 0.16	Uceda, Meilland, Berthier, 2011, 09-2176 (M-403873-01-1)
09-2176-03 Vendeuvre du poitou, France, 2009 (Gamay)	180 g/L SL	0.45	0.23	200	1	0 10 21 28 35	0.38 0.27 0.16 0.10 0.14	Uceda, Meilland, Berthier, 2011, 09-2176 (M-403873-01-1)
09-2176-04 Fonton, France, 2009 (Negrette)	180 g/L SL	0.45	0.23	200	1	0 9 21 28 35	0.31 0.57 0.32 0.18 0.18	Uceda, Meilland, Berthier, 2011, 09-2176 (M-403873-01-1)

Fig

Six supervised trials were conducted in 2004–2005 on figs in Brazil. For the trials conducted in 2004, brush application was carried out with a 240 g/L SL formulation at the harvest growth stage. For the trials conducted in 2005, application used a 720 g/L SL formulation at the harvest growth stage. In the trials conducted in 2004, residues of ethephon were determined using the analytical method referenced in "Analytical Methods for Pesticide Residues in Foodstuffs" 6th Edition, part II, The Netherlands, 1996, with some modifications. In the trials conducted in 2005, residues of ethephon were determined using the analytical method 11-94. The maximum period of storage of frozen samples at < –20 ºC was 8 months.

Table 52 Ethephon residues in figs resulting from supervised trials in Brazil

FIG	Application	DALT	Ethephon	Reference

Trial No Country, year (Variety)	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days	mg/kg	
GAP, Brazil	720 g/L SL		0.94		1	5		
1(R04MA1) Valinhos, Brazil, 2004 (Figo Roxo de Valinhos)	240 g/L SL		24	0.5	1	0 1 3 5 7	2.7 1.3 0.8 0.2 0.2	Trevizan, de Baptista, 2004, 102/5373/04 (M-284626-01-2)
	240 g/L SL		24	1.0	1	5	0.2	
2(R04MA01-P1) Monte Mor, Brazil, 2004 (Figo Roxo de Valinhos)	240 g/L SL		24	0.5	1	5	< 0.2	Trevizan, de Baptista, 2004, 102/5374/04 (M-284634-01-2)
	240 g/L SL		24	1.0	1	5	< 0.2	
3(R04MA01-P2) Caldas-MG, Brazil, 2004 (Figo Roxo de Valinhos)	240 g/L SL		24	0.5	1	5	0.6	Trevizan, de Baptista, 2004, 102/5375/04 (M-284637-01-2)
	240 g/L SL		24	1.0	1	5	0.9	
HR05BRA008-P1 Piracicaba, Brazil, 2005 (Roxo de Valinhos)	720 g/L SL		0.94	25	1	5	0.75	Galhiane, Santos, 2005, RA-925/05 (M-284675-01-2)
	720 g/L SL		1.9	25	1	5	1.32	
HR05BRA008-P2 Valinhos, Brazil, 2005 (Roxo de Valinhos)	720 g/L SL		0.94	25	1	5	0.71	Galhiane, Santos, 2005, RA-926/05 (M-284678-01-2)
	720 g/L SL		1.9	25	1	5	1.25	
HR05BRA008-P3 Itatiba, Brazil, 2005 (Roxo de Valinhos)	720 g/L SL		0.94	25	1	5	0.73	Galhiane, Santos, 2005, RA-927/05 (M-284681-01-2)
	720 g/L SL		1.9	25	1	5	1.34	

Olives

Eight supervised trials were conducted in 2007–2008 on olives in Spain. In the 2007 trials, a 480 g/L SL formulation was applied twice as a foliar spray to olives trees at BBCH 79–81 at a rate of 0.35–0.41 + 0.47–0.50 kg ai/ha and a 7-day interval between applications. In the 2008 trials, a 480 g/L SL formulation was applied twice as a foliar spray to olives trees at BBCH 78–87 at a rate of 0.48 + 0.62 kg ai/ha and a 7–8 day interval between applications. In the trials conducted in 2007, residues of ethephon were determined using method 00903. In the trials conducted in 2008, residues of ethephon were determined using method 00903, supplement E001. The maximum period of storage of frozen samples at < –18 ºC was 12 months for olives, 7 months for table olives and 11.5 months for oil.

Table 53 Ethephon residues in olives resulting from supervised trials in Europe

OLIVES Trial Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Formulation (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, Italy	480 g/L SL	1st 0.45 2nd 0.60	1st 36 2nd 48	1250	2	11		
07 D OL BY P01 Arahal, Spain, 2007 (Manzanillo)	480 g/L SL	0.35 0.47	0.036 0.048	968 971	2	11	4.3	Fernandez, 2009, 07 D OL BY P/A (M-352734-01-1)

OLIVES Trial Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Formulation (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
07 D OL BY P02 Huevar del Aljarafe, Spain, 2007 (Manzanillo)	480 g/L SL	0.41 0.50	0.036 0.048	1132 1045	2	11	2.2	Fernandez, 2009, 07 D OL BY P/A (M-352734-01-1)
07 D OL BY P03 La Puebla de Cazalla, Spain, 2007 (Hojiblanca)	480 g/L SL	0.35 0.47	0.036 0.048	974 983	2	11	2.5	Fernandez, 2009, 07 D OL BY P/A (M-352734-01-1)
07 D OL BY P04 Herrera, Spain, 2007 (Hojiblanca)	480 g/L SL	0.37 0.47	0.036 0.048	1020 981	2	11	1.6	Fernandez, 2009, 07 D OL BY P/A (M-352734-01-1)
08-2053-01 Sevilla, Spain, 2008 (Manzanillo)	480 g/L SL	0.48 0.62	0.044 0.057	1100 1100	2	11	0.90	Billian, 2009, 08-2053 (M-350265-02-1)
08-2053-02 Osuna, Spain, 2008 (Manzanillo)	480 g/L SL	0.48 0.62	0.044 0.057	1100 1100	2	11	2.60	Billian, 2009, 08-2053 (M-350265-02-1)
08-2053-03 Antequera, Spain, 2008 (Hojiblanco)	480 g/L SL	0.48 0.62	0.044 0.057	1100 1100	2	11	0.85	Billian, 2009, 08-2053 (M-350265-02-1)
08-2053-03 La Rambla, Spain, 2008 (Hojiblanco)	480 g/L SL	0.48 0.62	0.044 0.057	1100 1100	2	10	0.98	Billian, 2009, 08-2053 (M-350265-02-1)

Pineapple

Pineapple plants may be treated early to induce flowering or close to harvest to induce ripening/colouration of the pineapple fruit. The pre-flowering application is not expected to result in measurable residues. Treatment for fruit ripening/colouration close to harvest (typical PHI 1–14 days) is the most critical use and will result in the highest residues in the fruit. In the trials conducted in Brazil, Costa Rica and Côte d'Ivoire, pineapples have been treated close to harvest for fruit ripening/colouration.

Five supervised trials were conducted in Brazil. The plots were sprayed with a 240 g/L SL formulation once at 0.96 kg ai/ha or 1.92 kg ai/ha. All samples were analysed using ethylene release method (Method 11-94 for the 2005 trials). The maximum period of frozen storage of frozen samples was 1.5 months.

Two supervised trials have been conducted in 1998 in Costa Rica. The plots were sprayed with a 480 g/L SL formulation at an application rate of 1.59 kg ai/ha. Samples were separated into flesh and peel, after removal of the crown. The maximum period of storage of frozen samples at < –18 ºC was 3 months.

Two supervised trials were conducted in 1997 and 1999 in Côte d'Ivoire. The plots were sprayed with a 480 g/L SL formulation at a rate of 1.43–1.44 kg ai/ha.

Samples of peel and flesh of pineapple fruit from trials in Costa Rica and Côte d'Ivoire were analysed using method HVA 12/89. Residues in whole fruit were determined by calculation

from the residues in peel and flesh. The maximum period of storage of frozen samples was 6 months.

Six supervised trials have been conducted in 1989 in the USA (Hawaii). Four trials were conducted in Oahu, and two in Maui (no specific description about the locations). Each plot was divided into three subplots which were sprayed with a 480 g/L SL formulation at a rate of 2.24 + 1.12 kg ai/ha or 2× 2.24 kg ai/ha. Samples were analysed using method SOP 90070. The maximum period of storage of frozen samples was 11 months.

Table 54 Ethephon residues in pineapples resulting from supervised trials in Brazil, Costa Rica, Côte d'Ivoire and the USA

PINEAPPLE Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Belize, El Salvador, Honduras, Domenican Rep	480 g/L SL	1.92 [a]		2000–3000	1–2	7–14			[a] Can be divided into two applications (i.e., seasonal max: 1.92)
GAP, Brazil	720 g/L SL	0.94		30–500	1	14			
GAP, Costa Rica	480 SL	1.2		2000–3000	2	1			
GAP, Costa Rica, Panama, Guatemala	720 g/L SL	0.94		2000–3000	1	7–14			
GAP, Costa Rica, Panama, Guatemala	720 g/L SL	1.2		1000	1	7–14			
GAP, Kenya	480 g/L SL	1.92		3000	1	7			
BRAZIL									
039/94PC-01 Sao Paolo, Brazil, 1994 (variety not reported)	240 g/L SL	0.96	–	–	1	0 4 8 13 18	Fruit	0.47 0.41 0.46 0.20 0.13	Garcia, 1994, CP-1997 PA-081/94 (M-188144-02-1)
	240 g/L SL	1.90	–	–	1	0 4 8 13 18	Fruit	1.12 0.87 1.21 0.90 0.48	
060/96 PC-1 Faz Sao Carlos-Holambra, Brazil, 1996 (Pérola)	240 g/L SL	0.96	0.24	400	1	14	Fruit	< 0.05	Guimaraes, 1997, 4170 (M-421140-01-1)
	240 g/L SL	1.92	0.48	400	1	14	Fruit	< 0.05	
HR05BRA0004-P1 Frutal MG, Brazil, 2005 (Havaiana)	240 g/L SL	0.96	0.24	400	1	14	Fruit	0.15	Galhiane, Santos, 2005, RA-966/05 (M-284613-02-1)
	240 g/L SL	1.92	0.48	400	1	14	Fruit	0.22	
HR05BRA0004-P2 Uberlandia MG, Brazil, 2005 (Havai)	240 g/L SL	0.96	0.24	400	1	14	Fruit	0.11	Galhiane, Santos, 2005, RA-967/05 (M-284618-02-1)
	240 g/L SL	1.92	0.48	400	1	14	Fruit	0.21	

PINEAPPLE Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
HR05BRA0004-P3 Ribeirao SP, Brazil, 2005 (Havai)	240 g/L SL	0.96	0.24	400	1	14	Fruit	0.19	Galhiane, Santos, 2005, RA-968/05 (M-284623-02-1)
	240 g/L SL	1.92	0.48	400	1	14	Fruit	0.24	
Costa Rica									
98622XX1 Buenos Aires, Costa Rica, 1998 (Del Monte Gold)	480 g/L SL	1.59	0.13	1273	1	0 2 3 7 0 2 3 7 0 2 3 7	Pulp Peel Whole fruit, calculated	< 0.10 0.11 < 0.10 < 0.10 0.38 0.41 0.13 < 0.10 0.19 0.20 0.11 < 0.10	Maestracci, 1998, R&D/CRLD/ AN/msa/ 9816197 (M-165714-01-1)
98622XX2 Buenos Aires, Costa Rica, 1998 (Del Monte Gold)	480 g/L SL	1.59	0.13	1215	1	0 2 3 7 0 2 3 7 0 2 3 7	Pulp Peel Whole fruit, calculated	< 0.10 < 0.10 < 0.10 < 0.10 0.14 < 0.10 < 0.10 < 0.10 0.11 < 0.10 < 0.10 < 0.10	Maestracci, 1998, R&D/CRLD/ AN/msa/ 9816197 (M-165714-01-1)
Côte d'Ivoire									
97766CI1 Yamoussoukro, Côte d'Ivoire, 1997 (Cayenne Lisse)	480 g/L SL	1.43	0.048	2978	1	0 2 3 7 0 2 3 7 0 2 3 7	Pulp Peel Whole fruit, calculated	< 0.10 < 0.10 < 0.10 < 0.10 0.51 0.31 0.64 0.13 0.21 0.16 0.28 0.11	Maestracci, 1998, R&D/CRLD/ AN/msa/ 9816152 (M-165702-02-1)

PINEAPPLE Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
98761C1 Yamoussoukro Côte d'Ivoire, 1999 (Cayenne Lisse)	480 g/L SL	1.44	0.048	3000	1	0 2 3 7 0 2 3 7 0 2 3 7	Pulp Peel Whole fruit, calculated	0.21 0.25 0.13 0.13 1.7 1.6 1.6 2.7 0.72 0.67 0.59 0.97	Baudet 1998, R&D/CRLD/ AN/mr/ 9916533 (M-179309-01-1)
USA									
89-130-P2 Honolulu Co, HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 1.12	0.24 0.12	935 935	2	1 2 4 8	Whole fruit	0.06, 0.08, 0.15 [a] 0.05 0.04 0.03	Nygren, 1992, USA89E27, [M- 187578-01-1
89-130-P3 Honolulu Co, HI, USA,1989 (Smooth Cayenne)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	0.22 0.12 0.13 0.08	Nygren, 1992, USA89E27, [M- 187578-01-1
89-131-P2 Honolulu Co, HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 1.12	0.24 0.12	935 935	2	1 2 4 8	Whole fruit	0.17, 0.11, 0.22 0.11 0.03 < 0.02	Nygren, 1992, USA89E27, [M- 187578-01-1
89-131-P3 Honolulu Co, HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	0.38 0.07 0.09 0.06	Nygren, 1992, USA89E27, [M- 187578-01-1
89-132-P2 Oahu Co., HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 1.12	0.24 0.12	935 935	2	1 2 4 8	Whole fruit	n.a. 0.29 0.32 0.32	Nygren, 1992, USA89E27, [M- 187578-01-1
89-132-P3 Oahu Co., HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	0.67 0.41 0.98 0.72	Nygren, 1992, USA89E27, [M- 187578-01-1
89-133-P2 Oahu Co., HI, USA, 1989 (Smooth Cayenne)	480 g/L SL	2.24 1.12	0.24 0.12	935 935	2	1 2 4 8	Whole fruit	0.52, 0.71, 0.72 0.67 0.42 0.27	Nygren, 1992, USA89E27, [M- 187578-01-1
89-133-P3 Oahu Co., HI, USA,1989 (Smooth Cayenne)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	1.27 0.86 0.75 0.69	Nygren, 1992, USA89E27, [M- 187578-01-1

PINEAPPLE Trial No Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
89-134-P2 Maui Co., HI, USA, 1989 (Champaka)	480 g/L SL	2.45- 2.56 1.12	0.26- 0.27 0.12	935 935	2	1 2 4 8	Whole fruit	0.30, 0.19, 0.28 0.17 0.32 0.23	Nygren, 1992, USA89E27, [M- 187578-01-1
89-134-P3 Maui Co., HI, USA, 1989 (Champaka)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	0.62 0.40 0.36 0.76	Nygren, 1992, USA89E27, [M- 187578-01-1
89-135-P2 Maui Co., HI, USA, 1989 (Champaka)	480 g/L SL	2.62- 2.99 1.12	0.28- 0.32 0.12	935 935	2	1 2 4 8	Whole fruit	0.33, 0.42, 0.35 0.11 0.16 0.17	Nygren, 1992, USA89E27, [M- 187578-01-1
89-135-P3 Maui Co., HI, USA, 1989 (Champaka)	480 g/L SL	2.24 2.24	0.24 0.24	935 935	2	1 2 4 8	Whole fruit	0.74 0.26 0.59 0.48	Nygren, 1992, USA89E27, [M- 187578-01-1

[a] Results of three subplots. The highest residue concentration is selected.

Tomato

A total of twelve supervised trials were conducted on outdoor (field) grown tomatoes in Greece, Italy, Portugal and Spain. A total of nine supervised trials were conducted on indoor tomatoes in France, the Netherlands and Spain in 1999, 2000 and 2001. A 480 g/L SL formulation was applied as a foliar spray to outdoor (field) tomatoes at BBCH 84–89 at a rate of 1.68 kg ai/ha, or to indoor tomatoes at BBCH 60–89 at 1.42–1.47 kg ai/ha. In the 1999–2001 studies, residues of ethephon were determined using method HVA SOP 10071. In the 2004 study, residues of ethephon were determined using method 00903, supplement E001. The maximum period of storage of frozen samples was 642 days (21 months).

Twelve supervised trials were conducted in 1989–1991 on outdoor (field) grown tomato and three trials in 2005 on indoor tomato in the USA. A 240 g/L SL formulation was applied as a single foliar spray to outdoor (field) tomatoes at a rate of 1.73–2.14 kg ai/ha, or to indoor tomatoes at 1.38–1.42 kg ai/ha. In one field tomato trial (89-138), ethephon had been applied prior to the trial commencing, and the total ethephon application rate was 2.43 kg ai/ha. Residues of ethephon from the trials reported in 1991, 1992 and 2008 were determined using method SOP 90070. Residues of ethephon from the trials reported in 1995 were determined using method EC-92-228 (ethylene release method). The maximum period of storage frozen samples at –15 °C was 26 months.

Table 55 Ethephon residues in tomatoes resulting from supervised trials in Europe and the USA.

TOMATO Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, Italy	480 g/L SL	1.92 [b]		1000	1–2	7		)
EUROPE/OUTDOOR (FIELD)								
DR00EUS522 ESP0201 Brenes, Spain, 2000 (Inca)	480 g/L SL	1.68	0.17	1000	1	0 3 7	1.5 1.1 0.78	Hees, 2001, DR00EUS522 (M- 203527-01-1)
DR00EUS522 ITA0101 Bologna, Italy, 2000 (Nun 7491)	480 g/L SL	1.68	0.17	1000	1	0 3 7	1.2 0.23 0.24	Hees, 2001, DR00EUS522 (M- 203527-01-1)

TOMATO Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
DR00EUS522 ITA0201 Andria, Italy, 2000 (Faino)	480 g/L SL	1.68	0.17	1000	1	0 3 7	1.6 0.65 0.78	Hees, 2001, DR00EUS522 (M-203527-01-1)
DR00EUS522 GRC0101, Korifi-Imathia, Greece, 2000 (Titano M)	480 g/L SL	1.68	0.17	1000	1	0 3 7	0.56 0.52 0.62	Hees, 2001, DR00EUS522 (M-203527-01-1)
01R773-1 Utrea Sevilla, Spain, 2001 (Odin)	480 g/L SL	1.68	0.34	500	1	0 3 7	1.6 0.95 0.45	Davies, 2002, 01R773 (M-215341-01-1)
01R773-2 Brenes Sevilla, Spain, 2001 (Inca)	480 g/L SL	1.68	0.34	500	1	0 3 7	0.93 0.85 0.68	Davies, 2002, 01R773 (M-215341-01-1)
01R773-3 Molfetta, Italy, 2001 (Denaro)	480 g/L SL	1.68	0.24	700	1	0 3 7	1.9 1.1 0.5	Davies, 2002, 01R773 (M-215341-01-1)
01R773-4 Vrachia-Tessaloniki, Greece, 2001 (Titano)	480 g/L SL	1.68	0.34	500	1	0 3 7	0.35 0.45 0.46	Davies, 2002, 01R773 (M-215341-01-1)
01R773-5 Korifi-Imathia, Greece, 2001 (Rio Grande)	480 g/L SL	1.68	0.34	500	1	0 3 7	0.58 0.65 0.40	Davies, 2002, 01R773 (M-215341-01-1)
R 2004 0468/9 Gava, Spain, 2004 (Malpica)	480 g/L SL	1.68	0.21	800	1	0 4 7	0.95 0.46 0.30	Bardel, 2005, RA-2065/04 (M-261821-01-1)
R 2004 0469/7 Aldeia, Portugal, 2004 (H-9661)	480 g/L SL	1.68	0.21	800	1	0 3 7 10	1.1 0.80 0.57 0.17	Bardel, 2005, RA-2065/04 (M-261821-01-1)
R 2004 0470/0 Bolognia, Italy, 2004 (Missouri)	480 g/L SL	1.68	0.21	800	1	0 3 7 10	1.2 1.7 0.55 0.49	Bardel, 2005, RA-2065/04 (M-261821-01-1)
EUROPE/INDOOR								
DR00EUI520 FRA0301 Marcellus, France, 2000 (Vekio)	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.25 0.44 0.79	Hees, 2001, DR00EUI520 (M-202477-01-1)
DR00EUI520 FRA0302 Villefranche du Queyran, France, 2000 (Félicia)	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.45 0.48 0.45	Hees, 2001, DR00EUI520 (M-202477-01-1)
00582NL1 Huissen, Netherlands, 1999 (Elegance)	480 g/L SL	1.42	0.095	1488	1	7	0.51	Ballesteros, 2002, R&D/CRLD/AN/0215069 (M-210410-01-1)
00582NL2 Ooserhout, Netherlands, 1999 (Tomcat)	480 g/L SL	1.47	0.095	1538	1	7	0.69	Ballesteros, 2002, R&D/CRLD/AN/0215069 (M-210410-01-1)

TOMATO Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
01R791-1 Puebla de Vicar, Spain, 2001 (Eldiez)	480 g/L SL	1.44	0.12	1250	1	0 3 7	0.88 1.1 0.68	Davies, 2002, 01R791 (M-210553-01-1)
01R791-2 ND Zwaagdik, Netherlands, 2001 (Fergie (F6197))	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.86 1.4 0.66	Davies, 2002, 01R791 (M-210553-01-1)
01R791-3 ND Zwaagdik,Netherlands, 2001 (Rapsodie)	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.57 0.31 0.52	Davies, 2002, 01R791 (M-210553-01-1)
01R791-4 ND Zwaagdik,Netherlands, 2001 (Fergie (F6197))	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.61 0.34 0.31	Davies, 2002, 01R791 (M-210553-01-1)
01R791-5 ND Zwaagdik,Netherlands, 2001 (Rapsodie)	480 g/L SL	1.44	0.096	1500	1	0 3 7	0.41 0.16 0.36	Davies, 2002, 01R791 (M-210553-01-1)
GAP, Canada	240 g/L SL	1.54		30–500	1	No specific PHI set, harvest at maturity, generally 14–21 days after treatment		
USA/OOUTDOOR (FIELD)								
89-119 Imperial Co., CA, USA, 1989 (U.C. 82)	240 g/L SL	1.75	2.3	76	1	0 3 7	0.18 (0.14, 0.21,0.18) [a] 0.10 (0.14, 0.06, 0.10) 0.09 (0.07, 0.12, 0.08)	Nygren, 1991, USA89E30 (M-187599-01-1)
89-120 Imperial Co., CA, USA, 1989 (U.C. 82)	240 g/L SL	2.14	1.05	204	1	0 3 7	0.48 (0.71, 0.47, 0.26) 0.44 (0.65, 0.34, 0.32) 0.27 (0.23, 0.42, 0.17)	Nygren, 1991, USA89E30 (M-187599-01-1)
89-136 Solano Co., CA, USA, 1989 (Sun Seed 5715)	240 g/L SL	1.80	1.9	93	1	3 7 14	0.66 (0.34, 1.1, 0.54) 0.92 (1.0, 0.81, 0.95) 0.69 (0.63, 0.72, 0.73)	Nygren, 1991, USA89E30 (M-187599-01-1)
89-137 Solano Co., CA, USA, 1989 (Sun Seed 5715)	240 g/L SL	2.00	0.97	206	1	3 7 14	0.02 < 0.02 (< 0.02, < 0.02, < 0.02) 0.15 (0.05, 0.17, 0.22)	Nygren, 1991, USA89E30 (M-187599-01-1)
89-138 Sacrament Co., CA, USA, 1989 (1643)	240 g/L SL	1.27 1.16	1.3 0.93	93 125	2	3	0.73 (0.68, 0.86, 0.64)	Nygren, 1991, USA89E30 (M-187599-01-1)
90-492 Collier Co., FL, USA, 1990 (Sunny)	240 g/L SL	1.80	0.97	187	1	3 7 14	< 0.02 (< 0.02, < 0.02, < 0.02) < 0.02 (< 0.02, < 0.02, < 0.02) < 0.02 (< 0.02, < 0.02, < 0.02)	Nygren, 1992, USA90E16 (M-187596-01-1)
90-493 Collier Co., FL, USA, 1990 (Sunny)	240 g/L SL	1.80	1.9	93	1	3 7 14	0.32 (0.16, 0.47, 0.32) 0.06 (0.05, < 0.02, 0.11) 0.06 (0.05, 0.05, 0.07)	Nygren, 1992, USA90E16 (M-187596-01-1)

TOMATO Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
91-307 Stanislaus Co., CA, USA, 1991 (Ace)	240 g/L SL	1.75	0.53	329	1	3 7 14	1.66 (1.64, 2.24, 1.09) 0.97 (0.51, 1.24, 1.16) 0.63 (0.78, 0.66, 0.44)	Nygren, 1995, USA91E16 (M-187891-01-1)
91-308 Stanislaus Co., CA, USA, 1991 (Ace)	240 g/L SL	1.76	1.36	129	1	3 7 11	1.24 (1.06, 1.29, 1.37) 0.81 (0.93, 0.66, 0.83) 0.37 (0.29, 0.44, 0.39)	Nygren, 1995, USA91E16 (M-187891-01-1)
91-309 Stanislaus Co., CA, USA, 1991 (Ace)	240 g/L SL	1.80	0.55	329	1	3 7 14	0.55 (0.48, 0.61) 0.35 (0.43, 0.25, 0.36) 0.15 (0.22, 0.12, 0.12)	Nygren, 1995, USA91E16 (M-187891-01-1)
91-310 Stanislause Co., CA, USA, 1991 (Ace)	240 g/L SL	1.73	1.34	129	1	3 7 14	0.62 (0.69, 0.69, 0.49) 0.68 (0.75, 0.40, 0.89) 0.67 (0.40, 0.34, 1.27)	Nygren, 1995, USA91E16 (M-187891-01-1)
91-311 Collier Co., FL, USA, 1991 (BHN)	240 g/L SL	1.80	0.38	469	1	3 7 10	0.30 (0.17, 0.36, 0.37) 0.08 (0.12, 0.07, 0.04) 0.05 (0.06, 0.05, 0.04)	Nygren, 1995, USA91E16 (M-187891-01-1)
USA/INDOOR								
00250.05-CO13 Fort Collins, CO, USA, 2005 (Trust F1)	240 g/L SL	1.42	0.75	189	1	1 2	0.58 (0.56, 0.60) 0.70 (0.83, 0.56)	Dorschner, 2008, IR4 PR No 00250 (M-301374-01-1)
00250.05-FL37 Citra, FL, USA, 2005 (FL47)	240 g/L SL	1.41	0.49	289	1	1 2	0.60 (0.32, 0.88) 0.98 (0.85, 1.1)	Dorschner, 2008, IR4 PR No 00250 (M-301374-01-1)
00250.05-TX25 Weslaco, TX, USA, 2005 (Super sweet 100)	240 g/L SL	1.38	0.41	340	1	1 2	1.70 (2.0, 1.4) 1.80 (2.0, 1.6)	Dorschner, 2008, IR4 PR No 00250 (M-301374-01-1)

[a] Mean residue. Analytical results of replicate samples were in parentheses

[b] Can be divided into two applications (i.e., seasonal max, 1.92)

Cereal grains

Barley

A total of fifty-three supervised trials were conducted in Europe with a foliar spray:

- Fourteen at a rate of 1× 480 g ai/ha, application at BBCH 45–51 (one trial at BBCH 55), (determination using method HVA SOP 10071)
- Eight trials at a rate of 1× 225 g ai/ha, application at BBCH 39–41, (determination using method 00918)
- Ten trials at a rate of 1× 380 g ai/ha, application at BBCH 37–39, (determination using method 00918)
- Five trials at a rate of 1× 670–720 g ai/ha (nominal rate 720 g ai/ha), application at BBCH 37–39 (determination using method 00918).

In all studies, the maximum period of storage of frozen samples at around –18 °C was 14 months.

A total of 16 new trials were conducted to determine the magnitude of the residues of ethephon in/on barley (grain, green materials and straw) after one spraying application with ethephon SL 480 during the 2013 and 2014 seasons with one foliar application in Europe:

- Eight trials at a rate of 480 g ai/ha at BBCH 39
- Eight trials at 480 g ai/ha at BBCH 51.

The samples were stored frozen (–18 °C) for a maximum of 647 days. In these sixteen trials residues of ethephon and HEPA were determined by Method 01429, HPLC-MS/MS method in which grains and straw were extracted first with methanol and then by a mixture of concentrated hydrochloric acid and water (1/7, v/v) at 50 °C to convert conjugated ethephon and HEPA to free ethephon and HEPA. The extracts and acid hydrolysates were combined for analysis.

Table 56 Ethephon residues in barley grains resulting from supervised trials in Europe

BARLEY Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, Germany	660 g/L SL	0.462		100–300	1	–	Application timing BBCH 32–49	
GAP, UK	480 g/L SL	0.48		100–400	–	–	Application timing BBCH 32–49 Maximum total rate 0.48 kg ai/ha	
DR00EUS525 ITA0101 Bologna, Italy, 2000 (Express)	480 g/L SL	0.48 (BBCH 47)	0.16	300	1	48	< 0.05	Hees, 2001, DR00EUS525 (M-199982-01-1)
DR00EUS525 ITA0102 S. Mauro Pascoli, Italy, 2000 (Extra)	480 g/L SL	0.48 (BBCH 45)	0.16	300	1	47	< 0.05	Hees, 2001, DR00EUS525 (M-199982-01-1)
00547BX1 Marignac, France, 2000 (Sunrise)	480 g/L SL	0.48 (BBCH 45)	0.14	333	1	52	0.06	Ballasteros, 2001, R&D/CRLD/AN/mr/0115430 (M-208093-01-1)
00547TL1 Gardouch, France, 2000 (Esterel)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	62	0.06	Ballasteros, 2001, R&D/CRLD/AN/mr/0115430 (M-208093-01-1)
01R761-1 Ronchères, France, 2001 (Platine)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	69	< 0.05	Davies, 2002, 01R761 (M-209901-01-1)
01R761-2 Hargicourt, France, 2001 (Muscat)	480 g/L SL	0.48 (BBCH 49)	0.19	250	1	54	0.05	Davies, 2002, 01R761 (M-209901-01-1)
01R761-3 Braintree, UK, 2001 (Regina)	480 g/L SL	0.48 (BBCH 55)	0.19	252	1	58	0.23	Davies, 2002, 01R761 (M-209901-01-1)
01R761-4 Weilerswist, Germany, 2001 (Theresa)	480 g/L SL	0.48 (BBCH 51)	0.16	300	1	60	< 0.05	Davies, 2002, 01R761 (M-209901-01-1)
01R761-5 Zschortau, Germany, 2001 (Landi)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	66	< 0.05	Davies, 2002, 01R761 (M-209901-01-1)

BARLEY Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
01R771-1 Senestis, France, 2001 (Platine)	480 g/L SL	0.48 (BBCH 45)	0.19	250	1	64	< 0.05	Davies, 2002, 01R771 (M-210307-01-1)
01R771-2 Toussieux, France, 2001 (Ladoga)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	63	< 0.05	Davies, 2002, 01R771 (M-210307-01-1)
01R771-3 Genas, France, 2001 (Ladoga)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	57	< 0.05	Davies, 2002, 01R771 (M-210307-01-1)
01R771-4 Alberone Di Cento, Italy, 2001 (Sonora)	480 g/L SL	0.48 (BBCH 47)	0.14	350	1	35	0.29	Davies, 2002, 01R771 (M-210307-01-1)
01R771-5 Xirochori-Kilkis, Greece, 2001 (Athinaida)	480 g/L SL	0.48 (BBCH 47)	0.16	300	1	50	< 0.05	Davies, 2002, 01R771 (M-210307-01-1)
GAP, France	480 g/L SL	0.48		100–200	1	56	Application timing BBCH 32–39	
R 2004 0577/4 Monospita, Greece, 2004 (Kannon (distiho))	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	54	< 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0578/2 Bologna, Italy, 2004 (Marjorie)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	54	< 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0579/0 Vouillé, France, 2004 (Scarlette)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	56	< 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0580/4 Balaguer, Spain, 2004 (Prestige)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	53	< 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0572/3 Lund, Sweden, 2004 (Bombay)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	80	< 0.05	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0573/1 Leverkusen, Germany, 2004 (Condesse)	450 g/L SL [a]	0.38 (BBCH 37)	0.125	300	1	85	< 0.05	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0575/8 Weri-Obernergstraße, Germany, 2004 (Intro)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	77	< 0.05	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0576/6 Fresnoy les Roye, France, 2004 (Esterel)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	67	< 0.057	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2006 0126/3 Neuville de Poitou, France, 2006 (Abondance)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	56 59	< 0.05 (ear) < 0.05	Billian & Erler, 2007, RA-2519/06 (M-290151-01-1)
R 2006 0299/5 Tarascon, France, 2006 (Baraka)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	55 60	0.22 (ear) 0.09	Billian & Erler, 2007, RA-2519/06 (M-290151-01-1)

BARLEY Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, Poland	480 g/L SL	0.72		150– 300	1	–	Application timing BBCH 32–39	
R 2006 0117/4 Beuvraignes, France, 2006 (Colibri)	480 g/L SL	0.67 (BBCH 37)	0.22	300	1	56 76	< 0.05 < 0.05	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2006 0286/3 Welver-Flerke, Germany, 2006 (Duet)	480 g/L SL	0.67 (BBCH 37)	0.22	300	1	55 68	< 0.05 < 0.05	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2006 0285/5 Hoxne/Nreye, UK, 2006 (Sequel)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	56 74	< 0.05 < 0.05	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2007 0172/1 Chaussy, France, 2007 (Sibéria)	480 g/L SL	0.72 (BBCH 37)	0.24	300	1	56 75	< 0.05 < 0.05	Billian, 2008, RA-2573/07 (M-311809-01-1)
R 2007 0181/0 Lund, Sweden, 2007 (Bombay)	480 g/L SL	0.72 (BBCH 37)	0.24	300	1	56 70	< 0.05 < 0.05	Billian, 2008, RA-2573/07 (M-311809-01-1)
GAP, France	450 g/L SL [a]	0.23		100– 200	1	–	Application timing BBCH 31–37	
R 2004 0581/2 Le Thil en Vexin, France, 2004 (Scarlet)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	57	< 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0582/0 Staffanstorp, Sweden, 2004 (Pasadena)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	79	< 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0583/9 Burscheid, Germany, 2004 (Scarlett)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	61	< 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0584/7 Gersthofen, Germany, 2004 (Ursa)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	65	< 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0585/5 Saint Germain sur Renon, France, 2004 (Nevada)	450 g/L SL [a]	0.23 (BBCH 41)	0.075	300	1	52	< 0.05	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)
R 2004 0586/3 Bologna, Italy, 2004 (Federal)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	52	< 0.05	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)
R 2004 0587/1 Tarascon, France, 2004 (Baraka)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	44	< 0.05	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)
R 2004 0589/8 Golegã, Portugal, 2004 (Scarlett)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	61	< 0.05	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)

[a] 450 g/L SL formulation (150 g/L ethephon + 300 g/L chlormequat-chloride)

Table 57 Ethephon and HEPA residues in barley grains resulting from supervised trials in Europe obtained using an analytical method involving acid hydrolysis/extraction

BARLEY Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	HEPA mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Germay	660 g/L SL	0.462		100–300	1	–	Application timing BBCH 32–49		
GAP, UK	480 g/L SL	0.48		100–400	–	–	Application timing BBCH 32–49 Maximum total rate 0.48 kg ai/ha		
13-2027-01 Burscheid, Germany, 2013 (Duett)	480 SL	0.48 (BBCH 51)	0.16	300	1	59	0.13	0.019 (c, 0.013)	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-02 Diegem, Belgium, 2013 (Meridian)	480 SL	0.51 (BBCH 51)	0.19	267	1	55	0.067	< 0.01	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-03 Mijdrecht, Netherlands, 2013 (Malabar)	480 SL	0.48 (BBCH 51)	0.16	300	1	56	0.73	0.086	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-04 Cambridge, United Kingdom, 2013 (Cassata)	480 SL	0.48 (BBCH 51)	0.24	200	1	68	0.23	0.055	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
14-2022-01 Langenfeld, Germany, 2014 (Naomie)	480 SL	0.54 (BBCH 51)	0.16	336	1	78	0.031	0.016	Schulte & Berkum, 2015, 14-2022
14-2022-02 Burscheid, Germany, 2014 (Leibnitz)	480 SL	0.48 (BBCH 51)	0.16	300	1	64	0.41	0.055 (c, 0.054)	Schulte & Berkum, 2015, 14-2022
14-2022-03 Lyon Cedex 09, France, 2014 (Obite Winter)	480 SL	0.48 (BBCH 51)	0.16	300	1	56	0.090	0.021	Schulte & Berkum, 2015, 14-2022
14-2022-04 Cambridge CB4 0WB, United Kingdom, 2014 (Cassatta Typical UK variety)	480 SL	0.48 (BBCH 55)	0.24	200	1	73	0.16	0.047 (c, 0.011)	Schulte & Berkum, 2015, 14-2022
GAP, France	480 g/L SL	0.48		100–200	1	56	Application timing BBCH 32–39		
13-2028-01 Ceaux en Loudun, France, 2013 (Cervoise)	480 SL	0.48 (BBCH 39)	0.16	300	1	71	0.035	< 0.01	Schulte & Berkum, 2015, 13-2028 M-529491-01-1
13-2028-02 Les Franqueses del Valles, Spain, 2013 (Graphic)	480 SL	0.48 (BBCH 39)	0.16	400	1	72	0.21	0.069	Schulte & Berkum, 2015, 13-2028 M-529491-01-1
13-2028-03 Citavecchia, Italy, 2013 (Quench, Distichous barley)	480 SL	0.48 (BBCH 39)	0.16	300	1	62	0.041	0.012	Schulte & Berkum, 2015, 13-2028 M-529491-01-1
13-2028-04 Bologna, Italy, 2013 (Federal)	480 SL	0.48 (BBCH 39)	0.24	350	1	64	0.021	0.070 (c, 0.060)	Schulte & Berkum, 2015, 13-2028 M-529491-01-1
14-2020-01 Ceaux en Loudun, France, 2014 (Limpid Winter Barley)	480 SL	0.48 (BBCH 39)	0.16	300	1	72	0.14	0.026	Schulte & Berkum, 2015, 14-2020

BARLEY Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	HEPA mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
14-2020-02 Les Franqueses del Valles, Spain, 2014 (Graphic winterbarley)	480 SL	0.41 (BBCH 43)	0.12	342	1	64	0.039	0.013	Schulte & Berkum, 2015, 14-2020
14-2020-03 Bologna, Italy, 2014 (Lutece Winter variety)	480 SL	0.48 (BBCH 39)	0.12	400	1	64	0.047	< 0.01	Schulte & Berkum, 2015, 14-2020
14-2020-04 Kristoni Village, Greece, 2014 (Mucho Early, six row, USA)	480 SL	0.48 (BBCH 39)	0.16	300	1	63	0.034	0.014	Schulte & Berkum, 2015, 14-2020

Rye

Nine supervised trials were conducted in 2006–2007 in France, UK, Sweden and Germany. A 480 g/L SL formulation was applied as a foliar spray to rye at BBCH 49 at a rate of 0.67–0.72 kg ai/ha. Samples of green material were collected after 0, 7 and 20-21 days, ears and rest of plant after 42–49 days, and mature grain and straw after 70–103 days. Residues of ethephon were determined using method 00918.

The maximum period of storage of frozen samples at –18 °C was 11.4 months.

Table 58 Ethephon residues in rye grains resulting from supervised trials in Europe

RYE Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Germany	660 g/L SL	0.73		100–300	1	–	Application timing BBCH 37–49		
R 2006 0119/0 Le Plessier, France, 2006 (Picasso)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	49 75	Ear Grain	0.08 < 0.05	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0287/1 Thetford, UK, 2006 (Ursus)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	49 88	Ear Grain	0.11 0.07	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0289/8 Svedala, Sweden, 2006 (Matador)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	49 71	Ear Grain	0.07 < 0.05	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0290/1 Anneville Ambourville, France, 2006 (Canovus)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	49 70	Ear Grain	0.10 0.06	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0292/8 Beiersdorf, Germany, 2006 (Rekrut)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	49 77	Ear Grain	0.14 0.06	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2007 0174/8 Le Plessier Rosainvillers, France, 2007 (Picasso)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	49 85	Ear Grain Straw	0.12 < 0.05	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)

RYE Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
R 2007 0182/9 Burscheid, Germany, 2007 (Fernando)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	49 86	Ear Grain	< 0.05 < 0.05	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)
R 2007 0184/5 Anneville Ambourville, France, 2007 (Caroass)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	48 83	Ear Grain	0.09 < 0.05	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)
R 2007 0183/7 Thetford, UK, 2007 (Visello)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	42 103	Ear Grain	0.06 < 0.05	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)

Wheat

A total of forty-three supervised trials were conducted in Europe with one foliar application:

- Nine trials at a rate of 480 g ai/ha, application at BBCH 37–39 (method HVA SOP 10071)
- Five trials at a rate of 480 g ai/ha, application at BBCH 49–51 (method HVA SOP 10071)
- Eight trials at a rate of 375 g ai/ha, application at BBCH 37 (one trial at BBCH 41–45), (method 00918)
- Five trials at a rate of 670–720 g ai/ha (nominal rate 720 g ai/ha), application at BBCH 39 (one trial at BBCH 49) (method 00918).

In all above studies, the maximum period of storage of frozen samples at around –18 °C was 12.2 months.

During the 2013 and 2014 seasons, a total of 16 trials were conducted in Europe to determine the magnitude of the residues of ethephon in/on wheat, soft (grain, green materials and straw) after one spraying application with Ethephon SL 480:

- Eight at a rate of 480 g ai/ha at BBCH 51
- Eight at a rate of 480 g ai/ha at BBCH 39.

Residues of ethephon in trials in 2013 and 2014 were determined by Method 01429, HPLC-MS/MS method in which grains and straw were extracted first with methanol and then by a mixture of concentrated hydrochloric acid and water (1/7, v/v) at 50 °C to convert conjugated ethephon and HEPA to free ethephon and HEPA. The extracts and acid hydrolysates are combined for analysis.

The samples were stored frozen (–18 °C) for a maximum of 713 days.

Table 59 Ethephon residues in wheat grains resulting from supervised trials in Europe

WHEAT Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Germany	660 g/L SL	0.46		100–300	1	–	Application timing BBCH 37–51		
01R762-1 Braslou, France, 2001 (Isengrain)	480 g/L SL	0.48 (BBCH 51)	0.19	250	1	70	Grain	< 0.05	Davies, 2002, 01R762 (M-210306-01-1)

WHEAT Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
01R762-2 Courdoux, France, 2001 (Ritmo)	480 g/L SL	0.48 (BBCH 49)	0.24	200	1	66	Grain	< 0.05	Davies, 2002, 01R762 (M-210306-01-1)
01R762-3 Cambridge, UK, 2001 (Claire)	480 g/L SL	0.48 (BBCH 49)	0.16	302	1	72	Grain	< 0.05	Davies, 2002, 01R762 (M-210306-01-1)
01R762-4 Weilerswist, Germany, 2001 (Drifter)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	66	Grain	0.06	Davies, 2002, 01R762 (M-210306-01-1)
01R762-5 Zschortau, Germany, 2001 (Petrus)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	71	Grain	< 0.05	Davies, 2002, 01R762 (M-210306-01-1)
GAP, France	480 g/L SL	0.48		100–200	1	70	Application timing BBCH 32–39		
00548BX1 Chaunac, France, 2000 (Aztec)	480 g/L SL	0.48 (BBCH 38)	0.14	333	1	90	Grain	< 0.05	Ballasteros, 2002, R&D/CRLD/AN/mr/0115433 (M-208087-01-1)
00548LY1 La Boisse, France, 2000 (Cyrano)	480 g/L SL	0.48 (BBCH 39)	0.15	320	1	78	Grain	< 0.05	Ballasteros, 2002, R&D/CRLD/AN/mr/0115433 (M-208087-01-1)
00549BX1 Tugeras, France, 2000 (Hyno-valea)	480 g/L SL	0.47 (BBCH 39)	0.14	333	1	90	Grain	< 0.05	Ballasteros, 2002, R&D/CRLD/AN/mr/0115434 (M-208091-01-1)
00549TL1 Baziege, France, 2000 (Tremie)	480 g/L SL	0.48 (BBCH 37-39)	0.17	278	1	91	Grain	< 0.05	Ballasteros, 2002, R&D/CRLD/AN/mr/0115434 (M-208091-01-1)
01R772-1 Boe, France, 2001 (Soissons)	480 g/L SL	0.48 (BBCH 39)	0.19	250	1	74	Grain	< 0.05	Davies, 2002, 01R772 (M-210308-01-1)
01R772-2 Saint Romain De Jeolienas, France, 2001 (Aztec)	480 g/L SL	0.48 (BBCH 39)	0.19	250	1	74	Grain	< 0.05	Davies, 2002, 01R772 (M-210308-01-1)
01R772-3 Dodici Morelli, Italy, 2001 (Centauro)	480 g/L SL	0.48 (BBCH 39)	0.14	350	1	57	Grain	< 0.05	Davies, 2002, 01R772 (M-210308-01-1)
01R772-4 Paradas Sevilla, Spain, 2001 (Simeto)	480 g/L SL	0.48 (BBCH 39)	0.16	300	1	78	Grain	< 0.05	Davies, 2002, 01R772 (M-210308-01-1)
01R772-5 Alcala de Guadaira Sevilla, Spain, 2001 (Sula)	480 g/L SL	0.48 (BBCH 39)	0.16	300	1	76	Grain	< 0.05	Davies, 2002, 01R772 (M-210308-01-1)
GAP, France	450 g/L SL [a]	0.38		100–200	1	–	Application timing BBCH 31–37		

WHEAT Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
R 2004 0564/2 Staffanstorp, Sweden, 2004 (Marshall)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	85	Grain	< 0.05	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0565/0 Leverkusen, Germany, 2004 (Batis)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	92	Grain	< 0.05	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0566/9 Werl-Oberbergstraße, Germany, 2004 (Winnetou)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	81	Grain	< 0.05	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0567/7 Villettes, France, 2004 (Orvantis)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	84	Grain	< 0.05	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0568/5 Kilkis, Greece, 2004 (Mexicalli)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	57	Grain	< 0.05	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0569/3 Gargas, France, 2004 (Garric)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	77	Grain	< 0.05	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0570/7 Brenes, Spain, 2004 (Don Pedro)	450 g/L SL [a]	0.38 (BBCH 41–45)	0.12	300	1	78	Grain	< 0.05	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0571/5 Pereiro/Alenquer, Portugal, 2004 (Sula)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	82	Grain	< 0.05	Bardel, 2005, RA-2091/04 (M-251236-02-1)
GAP, Belgium	480 g/L SL	0.60		200–400	1	–	Application timing BBCH 37–45		
R 2006 0123/9 Chaussy, France, 2006 (Isengrain)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	56 64	Ear Grain	0.09 0.06	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2006 0293/6 Bury St Edmunds, UK, 2006 (Einstein)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	56 68	Ear Grain Straw	< 0.05 < 0.05	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2006 0294/4 Leverkusen, Germany, 2006 (Batis)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	56 73	Ear Grain	< 0.05 < 0.05	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2007 0175/6 Chambourg sur Indre, France, 2007 (Apache)	480 g/L SL	0.72 (BBCH 39)	0.24	300	1	56 85	Ear Grain	0.07 < 0.05	Billian, 2008, RA-2575/07 (M-312007-01-1)
R 2007 0186/1 Werl-Westönnen, Germany, 2007 (Ritmo)	480 g/L SL	0.77 (BBCH 49)	0.24	321	1	56 65	Ear Grain	0.09 < 0.05	Billian, 2008, RA-2575/07 (M-312007-01-1)

[a] 450 g/L SL formulation (150 g/L ethephon + 300 g/L chlormequat-chloride)

Table 60 Ethephon and HEPA residues in wheat grains resulting from supervised trials in Europe obtained using an analytical method involving acid hydrolysis/extraction

WHEAT Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	HEPA mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Germany	660 g/L SL	0.46		100–300	1	–	Application timing BBCH 37–51		
13-2029-01 Bursheid, Germany 2013 (Winnetou Soft)	480 SL	0.48 (BBCH 51)	0.16	300	1	75	0.059	0.027	Schulte & Berkum, 2015, 13-2029 M-529493-01-1
13-2029-02 Villars-Perwin, Belgium, 2013 (Matrix Soft)	480 SL	0.48 (BBCH 51)	0.16	300	1	61	0.059	0.029	Schulte & Berkum, 2015, 13-2029 M-529493-01-1
13-2029-03 Little Shelford CB22 5EU, United Kingdom 2013 (Claire Soft)	480 SL	0.48 (BBCH 51)	0.24	200	1	74	0.11	0.080	Schulte & Berkum, 2015, 13-2029 M-529493-01-1
14-2018-01 Vechta – Langförden, Germany, 2014 (Winnetou mass-wheat)	480 SL	0.48 (BBCH 51)	0.16	300	1	71	0.083	0.031 (c, 0.013)	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-02 Burscheid, Germany 2014 (Tobak)	480 SL	0.48 (BBCH 51)	0.16	300	1	68	0.14	0.040	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-03 SG8 8S Great Chishill, United Kingdom, 2014 (Solstice Milling)	480 SL	0.48 (BBCH 51)	0.24	200	1	64	0.23	0.089 (c, 0.043)	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-04 France Chambourg sur Indre, 2014 (Touareg Winter)	480 SL	0.48 (BBCH 51)	0.16	300	1	77	0.052	0.019 (c, 0.015)	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-05 Slootdorp, Netherlands 2014	480 SL	0.48 (BBCH 51)	0.12	400	1	54	0.31	0.046	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
GAP, France	480 g/L SL	0.48		100–200	1	70	Application timing BBCH 32–39		
14-2019-01 Gargas, France 2014 (Solehio Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	77	0.025	0.019 (c, 0.023)	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
14-2019-02 Brenes, Spain 2014 (Don Pedro)	480 SL	0.48 (BBCH 39)	0.16	400	1	72	0.011	0.019	Schulte & Berkum, 2015, 14-2019 M-532272-01-1

WHEAT Trial No Country, year (Variety)	Application					DALT days	Ethephon mg/kg	HEPA mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
14-2019-03 Bologna, Italy 2014 (Mieti Winter)	480 SL	0.48 (BBCH 39)	0.12	300	1	58	0.10	0.042	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
14-2019-04 Aramanha-Santarem, Portugal, 2014 (Artur Nick 2)	480 SL	0.48 (BBCH 39)	0.16	300	1	110	0.043	0.031 (c, 0.029)	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
13-2030-01 Castelnau d'estretefonds, France, 2013 (Hystar Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	80	0.049	0.037 (c, 0.017)	Schulte & Berkum, 2015, 13-2030 M-529488-01-1
13-2030-02 El Campillo, Spain, 2013 (Artur Nick Soft)	480 SL	0.52 (BBCH 39)	0.16	322	1	64	0.057	0.029	Schulte & Berkum, 2015, 13-2030 M-529488-01-1
13-2030-03 Tarquinia, Italy 2013 (Quality Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	63	0.13	0.044	Schulte & Berkum, 2015, 13-2030 M-529488-01-1
13-2030-04 Bologna, Italy 2013 (Serio Soft)	480 SL	0.48 (BBCH 39)	0.14	350	1	62	0.010	0.014	Schulte & Berkum, 2015, 13-2030 M-529488-01-1

Supervised trials in USA

Sixteen supervised trials were conducted in wheat.

In the 1981 trials, a 480 g/L SL formulation was applied as a single foliar broadcast spray to wheat at a rate of 0.56–0.59 or 0.84 kg ai/ha. Application was made at the early-late boot growth stage. Residues of ethephon were determined using a method similar to SOP 90074, entitled “Detailed Method of Analysis for residues of (2-Chloroethyl)Phosphonic Acid (Ethephon) in Wheat and Barley Grain, Straw and Milling Fractions”, dated December 1981.

In the 1989 trials, a 480 g/L SL formulation was applied as a single foliar spray to wheat at a rate of 0.56 kg ai/ha. Application was made at the late boot to inflorescence emergence growth stage. Residues of ethephon were determined using the same method as above.

The samples were stored frozen at approximately –20 °C for the maximum period of storage was 5 months for the 1981 study and 29 months for the 1989 study.

Table 61 Ethephon residues in wheat grains resulting from supervised trials in the USA

WHEAT Trial Country, year (Variety)	Application					DALT	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		
GAP, Canada	240 g/L SL	0.60		30–300	1	35	Application from BBCH 37–49	
10223-W1 Arkansas City, Kansas, USA, 1981 (Newton)	480 g/L SL	0.84 (late boot)	–	–	1	55	0.16 (0.17, 0.17, 0.15, 0.13) [a]	Harrison, 1981, 10223 (M-187972-01-1)

WHEAT Trial Country, year (Variety)	Application					DALT	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		
10223-W2 Landisville, Pennsylvania, USA, 1981 (Redcoat)	480 g/L SL	0.84 (boot)	–	–	1	49	0.07 (0.07, 0.08, 0.05, 0.09)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W3 Skaneateles, New York, USA, 1981 (Hauser)	480 g/L SL	0.84 (boot)	–	–	1	41	0.15 (0.15, 0.06, 0.12, 0.27)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W4 Newton, Iowa, USA, 1981 (Sage Hard Red)	480 g/L SL	0.56 (early boot)	–	–	1	54	0.04 (0.02, 0.06, 0.04)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W5 Sandusky, Michigan, USA, 1981 (Arthur)	480 g/L SL	0.56 (early boot)	–	–	1	62	0.15 (0.08, 0.18, 0.19)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W6 Newcastle, Ohio, USA, 1981 (Titan)	480 g/L SL	0.56 (early boot)	–	–	1	63	0.03 (0.04, 0.04, 0.03, < 0.02)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W7 Glyndon, Minnesota, USA, 1981 (Era)	480 g/L SL	0.56 (early boot)	–	–	1	57	0.02 (< 0.02, < 0.02, 0.02, 0.02)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W8 Powell, Wyoming, USA, 1981 (Prodax)	480 g/L SL	0.84 (boot)	–	–	1	57	0.34 (0.26, 0.36, 0.39)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W9 Warsaw, Illinois, USA, 1981 (Pioneer)	480 g/L SL	0.56 (mid boot)	–	–	1	64	< 0.02 (< 0.02,< 0.02,< 0.02)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W10 Rock Springs, Pennsylvania, USA, 1981 (Titan)	480 g/L SL	0.56	–	–	1	48	0.04 (0.05, 0.03, 0.04, 0.05)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W11 Elora, Ontario, Canada, 1981 (Frederick)	480 g/L SL	0.59	–	–	1	53	0.35	Harrison, 1981, 10223 (M-187972-01-1)
SARS-89-CO-24 Brighton, Colorado, USA, 1989 (Hawk)	480 g/L SL	0.56 (aerial) (late boot to 1/4 inflorescence emerged)	2.0	28	1	35 40 60	0.65 (0.65, 0.70, 0.60) 0.58 (0.58, 0.50, 0.67) 0.23 (0.29, 0.17, 0.23)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot to 1/4 inflorescence emerged)	0.83	67	1	35 40 60	0.61 (0.61, 0.61, 0.60) 0.40 (0.48, 0.42, 0.30) 0.16 (0.15, 0.18, 0.14)	

WHEAT Trial Country, year (Variety)	Application					DALT	Ethephon mg/kg	Reference
	Form. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		
SARS-89-KS-24 Sedan, Kansas, USA, 1989 (Thinderbird)	480 g/L SL	0.56 (aerial) (3/4 inflorescence emerged)	2.1	27	1	35 40 60	0.68 (0.94, 0.28, 0.82) 0.33 (0.35, 0.27, 0.38) 0.10 (0.08, 0.14, 0.09)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (3/4 inflorescence emerged)	0.86	65	1	35 40 60	0.53 (0.56, 0.52, 0.52) 0.33 (0.29, 0.34, 0.35) 0.10 (0.08, 0.09, 0.12)	
SARS-89-MN-24 East Grand Forks, Minnesota, USA, 1989 (Marshall)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	35 41 59	0.08 (0.07, 0.08, 0.08) 0.08 (0.07, 0.08, 0.10) < 0.05 (< 0.05, < 0.05, < 0.05)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot)	0.86	65	1	35 41 59	0.13 (0.12, 0.13, 0.14) 0.12 (0.11, 0.12, 0.14) 0.05 (< 0.05, 0.05, < 0.05)	
SARS-89-ND-24 Northwood, North Dakota, USA, 1989 (Butte 86)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	35 40 60	0.33 (0.30, 0.36, 0.32) 0.15 (0.18, 0.13, 0.15) 0.08 (0.09, 0.07, 0.07)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot)	0.86	65	1	35 40 60	0.25 (0.30, 0.24, 0.21) 0.14 (0.15, 0.14, 0.14) 0.08 (0.09, 0.06, 0.10)	
SARS-89-WA-24 Ephrata, Washington, USA, 1989 (Madson)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	40 60 70	0.15 (0.14, 0.12, 0.18) 0.14 (0.11, 0.14, 0.16) 0.07 (0.08, 0.07, 0.07)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot)	0.73	77	1	40 60 70	0.30 (0.31, 0.40, 0.20) 0.24 (0.24, 0.25, 0.23) 0.15 (0.14, 0.13, 0.19)	

[a] Mean residue. Analytical results of replicate samples were in parentheses.

Cotton seed

A total of ten supervised trials were conducted in Greece and Spain. A 540 g/L SC formulation was applied as a foliar spray to cotton at a nominal rate of 1.44 kg ai/ha (actual rate range 1.41–1.53 kg ai/ha). In the trials conducted in Greece in 1993 and 1995, an additional plot was treated at a nominal rate of 2.88 kg ai/ha (actual rate range 2.79–2.93 kg ai/ha). In the 1993–1995 studies, residues of ethephon were determined using method HVA 12/89. In the 2008 study, residues of ethephon were determined using method 00918. The maximum period of storage of frozen cotton seed samples, except described below, at < –18 °C was 14 months.

In trial 93739GR1, samples were stored at room temperature for 3 months and then frozen (–20 °C) for 13 months prior to analysis. As storage stability data indicate that residues of ethephon are not stable in cotton seed when stored at room temperature, these data will not be considered in the estimation of maximum residue level. In trials 94681SE1, 94681SE2 and 94681SE3, samples were stored in a cold room for 1 month and then frozen (–20 °C) for 4 months prior to analysis.

A total of forty-one supervised trials were conducted in the USA. In the 1989 trials, a 720 g/L SL formulation was applied as a single foliar spray to cotton at a rate of 2.24 kg ai/ha by ground or aerial application. Residues of ethephon were determined using method SOP 90075. In the 1993 trials, a 540 g/L SC formulation was applied as a single foliar spray to cotton at a nominal rate of 2.24 kg ai/ha by ground application. Residues of ethephon were determined using method EC-92-228. In the 1994 trials, a 540 g/L SC formulation was applied as a single foliar

spray to cotton at a nominal rate of 2.24 kg ai/ha by ground application. Residues of ethephon in seed and gin trash were determined using method EC-92-228. The maximum period of storage of frozen samples at < –10 °C was 12 months for seed and 6.3 months for gin trash.

A total of seven supervised trials were conducted in Brazil. In the 1996 trials, a 480 g/L SL formulation was applied as a foliar spray to cotton at a nominal rate of 1.44 kg ai/ha in one plot and at 2.88 kg ai/ha in the other. In the 2006 trials (HR06BR008-P1 to -P4), a 540 g/L SC formulation was applied as a foliar spray to cotton at a nominal rate of 1.20 kg ai/ha. Residues of ethephon were determined using method 11-94 (ethylene release). The maximum period of storage of frozen samples at < –10 °C was 12 months.

Table 62 Ethephon residues in cotton seed resulting from supervised trials in Europe, the USA and Brazil

COTTON Trial No. Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
GAP, Greece	480 g/L SL	1.44		500–600	1	7		
EUROPE								
93739GR1 Arma Thiva-Viotia, Greece, 1993 (Zeta II)	540 g/L SC [a]	1.44	0.36	400	1	7	< 0.10	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515891 (M-163122-01-1)
	540 g/L SC [a]	2.88	0.72	400	1	7	0.12	
94681SE1 Carlota-AL, Spain, 1994 (Cnema 111)	540 g/L SC [a]	1.44	0.36	400	1	0 3 7	< 0.10 0.35 0.59	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
94681SE2 Carlota-ZA, Spain, 1994 (Cnema 111)	540 g/L SC [a]	1.44	0.36	400	1	0 3 7	< 0.10 0.15 0.30	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
94681SE3 Ecija, Spain, 1994 (Cnema 111)	540 g/L SC [a]	1.44	0.36	400	1	0 3 7	2.09 0.29 1.13	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
95723SE1 Ciatr Sevilla, Spain, 1995 (Corona)	540 g/L SC [a]	1.44	0.33	440	1	7	0.19	Muller, 1996, R&D/CRLD/AN/bd/ 9516706 (M-163236-01-1)
95705GR1 Nicaea-Larissa, Greece, 1995 (Zeta 2)	540 g/L SC [a]	1.48	0.16	911	1	8	< 0.10	Muller, 1996, R&D/CRLD/AN/vg/ 9516705 (M-163240-01-1)
	540 g/L SC [a]	2.79	0.31	911	1	8	0.20	
95705GR2 Larissa, Greece, 1995 (Zeta 2)	540 g/L SC [a]	1.46	0.16	912	1	8	< 0.10	Muller, 1996, R&D/CRLD/AN/vg/ 9516705 (M-163240-01-1)
	540 g/L SC [a]	2.93	0.32	912	1	8	< 0.10	
95705GR3 Stavros-Lamia, Greece, 1995 (Zeta 2)	540 g/L SC [a]	1.41	0.16	892	1	8	0.35	Muller, 1996, R&D/CRLD/AN/vg/ 9516705 (M-163240-01-1)
	540 g/L SC [a]	2.93	0.33	892	1	8	0.23	

COTTON Trial No. Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
08-2023-01 Aiginion-Pieria, Greece, 2008 (Carmen)	540 g/L SC [a]	1.44	0.29	500	1	0 7	2.3 (boll) 0.10	Billian, Reineke, Krusell, 2009, 08-2023 (M-360139-01-1)
08-2023-02 Lebrija, Spain, 2008 (Celia)	540 g/L SC [a]	1.53	0.29	533	1	0 7	1.7 (boll) 0.07	Billian, Reineke, Krusell, 2009, 08-2023 (M-360139-01-1)
GAP, USA	765 g/L SC [b]	2.24		28–234	1	7		
GAP, USA	720 g/L SC	2.24		19–94	1	7		
USA								
89-156 Harmon Co., OK, USA, 1989 (Stoneville 483)	720 g/L SL	2.24 (aerial)	11.4	19.7	1	7 10 14	0.23 (0.24, 0.26, 0.20) 0.47 (0.45, 0.51, 0.45) 0.56 (0.77, 0.76, 0.14)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-157 Harmon Co., OK, USA, 1989 (Stoneville 483)	720 g/L SL	2.24 (ground)	1.34	167	1	7 10 14	0.58 (0.64, 0.52, 0.59) 0.75 (0.78, 0.75, 0.72) 0.70 (0.65, 0.83, 0.62)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-159 Maricopa Co., AZ, USA, 1989 (DP-L90)	720 g/L SL	2.24 (aerial)	4.79	46.7	1	7 10 14	0.55 (0.49, 0.57, 0.58) 0.95 (1.2, 0.64, 1.0) 0.45 (0.55, 0.10, 0.71)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-160 Maricopa Co., AZ, USA, 1989 (DP-L70)	720 g/L SL	2.24 (ground)	2.08	107	1	7 10 14	2.4 (2.1, 2.9, 2.1) 2.2 (2.7, 1.8, 2.0) 1.9 (2.4, 2.0, 1.4)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-161 Lonoke Co., AR, USA, 1989 (Stoneville 506)	720 g/L SL	2.24 (ground)	1.60	140	1	7 10 14	0.10 (0.10, 0.09, 0.10) 0.18 (0.20, 0.17, 0.16) 0.24 (0.22, 0.33, 0.18)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-162 Tulare Co., CA, USA, 1989 (Acala GC-510)	720 g/L SL	2.24 (aerial)	4.79	46.7	1	7 10 14	0.10 (0.08, 0.09, 0.12) 0.09 (0.16, 0.05, 0.07) 0.16 (0.22, 0.12, 0.15)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-163 Wharton Co., TX, USA, 1989 (DES 119)	720 g/L SL	2.24 (ground)	1.58	142	1	7 10 14	0.06 (0.07, 0.05, 0.06) 0.05 (0.05, 0.04, 0.06) 0.02 (< 0.02, < 0.02, 0.03)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-164 Wharton Co., TX, USA, 1989 (DES 119)	720 g/L SL	2.24 (aerial)	12.0	18.7	1	7 10 14	0.03 (< 0.02, 0.06, < 0.02) < 0.02 (< 0.02, < 0.02, < 0.02) < 0.02 (< 0.02,< 0.02, < 0.02)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-165 Burke Co., GA, USA, 1989 (DPL 90)	720 g/L SL	2.24 (ground)	1.44	155	1	7 10 14	0.31 (0.35, 0.36, 0.21) 0.34 (0.38, 0.37, 0.27) < 0.02 (< 0.02, < 0.02, < 0.02)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-166 Burke Co., GA, USA, 1989 (DPL 90)	720 g/L SL	2.24 (aerial)	10.4	21.5	1	7 10 14	0.65 (0.82, 0.51, 0.61) 0.35 (0.54, 0.07, 0.45) 0.36 (0.43, 0.26, 0.39)	Nygren, 1991, USA89I03 (M-187602-01-1)

COTTON Trial No. Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
89-167 Hale Co., TX, USA, 1989 (Paymaster 145)	720 g/L SL	2.24 (aerial)	12.0	18.6	1	7 10 14	0.54 (0.42, 1.0, 0.21) 0.91 (0.42, 1.5, 0.82) 1.42 (0.25, 2.0, 2.0)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-168 Lynn Co., TX, USA, 1989 (Paymaster HS26)	720 g/L SL	2.24 (ground)	1.70	132	1	7 10 14	0.46 (0.42, 0.50, 0.47) 0.86 (0.78, 0.69, 1.1) 0.70 (0.58, 0.71, 0.80)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-169 Curry Co., NM, USA, 1989 (Paymaster 792)	720 g/L SL	2.24 (ground)	1.70	132	1	7 10 14	1.5 (1.6, 1.6, 1.4) 1.1 (1.3, 0.92, 1.1) 1.5 (1.6, 1.2, 1.8)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-170 Sharkey Co., MS, USA, 1989 (DPL 50)	720 g/L SL	2.24 (ground)	1.63	137	1	7 10 14	0.50 (0.69, 0.35, 0.45) 0.09 (0.10, 0.05, 0.12) 0.10 (0.12, 0.08, 0.11)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-171 Sharkey Co., MS, USA, 1989 (DPL 50)	720 g/L SL	2.24 (ground)	1.63	137	1	7 10 14	0.61 (0.54, 0.80, 0.49) 0.42 (0.21, 0.90, 0.16) 0.07 (0.09, 0.11, < 0.02)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-172 Sharkey Co., MS, USA, 1989 (DPL 50)	720 g/L SL	2.24 (aerial)	12.1	18.5	1	7 11 14	0.44 (0.42, 0.34, 0.56) 0.16 (0.24, 0.12, 0.11) 0.22 (0.03, 0.58, 0.04)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-173 Tulare Co., CA, USA, 1989 (Acala GC510)	720 g/L SL	2.24 (aerial)	4.89	45.8	1	7 10 14	0.35 (0.25, 0.28, 0.53) 0.21 (0.28, 0.12, 0.22) 0.05 (0.04, 0.05, 0.05)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-174 Fresno Co., CA, USA, 1989 (GC-510)	720 g/L SL	2.24 (ground)	1.20	187	1	7 10 14	0.36 (0.54, 0.30, 0.25) 0.16 (0.19, 0.12, 0.18) 0.19 (0.14, 0.22, 0.21)	Nygren, 1991, USA89I03 (M-187602-01-1)
89-175 Lonoke Co., AR, USA, 1989 (DPL 50)	720 g/L SL	2.24 (aerial)	11.5	19.5	1	7 11 14	0.03 (< 0.02, 0.03, 0.03) < 0.02 (< 0.02, < 0.02, < 0.02) 0.11 (0.06, 0.18, 0.10)	Nygren, 1991, USA89I03 (M-187602-01-1)
93-0257 Hale Co., TX, USA, 1993 (Paymaster HS-200)	540 g/L SC	2.20 (ground)	1.30	168	1	7	0.59 (0.50, 0.52, 0.76)	See, 1994, USA93I03R (M-252199-01-1)
93-0258 Lenoir, NC, USA, 1993 (Chembred 1135)	540 g/L SC	2.26 (ground)	1.61	140	1	7	0.23 (0.20, 0.23, 0.26)	See, 1994, USA93I03R (M-252199-01-1)
93-0259 Yuma Co., AZ, USA, 1993 (Deltapine 50)	540 g/L SC	2.22 (ground)	1.58	140	1	7	2.42 (2.20, 2.59, 2.48)	See, 1994, USA93I03R (M-252199-01-1)
93-0260 Fresno, CA, USA, 1993 (Acala SJ-2)	540 g/L SC	3.18 (ground)	2.27	140	1	7	0.59 (1.25, 0.23, 0.29)	See, 1994, USA93I03R (M-252199-01-1)
93-0261 Backgate, AR, USA, 1993 (D&PL50)	540 g/L SC	2.35 (ground)	1.68	140	1	7	0.11 (0.12, 0.10, 0.12)	See, 1994, USA93I03R (M-252199-01-1)

COTTON Trial No. Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
93-0262 Barnwell Co., SC, USA, 1993 (Delta Pine 90-Acala)	540 g/L SC	2.33 (ground)	1.66	140	1	7	0.55 (0.69, 0.56, 0.40)	See, 1994, USA93I03R (M-252199-01-1)
93-0263 Mitchel Co., GA, USA, 1993 (Deltapine 90-Acala)	540 g/L SC	2.24 (ground)	1.20	187	1	7	0.10 (0.12, 0.11, 0.06)	See, 1994, USA93I03R (M-252199-01-1)
93-0264 Fresno Co., CA, USA, 1993 (GS 10)	540 g/L SC	3.77 (ground)	2.02	187	1	7	0.99 (1.06, 1.12, 0.80)	See, 1994, USA93I03R (M-252199-01-1)
93-0265 Crittenden Co., AR, USA, 1993 (Stoneville 453)	540 g/L SC	2.13 (ground)	1.52	140	1	7	0.41 (0.42, 0.41, 0.41)	See, 1994, USA93I03R (M-252199-01-1)
93-0266 St. Landry, LA, USA, 1993 (Deltapine 50)	540 g/L SC	2.26 (ground)	1.61	140	1	7	0.26 (0.21, 0.34, 0.22)	See, 1994, USA93I03R (M-252199-01-1)
94-0284 Wharton Co., TX, USA, 1994 (Deltapine 20)	540 g/L SC	2.31 (ground)	1.54	150	1	7	0.16 (0.17, 0.14)	See, 1995, USA94I01R (M-253436-01-1)
94-0285 Castro Co., TX, USA, 1994 (Paymaster 145)	540 g/L SC	2.25 (ground)	1.53	147	1	7	2.88 (2.48, 3.28)	See, 1995, USA94I01R (M-253436-01-1)
94-0286 Floyd Co., TX, USA, 1994 (Paymaster HS-200)	540 g/L SC	2.43 (ground)	1.54	158	1	7	0.69 (0.70, 0.67)	See, 1995, USA94I01R (M-253436-01-1)
94-0287 Fresno, CA, USA, 1994 (Maxxa)	540 g/L SC	2.22 (ground)	1.59	139	1	7	0.18 (0.15, 0.21)	See, 1995, USA94I01R (M-253436-01-1)
94-0288 Washington Co., MS, USA, 1994 (DPL 50)	540 g/L SC	2.26 (ground)	1.59	142	1	7	0.54 (0.56, 0.52)	See, 1995, USA94I01R (M-253436-01-1)
94-0289 Houseton Co., AL, USA, 1994 (DPL 5415)	540 g/L SC	2.28 (ground)	1.64	139	1	8	0.26 (0.29, 0.22)	See, 1995, USA94I01R (M-253436-01-1)
94-0290 Madera Co., CA, USA, 1994 (Maxa)	540 g/L SC	2.17 (ground)	1.18	184	1	6	2.73 (2.34, 3.12)	See, 1995, USA94I01R (M-253436-01-1)
94-0291 Fayette Co., TN, USA, 1994 (Stoneville 453)	540 g/L SC	2.25 (ground)	1.57	143	1	7	1.18 (1.38, 0.97)	See, 1995, USA94I01R (M-253436-01-1)
94-0292 Crittenden Co., AR, USA, 1994 (Stoneville 453)	540 g/L SC	2.27 (ground)	1.62	140	1	7	0.09 (0.096, 0.080)	See, 1995, USA94I01R (M-253436-01-1)

COTTON Trial No. Country, year (Variety)	Application					DALT days	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No			
94-0293 Burleson Co., TX, USA, 1994 (DP&L 5415)	540 g/L SC	2.24 (ground)	1.56	144	1	9	0.12 (0.12, 0.12)	See, 1995, USA94I01R (M-253436-01-1)
94-0393 Hale Co., TX, USA, 1994 (Paymaster HS-200)	540 g/L SC	2.32 (ground)	1.53	151	1	7	4.93 (4.21, 5.65)	See, 1995, USA94I01R (M-253436-01-1)
94-0394 Hale Co., TX, USA, 1994 (Paymaster 145)	540 g/L SC	2.27 (ground)	1.45	157	1	7	2.29 (2.32, 2.26)	See, 1995, USA94I01R (M-253436-01-1)
GAP, Brazil	540 g/L SC [a]	1.20		200–500	1	7		
GAP, Peru	720 g/L SL	1.44			1	7–14		
BRAZIL								
003/97-PC-01 Holambra SP, Brazil, 1996 (IAC-20)	480 g/L SL	1.44	–	–	1	7	< 0.20	Garcia, 1997, CP-2466/97 (M-188222-01-1)
	480 g/L SL	2.88	–	–	1	7	< 0.20	
055/96-PC EAE Paulinia SP, Brazil, 1996 (IAC-22)	480 g/L SL	1.44	0.36	400	1	7	< 0.20	Garcia & Oliverira, 1997, CP-2435/97 (M-253467-02-1)
	480 g/L SL	2.88	0.72	400	1	7	< 0.20	
056/96-PC Holambra SP, Brazil, 1996 (IAC-20)	480 g/L SL	1.44	0.36	400	1	7	< 0.20	Garcia & Oliverira, 1997, CP-2436/97 (M-253470-02-1)
	480 g/L SL	2.88	0.72	400	1	7	< 0.20	
HR06BRA008-P1 Paulinia SP, Brazil, 2006 (Delta Opal)	540 g/L SC [a]	1.20	0.24	500	1	7	< 0.10	Galhiane & Santos, 2006, RA-218/06 (M-285068-01-2)
HR06BRA008-P2 Rondonopolis MT Brazil, 2006 (Delta Opal)	540 g/L SC [a]	1.20	0.24	500	1	7	< 0.10	Galhiane & Santos, 2006, RA-219/06 (M-285070-01-2)
HR06BRA008-P3 Costa Rica MS, Brazil, 2006 (Delta Opal)	540 g/L SC [a]	1.20	0.24	500	1	7	< 0.10	Galhiane & Santos, 2006, RA-220/06 (M-285073-01-2)
HR06BRA008-P4 Rio Verde GO, Brazil, 2006 (FMX 966)	540 g/L SC [a]	1.20	0.24	500	1	7	< 0.10	Galhiane & Santos, 2006, RA-221/06 (M-285075-01-2)

[a] 540 g/L SC formulation (480 g/L ethephon + 60 g/L cyclanilide)

[b] 765 g/L SC formulation (720 g/L ethephon + 45 g/L cyclanilide)

Primary feed commodities

Barley forage and straw

Thirty-seven supervised trials have been conducted in barley in Europe.

Table 63 Ethephon residues in barley forage and straw resulting from supervised trials in Europe

BARLEY	Application					DALT	Portion analysed	Ethephon	Reference
Trial No. Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
GAP, Germay	660 g/L SL	0.462		100– 300	1	–	Application timing BBCH 32–49		
GAP, UK	480 g/L SL	0.48		100– 400	–	–	Application timing BBCH 32–49 Maximum total rate 0.48 kg ai/ha		
DR00EUS525 ITA0101 Bologna, Italy, 2000 (Express)	480 g/L SL	0.48 (BBCH 47)	0.16	300	ß1	0 11 48	Green plant Green plant Straw	10 0.23 0.08	Hees, 2001, DR00EUS525 (M-199982-01-1)
DR00EUS525 ITA0102 S. Mauro Pascoli, Italy, 2000 (Extra)	480 g/L SL	0.48 (BBCH 45)	0.16	300	1	0 18 47	Green plant Green plant Straw	11 0.35 0.63	Hees, 2001, DR00EUS525 (M-199982-01-1)
00547BX1 Marignac, France, 2000 (Sunrise)	480 g/L SL	0.48 (BBCH 45)	0.14	333	1	0 14 27 52	Green plant Green plant Green plant Straw	8.1 1.3 0.47 0.25	Ballasteros, 2001, R&D/CRLD/AN/mr/0115430 (M-208093-01-1)
00547TL1 Gardouch, France, 2000 (Esterel)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	0 14 25 62	Green plant Green plant Green plant Straw	5.1 1.9 0.90 0.43	Ballasteros, 2001, R&D/CRLD/AN/mr/0115430 (M-208093-01-1)
01R761-1 Ronchères, France, 2001 (Platine)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	0 69	Green plant Straw	5.7 0.06	Davies, 2002, 01R761 (M-209901-01-1)
01R761-2 Hargicourt, France, 2001 (Muscat)	480 g/L SL	0.48 (BBCH 49)	0.19	250	1	0 12 28 54	Green plant Green plant Green plant Straw	2.6 0.86 0.48 0.21	Davies, 2002, 01R761 (M-209901-01-1)
01R761-3 Braintree, UK, 2001 (Regina)	480 g/L SL	0.48 (BBCH 55)	0.19	252	1	0 6 28 58	Green plant Green plant Green plant Straw	9.3 5.8 1.6 0.95	Davies, 2002, 01R761 (M-209901-01-1)
01R761-4 Weilerswist, Germany, 2001 (Theresa)	480 g/L SL	0.48 (BBCH 51)	0.16	300	1	0 9 35 60	Green plant Green plant Green plant Straw	6.2 0.80 0.66 1.1	Davies, 2002, 01R761 (M-209901-01-1)
01R761-5 Zschortau, Germany, 2001 (Landi)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	0 66	Green plant Straw	4.2 0.33	Davies, 2002, 01R761 (M-209901-01-1)
01R771-1 Senestis, France, 2001 (Platine)	480 g/L SL	0.48 (BBCH 45)	0.19	250	1	0 64	Green plant Straw	9.4 < 0.05	Davies, 2002, 01R771 (M-210307-01-1)
01R771-2 Toussieux, France, 2001 (Ladoga)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	0 20 27 63	Green plant Green plant Green plant Straw	8.4 1.1 0.81 0.09	Davies, 2002, 01R771 (M-210307-01-1)
01R771-3 Genas, France, 2001 (Ladoga)	480 g/L SL	0.48 (BBCH 47)	0.19	250	1	0 14 33 57	Green plant Green plant Green plant Straw	4.8 2.1 1.4 0.36	Davies, 2002, 01R771 (M-210307-01-1)

BARLEY	Application					DALT	Portion analysed	Ethephon	Reference
Trial No. Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
01R771-4 Alberone Di Cento, Italy, 2001 (Sonora)	480 g/L SL	0.48 (BBCH 47)	0.14	350	1	0 9 20 35	Green plant Green plant Green plant Straw	4.4 5.2 1.7 0.24	Davies, 2002, 01R771 (M-210307-01-1)
01R771-5 Xirochori-Kilkis, Greece, 2001 (Athinaida)	480 g/L SL	0.48 (BBCH 47)	0.16	300	1	0 50	Green plant Straw	3.0 < 0.05	Davies, 2002, 01R771 (M-210307-01-1)
GAP, France	480 g/L SL	0.48		100–200	1	56	Application timing BBCH 32–39		
R 2004 0577/4 Monospita, Greece, 2004 (Kannon (distiho))	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 11 54	Green plant Green plant Straw	8.1 0.20 < 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0578/2 Bologna, Italy, 2004 (Marjorie)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 12 54	Green plant Green plant Straw	6.0 0.09 < 0.05	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0579/0 Vouillé, France, 2004 (Scarlette)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 20 56	Green plant Green plant Straw	6.7 0.21 0.12	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0580/4 Balaguer, Spain, 2004 (Prestige)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 15 53	Green plant Green plant Straw	5.2 0.30 0.27	Bardel & Wolters, 2005, RA-2093/04 (M-251235-01-1)
R 2004 0572/3 Lund, Sweden, 2004 (Bombay)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 21 80	Green plant Green plant Straw	9.5 0.45 0.07	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0573/1 Leverkusen, Germany, 2004 (Condesse)	450 g/L SL [a]	0.38 (BBCH 37)	0.125	300	1	0 19 85	Green plant Green plant Straw	3.9 < 0.05 < 0.05	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0575/8 Weri-Obernergstraße, Germany, 2004 (Intro)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 17 77	Green plant Green plant Straw	5.3 0.11 < 0.05	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2004 0576/6 Fresnoy les Roye, France, 2004 (Esterel)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 17 67	Green plant Green plant Straw	6.2 0.38 0.07	Bardel & Wolters, 2005, RA-2092/04 (M-251366-01-1)
R 2006 0126/3 Neuville de Poitou, France, 2006 (Abondance)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 7 21 59	Green plant Green plant Green plant Straw	5.6 1.1 0.22 0.13	Billian & Erler, 2007, RA-2519/06 (M-290151-01-1)
R 2006 0299/5 Tarascon, France, 2006 (Baraka)	450 g/L SL [a]	0.38 (BBCH 39)	0.125	300	1	0 7 21 60	Green plant Green plant Green plant Straw	8.3 3.4 2.1 1.6	Billian & Erler, 2007, RA-2519/06 (M-290151-01-1)

BARLEY	Application					DALT	Portion analysed	Ethephon	Reference
Trial No. Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
GAP, Poland	480 g/L SL	0.72		150– 300	1	–	Application timing BBCH 32–39		
R 2006 0117/4 Beuvraignes, France, 2006 (Colibri)	480 g/L SL	0.67 (BBCH 37)	0.22	300	1	0 7 21 76	Green plant Green plant Green plant Straw	13 1.1 0.26 < 0.05	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2006 0286/3 Welver-Flerke, Germany, 2006 (Duet)	480 g/L SL	0.67 (BBCH 37)	0.22	300	1	0 7 21 68	Green plant Green plant Green plant Straw	7.1 0.28 0.07 < 0.05	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2006 0285/5 Hoxne/Nreye, UK, 2006 (Sequel)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	0 6 20 74	Green plant Green plant Green plant Straw	9.6 0.60 0.22 0.13	Billian & Telscher, 2007, RA-2515/06 (M-294373-01-1)
R 2007 0172/1 Chaussy, France, 2007 (Sibéria)	480 g/L SL	0.72 (BBCH 37)	0.24	300	1	0 7 21 56 75	Green plant Green plant Green plant Rest of plant Straw	8.9 4.3 0.24 < 0.05 < 0.05	Billian, 2008, RA-2573/07 (M-311809-01-1)
R 2007 0181/0 Lund, Sweden, 2007 (Bombay)	480 g/L SL	0.72 (BBCH 37)	0.24	300	1	0 7 21 56 70	Green plant Green plant Green plant Rest of plant Straw	6.0 0.39 0.08 < 0.05 < 0.05	Billian, 2008, RA-2573/07 (M-311809-01-1)
GAP, France	450 g/L SL [a]	0.23		100– 200	1	–	Application timing BBCH 31–37		
R 2004 0581/2 Le Thil en Vexin, France, 2004 (Scarlet)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 21 57	Green plant Green plant Straw	3.7 0.28 < 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0582/0 Staffanstorp, Sweden, 2004 (Pasadena)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 15 79	Green plant Green plant Straw	5.9 0.16 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0583/9 Burscheid, Germany, 2004 (Scarlett)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 11 61	Green plant Green plant Straw	4.5 0.21 < 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0584/7 Gersthofen, Germany, 2004 (Ursa)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 10 65	Green plant Green plant Straw	3.0 0.11 < 0.05	Bardel & Wolters, 2005, RA-2094/04 (M-249305-02-1)
R 2004 0585/5 Saint Germain sur Renon, France, 2004 (Nevada)	450 g/L SL [a]	0.23 (BBCH 41)	0.075	300	1	0 17 52	Green plant Green plant Straw	5.2 0.27 < 0.05	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)
R 2004 0586/3 Bologna, Italy, 2004 (Federal)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 14 52	Green plant Green plant Straw	5.4 0.28 0.10	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)
R 2004 0587/1 Tarascon, France, 2004 (Baraka)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 6 44	Green plant Green plant Straw	7.5 3.9 3.7	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)

BARLEY	Application					DALT	Portion analysed	Ethephon	Reference
Trial No. Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
R 2004 0589/8 Golegã, Portugal, 2004 (Scarlett)	450 g/L SL [a]	0.23 (BBCH 39)	0.075	300	1	0 21 61	Green plant Green plant Straw	4.1 0.16 0.19	Bardel & Wolters, 2005, RA-2095/04 (M-251234-01-1)

[a] 450 g/L SL formulation (150 g/L ethephon + 300 g/L chlormequat-chloride)

Table 64 Ethephon residues in barley forage and straw resulting from supervised trials in Europe obtained using an analytical method involving acid hydrolysis/extraction

BARLEY Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
13-2027-01 Burscheid, Germany, 2013 (Duett)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 7 14 21 24 59	Green plant Green plant Green plant Green plant Green plant Straw	6.2 0.61 0.55 0.26 0.43 0.51	0.091 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-02 Diegem, Belgium, 2013 (Meridian)	480 SL	0.51 (BBCH 51)	0.19	267	1	0 33 55	Green plant Green plant Straw	3.2 < 0.05 0.35	< 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-03 Mijdrecht, Netherlands, 2013 (Malabar)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 7 14 21 43 56	Green plant Green plant Green plant Green plant Green plant Straw	7.9 3.8 0.85 0.57 0.27 1.5	0.094 0.088 0.085 0.076 0.059 < 0.05	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
13-2027-04 Cambridge, United Kingdom, 2013 (Cassata)	480 SL	0.48 (BBCH 51)	0.24	200	1	0 34 68	Green plant Green plant Straw	6.6 0.36 3.6	0.093 < 0.05 0.066	Schulte & Berkum, 2015, 13-2027 M-526906-01-1
14-2022-01 Langenfeld, Germany, 2014 (Naomie)	480 SL	0.54 (BBCH 51)	0.16	336	1	0 7 14 21 36 78	Green plant Green plant Green plant Green plant Green plant Straw	6.2 0.50 0.29 0.17 0.086 0.64	0.12 < 0.05 < 0.05 < 0.05 < 0.05 0.055	Schulte & Berkum, 2015, 14-2022
14-2022-02 Burscheid, Germany, 2014 (Leibnitz)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 21 64	Green plant Green plant Straw	7.7 0.37 1.2	0.12 < 0.05 0.063 (c, 0.061)	Schulte & Berkum, 2015, 14-2022
14-2022-03 Lyon Cedex 09, France, 2014 (Obite Winter)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 7 14 21 28 56	Green plant Green plant Green plant Green plant Green plant Straw	6.6 0.34 0.15 0.10 < 0.05 0.43	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 14-2022
14-2022-04 Cambridge CB4 0WB, United Kingdom, 2014 (Cassatta Typical UK variety)	480 SL	0.48 (BBCH 55)	0.24	200	1	0 34 73	Green plant Green plant Straw	7.3 0.13 0.78 (c, 0.088)	0.072 0.050 < 0.05	Schulte & Berkum, 2015, 14-2022

BARLEY Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
GAP, France	480 g/ L SL	0.48		100–200	1	56	Application timing BBCH 32-39			
13-2028-01 Ceaux en Loudun, France, 2013 (Cervoise)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 12 21 39 71	Green plant Green plant Green plant Green plant Green plant Straw	4.5 0.24 0.15 0.092 < 0.05 0.23	0.053 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 13- 2028 M-529491- 01-1
13-2028-02 Les Franqueses del Valles, Spain, 2013 (Graphic)	480 SL	0.48 (BBCH 39)	0.16	400	1	0 27 72	Green plant Green plant Straw	4.2 0.26 1.7	0.058 (c, 0.081) < 0.05 0.17 (c, 0.17)	Schulte & Berkum, 2015, 13- 2028 M-529491- 01-1
13-2028-03 Citavecchia, Italy, 2013 (Quench, Distichous barley)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 14 21 24 62	Green plant Green plant Green plant Green plant Green plant Straw	5.9 0.44 0.087 0.078 0.051 0.39	0.051 < 0.05 < 0.05 < 0.05 < 0.05 0.054	Schulte & Berkum, 2015, 13- 2028 M-529491- 01-1
13-2028-04 Bologna, Italy, 2013 (Federal)	480 SL	0.48 (BBCH 39)	0.24	350	1	0 29 64	Green plant Green plant Straw	3.5 < 0.05 0.24	< 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 13- 2028 M-529491- 01-1
14-2020-01 Ceaux en Loudun, France, 2014 (Limpid Winter Barley)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 14 21 42 72	Green plant Green plant Green plant Green plant Green plant Straw	5.6 3.0 3.0 0.38 0.095 1.1	0.069 0.055 0.055 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 14- 2020
14-2020-02 Les Franqueses del Valles, Spain, 2014 (Graphic winterbarley)	480 SL	0.41 (BBCH 43)	0.12	342	1	0 29 64	Green plant Green plant Straw	6.6 0.36 0.97	0.14 < 0.05 0.080	Schulte & Berkum, 2015, 14- 2020
14-2020-03 Bologna, Italy, 2014 (Lutece Winter variety)	480 SL	0.48 (BBCH 39)	0.12	400	1	0 6 14 20 29 64	Green plant Green plant Green plant Green plant Green plant Straw	3.3 1.2 0.34 0.10 < 0.05 0.39	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 14- 2020
14-2020-04 Kristoni Village, Greece, 2014 (Mucho Early, six row, USA)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 48 63	Green plant Green plant Straw	8.2 < 0.05 0.35	0.14 < 0.05 < 0.05	Schulte & Berkum, 2015, 14- 2020

Rye forage and straw

Nine supervised trials have been conducted in rye in Europe.

Table 65 Ethephon residues in rye forage and straw resulting from supervised trials in Europe

RYE	Application					DALT	Portion analysed	Ethephon	Reference
Trial Country, year (Variety)	Formul. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	

RYE	Application					DALT	Portion analysed	Ethephon	Reference
Trial Country, year (Variety)	Formul. (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
GAP, Austria	660 g/L SL	0.73		100–300	1	–	Application timing BBCH 37–49		
GAP, Germany	660 g/L SL	0.73		100–300	1	–	Application timing BBCH 37–49		
R 2006 0119/0 Le Plessier, France, 2006 (Picasso)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	0 7 21 75	Green plant Green plant Green plant Straw	6.4 0.31 0.18 0.26	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0287/1 Thetford, UK, 2006 (Ursus)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	0 7 21 88	Green plant Green plant Green plant Straw	9.6 0.76 0.51 0.34	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0289/8 Svedala, Sweden, 2006 (Matador)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	0 7 21 71	Green plant Green plant Green plant Straw	13 0.66 0.31 0.33	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0290/1 Anneville Ambourville, France, 2006 (Canovus)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	0 7 21 70	Green plant Green plant Green plant Straw	7.7 0.53 0.25 0.21	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2006 0292/8 Beiersdorf, Germany, 2006 (Rekrut)	480 g/L SL	0.67 (BBCH 49)	0.22	300	1	0 7 21 77	Green plant Green plant Green plant Straw	9.2 1.1 0.47 0.12	Billian & Telscher, 2007, RA-2516/06 (M-294780-02-1)
R 2007 0174/8 Le Plessier Rosainvillers, France, 2007 (Picasso)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	0 7 21 49 85	Green plant Green plant Green plant Rest of plant Straw	7.2 1.8 0.24 0.69 0.11	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)
R 2007 0182/9 Burscheid, Germany, 2007 (Fernando)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	0 7 21 49 86	Green plant Green plant Green plant Rest of plant Straw	4.4 2.5 0.12 0.07 < 0.05	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)
R 2007 0184/5 Anneville Ambourville, France, 2007 (Caroass)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	0 7 20 48 83	Green plant Green plant Green plant Rest of plant Straw	9.4 1.2 0.28 0.21 0.14	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)
R 2007 0183/7 Thetford, UK, 2007 (Visello)	480 g/L SL	0.72 (BBCH 49)	0.24	300	1	0 7 21 42 103	Green plant Green plant Green plant Rest of plant Straw	9.1 0.52 0.34 0.16 0.07	Billian, Erler & Wolters, 2008, RA-2574/07 (M-318501-01-1)

Wheat forage and straw

Twenty-six supervised trials have been conducted in wheat in Europe and sixteen supervised trials have been conducted in wheat in the USA, which support the use on wheat in Canada.

Table 66 Ethephon residues in wheat forage and straw resulting from supervised trials in Europe

WHEAT	Application					DALT	Portion analysed	Ethephon	Reference
Trial Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
GAP, Austria	660 g/L SL	0.46		100–300	1	–	Application timing BBCH 37–51		
GAP, Germany	660 g/L SL	0.46		100–300	1	–	Application timing BBCH 37–51		
01R762-1 Braslou, France, 2001 (Isengrain)	480 g/L SL	0.48 (BBCH 51)	0.19	250	1	0 70	Green plant Straw	5.2 0.22	Davies, 2002, 01R762 (M-210306-01-1)
01R762-2 Courdoux, France, 2001 (Ritmo)	480 g/L SL	0.48 (BBCH 49)	0.24	200	1	0 8 23 66	Green plant Green plant Green plant Straw	3.5 3.5 1.5 0.14	Davies, 2002, 01R762 (M-210306-01-1)
01R762-3 Cambridge, UK, 2001 (Claire)	480 g/L SL	0.48 (BBCH 49)	0.16	302	1	0 17 29 72	Green plant Green plant Green plant Straw	6.5 0.77 0.56 0.13	Davies, 2002, 01R762 (M-210306-01-1)
01R762-4 Weilerswist, Germany, 2001 (Drifter)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	0 66	Green plant Straw	6.2 0.51	Davies, 2002, 01R762 (M-210306-01-1)
01R762-5 Zschortau, Germany, 2001 (Petrus)	480 g/L SL	0.48 (BBCH 49)	0.16	300	1	0 15 40 71	Green plant Green plant Green plant Straw	4.0 1.5 0.58 0.38	Davies, 2002, 01R762 (M-210306-01-1)
GAP, France	480 g/L SL	0.48		100–200	1	70	Application timing BBCH 32-39		
00548BX1 Chaunac, France, 2000 (Aztec)	480 g/L SL	0.48 (BBCH 38)	0.14	333	1	0 14 34 90	Green plant Green plant Green plant Straw	7.7 2.2 1.2 0.15	Ballasteros, 2002, R&D/CRLD/AN/mr/ 0115433 (M-208087-01-1)
00548LY1 La Boisse, France, 2000 (Cyrano)	480 g/L SL	0.48 (BBCH 39)	0.15	320	1	0 16 34 78	Green plant Green plant Green plant Straw	7.0 1.2 0.71 0.15	Ballasteros, 2002, R&D/CRLD/AN/mr/ 0115433 (M-208087-01-1)
00549BX1 Tugeras, France, 2000 (Hyno-valea)	480 g/L SL	0.47 (BBCH 39)	0.14	333	1	90	Straw	0.22	Ballasteros, 2002, R&D/CRLD/AN/mr/ 0115434 (M-208091-01-1)
00549TL1 Baziege, France, 2000 (Tremie)	480 g/L SL	0.48 (BBCH 37–39)	0.17	278	1	91	Straw	0.075	Ballasteros, 2002, R&D/CRLD/AN/mr/ 0115434 (M-208091-01-1)
01R772-1 Boe, France, 2001 (Soissons)	480 g/L SL	0.48 (BBCH 39)	0.19	250	1	0 74	Green plant Straw	7.4 0.56	Davies, 2002, 01R772 (M-210308-01-1)

WHEAT	Application					DALT	Portion analysed	Ethephon	Reference
Trial Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
01R772-2 Saint Romain De Jeolienas, France, 2001 (Aztec)	480 g/L SL	0.48 (BBCH 39)	0.19	250	1	0 25 35 74	Green plant Green plant Green plant Straw	14 1.5 1.1 < 0.05 0.45	Davies, 2002, 01R772 (M-210308-01-1)
01R772-3 Dodici Morelli, Italy, 2001 (Centauro)	480 g/L SL	0.48 (BBCH 39)	0.14	350	1	0 10 31 57	Green plant Green plant Green plant Straw	12 3.1 1.2 1.3	Davies, 2002, 01R772 (M-210308-01-1)
01R772-4 Paradas Sevilla, Spain, 2001 (Simeto)	480 g/L SL	0.48 (BBCH 39)	0.16	300	1	0 16 29 78	Green plant Green plant Green plant Straw	18 5.7 2.9 0.46	Davies, 2002, 01R772 (M-210308-01-1)
01R772-5 Alcala de Guadaira Sevilla, Spain, 2001 (Sula)	480 g/L SL	0.48 (BBCH 39)	0.16	300	1	0 15 29 76	Green plant Green plant Green plant Straw	14 4.3 3.0 0.12	Davies, 2002, 01R772 (M-210308-01-1)
GAP, France	450 g/L SL [a]	0.38		100–200	1	–	Application timing BBCH 31–37		
R 2004 0564/2 Staffanstorp, Sweden, 2004 (Marshall)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	0 28 85	Green plant Green plant Straw	7.2 0.27 0.18	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0565/0 Leverkusen, Germany, 2004 (Batis)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	0 42 92	Green plant Green plant Straw	4.9 < 0.05 < 0.05	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0566/9 Werl-Oberbergstraße, Germany, 2004 (Winnetou)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	0 23 81	Green plant Green plant Straw	3.1 0.09 0.06	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0567/7 Villettes, France, 2004 (Orvantis)	450 g/L SL [a]	0.38 (BBCH 37)	0.13	300	1	0 36 84	Green plant Green plant Straw	4.5 0.41 0.45	Bardel, 2005, RA-2090/04 (M-251226-01-1)
R 2004 0568/5 Kilkis, Greece, 2004 (Mexicalli)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	0 9 57	Green plant Green plant Straw	8.3 8.5 0.10	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0569/3 Gargas, France, 2004 (Garric)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	0 25 77	Green plant Green plant Straw	6.1 0.09 0.15	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0570/7 Brenes, Spain, 2004 (Don Pedro)	450 g/L SL [a]	0.38 (BBCH 41-45)	0.12	300	1	0 14 78	Green plant Green plant Straw	10 0.26 0.10	Bardel, 2005, RA-2091/04 (M-251236-02-1)
R 2004 0571/5 Pereiro/Alenquer, Portugal, 2004 (Sula)	450 g/L SL [a]	0.38 (BBCH 37)	0.12	300	1	0 35 82 82	Green plant Green plant Straw	6.0 0.07 0.11	Bardel, 2005, RA-2091/04 (M-251236-02-1)
GAP, Belgium	480 g/L SL	0.60		200–400	1	–	Application timing BBCH 37–45		

WHEAT	Application					DALT	Portion analysed	Ethephon	Reference
Trial Country, year (Variety)	Form (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days		mg/kg	
R 2006 0123/9 Chaussy, France, 2006 (Isengrain)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	0 7 21 64	Green plant Green plant Green plant Straw	8.9 0.82 0.54 0.37	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2006 0293/6 Bury St Edmunds, UK, 2006 (Einstein)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	0 7 21 68	Green plant Green plant Green plant Straw	9.0 0.22 0.11 0.18	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2006 0294/4 Leverkusen, Germany, 2006 (Batis)	480 g/L SL	0.67 (BBCH 39)	0.22	300	1	0 7 21 73	Green plant Green plant Green plant Straw	8.1 0.28 0.14 0.08	Billian & Telscher, 2007, RA-2517/06 (M-294528-01-1)
R 2007 0175/6 Chambourg sur Indre, France, 2007 (Apache)	480 g/L SL	0.72 (BBCH 39)	0.24	300	1	0 7 21 56 85	Green plant Green plant Green plant Rest of plant Straw	11 6.0 0.40 0.23 0.29	Billian, 2008, RA-2575/07 (M-312007-01-1)
R 2007 0186/1 Werl-Westönnen, Germany, 2007 (Ritmo)	480 g/L SL	0.77 (BBCH 49)	0.24	321	1	0 7 21 56 65	Green plant Green plant Green plant Rest of plant Straw	7.6 0.45 0.21 0.18 0.18	Billian, 2008, RA-2575/07 (M-312007-01-1)

[a] 450 g/L SL formulation (150 g/L ethephon + 300 g/L chlormequat-chloride)

Table 67 Ethephon and HEPA residues in wheat forage and straw resulting from supervised trials in Europe obtained using an analytical method involving acid hydrolysis/extraction

WHEAT Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
GAP, Germany	660 g/L SL	0.46		100–300	1	–	Application timing BBCH 37–51			
13-2029-01 Bursheid, Germany 2013 (Winnetou Soft)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 7 14 21 23 75	Green plant Green plant Green plant Green plant Green plant Straw	3.3 0.46 0.21 0.17 0.17 0.36	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 0.050	Schulte & Berkum, 2015, 13-2029 M-529493-01-1

WHEAT Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
13-2029-02 Villars-Perwin, Belgium, 2013 (Matrix Soft)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 8 14 21 29 61	Green plant Green plant Green plant Green plant Green plant Straw	3.1 0.16 0.11 0.11 0.11 0.66	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 13-2029 M-529493-01-1
13-2029-03 Little Shelford CB22 5EU, United Kingdom 2013 (Claire Soft)	480 SL	0.48 (BBCH 51)	0.24	200	1	0 38 74	Green plant Green plant Straw	7.5 0.32 1.3	0.076 0.050 0.083	Schulte & Berkum, 2015, 13-2029 M-529493-01-1
14-2018-01 Vechta – Langförden, Germany, 2014 (Winnetou mass-wheat)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 8 14 21 29 71	Green plant Green plant Green plant Green plant Green plant Straw	4.9 0.28 0.29 0.23 0.22 0.44	0.085 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-02 Burscheid, Germany 2014 (Tobak)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 26 68	Green plant Green plant Straw	7.0 0.23 1.2	0.078 < 0.05 0.15 (c, 0.23)	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-03 SG8 8S Great Chishill, United Kingdom, 2014 (Solstice Milling)	480 SL	0.48 (BBCH 51)	0.24	200	1	0 7 15 22 36 64	Green plant Green plant Green plant Green plant Green plant Straw	7.0 0.39 0.27 0.17 0.12 1.2	0.073 < 0.05 < 0.05 < 0.05 < 0.05 0.055	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-04 France Chambourg sur Indre, 2014 (Touareg Winter)	480 SL	0.48 (BBCH 51)	0.16	300	1	0 35 77	Green plant Green plant Straw	7.2 0.071 0.57	0.087 < 0.05 < 0.05	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
14-2018-05 Slootdorp, Netherlands 2014	480 SL	0.48 (BBCH 51)	0.12	400	1	0 32 54	Green plant Green plant Straw	5.9 0.23 1.5	0.062 < 0.05 < 0.05	Schulte & Berkum, 2015, 14-2018 M-532267-01-1
GAP, France	480 g/L SL	0.48		100–200	1	70	Application timing BBCH 32–39			

WHEAT Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
14-2019-01 Gargas, France 2014 (Solehio Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 14 21 41 77	Green plant Green plant Green plant Green plant Green plant Straw	7.1 0.27 0.16 0.12 < 0.05 0.29	0.13 < 0.05 < 0.05 < 0.05 < 0.05 0.079	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
14-2019-02 Brenes, Spain 2014 (Don Pedro)	480 SL	0.48 (BBCH 39)	0.16	400	1	0 39 72	Green plant Green plant Straw	6.4 < 0.05 0.21	0.087 < 0.05 0.092 (c, 0.12)	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
14-2019-03 Bologna, Italy 2014 (Mieti Winter)	480 SL	0.48 (BBCH 39)	0.12	300	1	0 7 14 21 30 58	Green plant Green plant Green plant Green plant Green plant Straw	10 0.82 0.30 0.30 0.26 1.2	0.12 < 0.05 < 0.05 < 0.05 < 0.05 < 0.05	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
14-2019-04 Aramanha-Santarem, Portugal, 2014 (Artur Nick 2)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 60 110	Green plant Green plant Straw	16 0.075 0.44	0.21 < 0.05 0.084 (c, 0.061)	Schulte & Berkum, 2015, 14-2019 M-532272-01-1
13-2030-01 Castelnau d'estretefonds, France, 2013 (Hystar Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 14 21 45 80	Green plant Green plant Green plant Green plant Green plant Straw	5.7 0.50 0.31 0.24 0.16 0.86	0.27 < 0.05 < 0.05 < 0.05 < 0.05 0.051	Schulte & Berkum, 2015, 13-2030 M-529488-01-1
13-2030-02 El Campillo, Spain, 2013 (Artur Nick Soft)	480 SL	0.52 (BBCH 39)	0.16	322	1	0 43 64	Green plant Green plant Straw	17 0.21 0.84	0.24 < 0.05 < 0.05	Schulte & Berkum, 2015, 13-2030 M-529488-01-1

WHEAT Trial No Country, year (Variety)	Application					DALA days	Portion analysed	Ethephon mg/kg	HEPA mg/kg	Reference
	Form.(g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No					
13-2030-03 Tarquinia, Italy 2013 (Quality Soft)	480 SL	0.48 (BBCH 39)	0.16	300	1	0 7 14 21 24 63	Green plant Green plant Green plant Green plant Green plant Straw	6.9 0.48 0.17 0.19 0.16 1.7	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05 0.12	Schulte & Berkum, 2015, 13-2030 M-529488-01-1
13-2030-04 Bologna, Italy 2013 (Serio Soft)	480 SL	0.48 (BBCH 39)	0.14	350	1	0 25 62	Green plant Green plant Straw	5.6 0.050 0.30	0.11 < 0.05 0.058	Schulte & Berkum, 2015, 13-2030 M-529488-01-1

Table 68 Residues of ethephon in wheat straw resulting from supervised trials in the USA

WHEAT	Application					DALT	Ethephon	Reference
Trial Country, year (Variety)	Formulation (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days	mg/kg	
GAP, Canada	240 g/L SL	0.60		30–300	1	35	Application from BBCH 37–49	
10223-W1 Arkansas City, Kansas, USA, 1981 (Newton)	480 g/L SL	0.84 (late boot)	–	–	1	55	0.28 (0.08, 0.63, 0.27, 0.14) [a]	Harrison, 1981, 10223 (M-187972-01-1)
10223-W2 Landisville, Pennsylvania, USA, 1981 (Redcoat)	480 g/L SL	0.84 (boot)	–	–	1	49	0.59 (< 0.02, 0.30, 0.81, 1.21)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W3 Skaneateles, New York, USA, 1981 (Hauser)	480 g/L SL	0.84 (boot)	–	–	1	41	5.84 (7.60, 3.43, 4.61, 7.71)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W4 Newton, Iowa, USA, 1981 (Sage Hard Red)	480 g/L SL	0.56 (early boot)	–	–	1	54	0.39 (0.29, 0.40, 0.49)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W5 Sandusky, Michigan, USA, 1981 (Arthur)	480 g/L SL	0.56 (early boot)	–	–	1	62	3.37 (4.44, 2.19, 3.48)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W6 Newcastle, Ohio, USA, 1981 (Titan)	480 g/L SL	0.56 (early boot)	–	–	1	57	0.05 (< 0.02, 0.11, 0.06)	Harrison, 1981, 10223 (M-187972-01-1)

WHEAT	Application					DALT	Ethephon	Reference
Trial Country, year (Variety)	Formulation (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days	mg/kg	
10223-W7 Glyndon, Minnesota, USA, 1981 (Era)	480 g/L SL	0.84 (boot)	–	–	1	57	4.24 (4.51, 3.66, 3.66, 5.11)	Harrison, 1981, 10223 (M-187972-01-1)
10223-W8 Powell, Wyoming, USA, 1981 (Prodax)	480 g/L SL	0.56 (mid boot)	–	–	1	64	0.16	Harrison, 1981, 10223 (M-187972-01-1)
10223-W9 Warsaw, Illinois, USA, 1981 (Pioneer)	480 g/L SL	0.56	–	–	1	48	1.33 (1.36, 1.28, 1.40, 1.30)	Harrison, 1981, 10223 (M-187972-01-1)
SARS-89-CO-24 Brighton, Colorado, USA, 1989 (Hawk)	480 g/L SL	0.56 (aerial) (late boot to 1/4 inflorescence emerged)	2.0	28	1	35 40 60	1.3 (1.1, 1.4, 1.5) 1.7 (1.5, 1.7, 1.9) 3.4 (4.5, 3.3, 2.3)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot to 1/4 inflorescence emerged)	0.83	67	1	35 40 60	1.5 (1.5, 1.5, 1.6) 1.5 (1.6, 1.4, 1.4) 1.3 (1.2, 1.3, 1.4)	
SARS-89-KS-24 Sedan, Kansas, USA, 1989 (Thinderbird)	480 g/L SL	0.56 (aerial) (3/4 inflorescence emerged)	2.1	27	1	35 40 60	3.2 (4.3, 2.4, 3.0) 1.1 (0.99, 0.83, 1.4) 0.31 (0.39, 0.34, 0.21)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (3/4 inflorescence emerged)	0.86	65	1	35 40 60	2.7 (2.5, 3.1, 2.6) 1.3 (1.1, 1.5, 1.3) 0.78 (0.56, 0.86, 0.91)	
SARS-89-MN-24 East Grand Forks, Minnesota, USA, 1989 (Marshall)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	35 41 59	1.0 (1.1, 0.98, 0.96) 1.3 (1.0, 1.2, 1.6) 0.29 (0.25, 0.39, 0.24)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot)	0.86	65	1	35 41 59	1.4 (0.84, 1.9, 1.5) 1.7 (1.6, 1.6, 1.8) 0.66 (0.56, 0.77, 0.64)	
SARS-89-ND-24 Northwood, North Dakota, USA, 1989 (Butte 86)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	35 40 60	2.7 (3.4, 2.3, 2.5) 1.6 (2.4, 0.72, 1.7)) 0.20 (0.39, 0.09, 0.11)	Conn, 1992, SARS-89-24 (M-187553-01-1)

WHEAT	Application					DALT	Ethephon	Reference
Trial Country, year (Variety)	Formulation (g ai/L)	kg ai/ha	kg ai/hL	Water (L/ha)	No	days	mg/kg	
		0.56 (ground) (late boot)	0.86	65	1	35 40 60	2.0 (2.5, 1.6, 1.9) 1.4 (1.3, 1.5, 1.5) 0.33 (0.43, 0.34, 0.23)	
SARS-89-WA-24 Ephrata, Washington, USA, 1989 (Madson)	480 g/L SL	0.56 (aerial) (late boot)	2.0	28	1	40 60 70	0.95 (1.5, 0.63, 0.73) 0.95 (0.85, 0.90, 1.1) 1.5 (1.7, 1.2, 1.5)	Conn, 1992, SARS-89-24 (M-187553-01-1)
		0.56 (ground) (late boot)	0.73	77	1	40 60 70	1.2 (0.41, 1.4, 1.8) 1.8 (1.9, 1.7, 1.9) 1.3 (1.3, 1.1, 1.6)	

[a] Mean residue. Analytical results of replicate samples are in parentheses

Table 69 Ethephon residues in cotton lint and gin trash resulting from supervised trials in Europe, the USA and Brazil

COTTON Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
GAP, Greece	480 g/L SL	1.44		500–600	1	7			
EUROPE									
94681SE1 Carlota-AL, Spain, 1994 (Cnema 111)	540 g/L SC [b]	1.44	0.36	400	1	0 3 7	Lint	0.12 11.5 10.1	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
94681SE2 Carlota-ZA, Spain, 1994 (Cnema 111)	540 g/L SC [b]	1.44	0.36	400	1	0 3 7	Lint	< 0.10 8.08 1.92	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
94681SE3 Ecija, Spain, 1994 (Cnema 111)	540 g/L SC [b]	1.44	0.36	400	1	0 3 7	Lint	< 0.10 33.3 14.4	Richard & Muller, 1995, R&D/CRLD/AN/bd/ 9515911 (M-163133-01-1)
95723SE1 Ciatr Sevilla, Spain, 1995 (Corona)	540 g/L SC [b]	1.44	0.33	440	1	7	Lint	2.06	Muller, 1996, R&D/CRLD/AN/bd/ 9516706 (M-163236-01-1)
GAP, USA	765 g/L SC	2.24		28-234	1	7			
GAP, USA	720 g/L SC	2.24		19-94	1	7			
USA									

COTTON Trial No. Country, year (Variety)	Application					DALT days	Portion analysed	Ethephon mg/kg	Reference
	Form. (g ai/L & type)	kg ai/ha	kg ai/hL	Water (L/ha)	No				
94-0284 Wharton Co., TX, USA, 1994 (Deltapine 20)	540 g/L SC	2.31 (ground)	1.54	150	1	7	Gin trash	8.41 (8.63, 8.18) [a]	See, 1995, USA94I01R (M-253436-01-1)
94-0285 Castro Co., TX, USA, 1994 (Paymaster 145)	540 g/L SC	2.25 (ground)	1.53	147	1	7	Gin trash	40.5 (43.4, 37.5)	See, 1995, USA94I01R (M-253436-01-1)
94-0286 Floyd Co., TX, USA, 1994 (Paymaster HS-200)	540 g/L SC	2.43 (ground)	1.54	158	1	7	Gin trash	11.1 (10.5, 11.7)	See, 1995, USA94I01R (M-253436-01-1)
94-0287 Fresno, CA, USA, 1994 (Maxxa)	540 g/L SC	2.22 (ground)	1.59	139	1	7	Gin trash	17.1 (15.3, 18.8)	See, 1995, USA94I01R (M-253436-01-1)
94-0288 Washington Co., MS, USA, 1994 (DPL 50)	540 g/L SC	2.26 (ground)	1.59	142	1	7	Gin trash	54.2 (56.3, 52.0)	See, 1995, USA94I01R (M-253436-01-1)
94-0289 Houseton Co., AL, USA, 1994 (DPL 5415)	540 g/L SC	2.28 (ground)	1.64	139	1	8	Gin trash	45.5 (41.1, 49.8)	See, 1995, USA94I01R (M-253436-01-1)
94-0290 Madera Co., CA, USA, 1994 (Maxa)	540 g/L SC	2.17 (ground)	1.18	184	1	6	Gin trash	150 (141, 158)	See, 1995, USA94I01R (M-253436-01-1)
94-0291 Fayette Co., TN, USA, 1994 (Stoneville 453)	540 g/L SC	2.25 (ground)	1.57	143	1	7	Gin trash	25.1 (25.8, 24.4)	See, 1995, USA94I01R (M-253436-01-1)
94-0292 Crittenden Co., AR, USA, 1994 (Stoneville 453)	540 g/L SC	2.27 (ground)	1.62	140	1	7	Gin trash	13.5 (12.0, 15.0)	See, 1995, USA94I01R (M-253436-01-1)
94-0293 Burleson Co., TX, USA, 1994 (DP&L 5415)	540 g/L SC	2.24 (ground)	1.56	144	1	9	Gin trash	6.66 (6.46, 6.86)	See, 1995, USA94I01R (M-253436-01-1)
94-0393 Hale Co., TX, USA, 1994 (Paymaster HS-200)	540 g/L SC	2.32 (ground)	1.53	151	1	7	Gin trash	55.7 (44.5, 66.8)	See, 1995, USA94I01R (M-253436-01-1)
94-0394 Hale Co., TX, USA, 1994 (Paymaster 145)	540 g/L SC	2.27 (ground)	1.45	157	1	7	Gin trash	28.9 (26.9, 30.8)	See, 1995, USA94I01R (M-253436-01-1)

[a] Mean residue. Analytical results in parentheses

[b] 540 g/L SL formulation (180 g/L ethephon + 360 g/L chlormequat-chloride)

FATE OF RESIDUES IN STORAGE AND IN PROCESSING

Information and Data from Residues in Processed Commodities

The Meeting received information on hydrolysis relevant to food processing; and processing of apples, grapes, olives, tomatoes, barley, wheat, and cotton seed to their respective processed commodities.

Hydrolysis

The hydrolytic behaviour of ethephon was investigated under conditions relevant to major food processing operations such as pasteurization (20 minutes at 90 °C, pH 4), brewing, baking and boiling (60 minutes at 100 °C, pH 5) and sterilisation (20 minutes at 120 °C, pH 6) using [^{14}C]ethephon (Selzer, 2002, CP02/001, [M-211072-01-1).

[^{14}C]Ethephon was spiked into citrate buffer solutions which were adjusted to the required pH-value with sodium hydroxide. For each set of conditions there were two trials at a spiking level of 0.1 mg/L and two trials at a level of 1.0 mg/L. The spiked buffer solutions were heated in closed stainless steel reaction vessels using either a water bath or an autoclave. The heating time was measured from the moment when the temperature inside the vessels reached the required value. At the end of the fixed time the vessels were immersed immediately in an ice bath. After cooling, the outlets of the vessels were connected to a series of adsorption bottles containing a saturated solution of pyridinium hydrobromide perbromide (PHB) and the headspace gas was passed through the bottles in order to trap the ethylene formed during the test.

The total radioactivity remaining in the buffer solutions and the radioactivity trapped in the bottles were measured by LSC. The individual compounds present in the buffer solutions were identified and quantified by HPLC against reference standards. In order to characterize the radioactive compounds released in the gaseous phase, a series of trials was performed under the same conditions with unlabelled ethephon and the gaseous phase was analysed by GC/FID.

The overall radioactivity recovery was in the range of 82 to 95%, except in three trials where the recovery was only about 50% because of losses during the gas trapping procedure (Table 70).

Under the conditions representative of pasteurization, more than 80% of the ethephon remained unchanged and about 10% was decomposed to ethylene. Besides the parent compound, very small amounts of HEPA and an unknown compound were formed in the buffer solution. Under the conditions representative of brewing, baking, boiling and sterilization, degradation of ethephon was complete. Based on the trials which gave acceptable overall recoveries, at least 75% of the substance was decomposed to ethylene. The buffer solutions contained small quantities of HEPA and an unknown compound, but these amounted to less than 10% of the initial radioactivity.

Table 70 Quantification and characterization of radioactivity recovered under hydrolysis conditions simulating processing

Simulated process	Initial level of ethephon	Total radioactivity recovered (%[a])	Radioactivity in solution (%[a])				Ethylene (%[a])
			Total	Ethephon	HEPA	Unknown	
Pasteurisation (90 °C, pH 4, 20 min)	0.1 mg/L	93.0	83.31	80.29	1.46	1.56	9.67
	1.0 mg/L	93.4	82.55	80.74	0.93	0.66	10.82
Baking, brewing, boiling (100 °C, pH 5, 60 min)	0.1 mg/L	82.6	6.94	n.d.	4.70	2.24	75.64
	1.0 mg/L	85.7	8.76	n.d.	7.86	0.90	76.93

Simulated process	Initial level of ethephon	Total radioactivity recovered (%[a])	Radioactivity in solution (%[a])				Ethylene (%[a])
			Total	Ethephon	HEPA	Unknown	
Sterilization (120 °C, pH 6, 20 min)	0.1 mg/L	51.2 [b]	11.72	n.d.	2.66	5.44	39.45 [b]
	1.0 mg/L	82.6	4.14	n.d.	2.91	1.23	78.45

[a] All results are expressed as percentage of initial radioactivity and represent the mean of two replicates, except for brewing, baking and boiling at 1.0 mg/L, for which the results of only one trial are shown, due to low overall recovery in the other trial (49.0% of initial radioactivity).

[b] For sterilisation at 0.1 mg/L both trials resulted in low overall recoveries, probably due to a leak in the gas trapping system and underestimation of the ethylene released.

Apples

The first study was conducted in the USA during 1989–1990 on processing of apples harvested at a DALT of 7 days in one trial in Washington into juice and wet and dry pomace (Nygren, 1990, USA89E32, [M-187583-01-1]). Apples were stored frozen prior to processing. The processing procedure consisted of first washing the thawed apples. The use of frozen apples resulted in a high yield of juice end compared to normal commercial processing attributed to the partial destruction of cell walls during freezing. A flow chart of the processing operations is shown below with analysed fractions underlined.

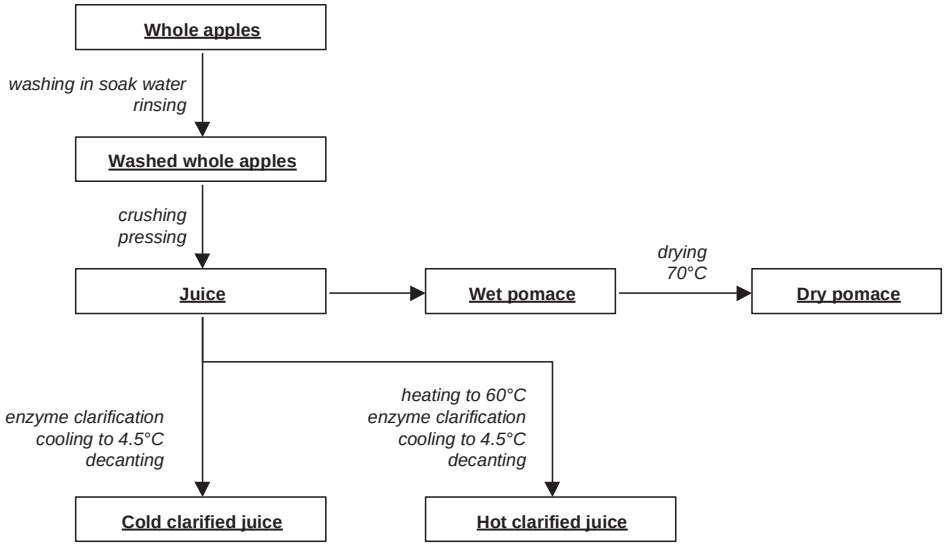


Figure 5 Apple processing

Residues of ethephon were determined using method SOP 90070. The LOQ was 0.05 mg/kg in apples and processed fractions. In the method validation, recoveries at fortification levels of 0.20–2.0 mg/kg were 104% in fruit, 76–85% in wet pomace, 105% in dry pomace, 98% in fresh juice, 64–107% in cold clarified juice and 95% in hot clarified juice.

The samples were frozen after collection (< –16 °C) and stored frozen until extraction and analysis. The maximum period of storage was 13 months for apple fruit and 9 months for processed commodities.

Residues determined in apple fruit and processed fractions are shown in Table 71. Results indicate that ethephon residues concentrate from whole fresh fruit to juice with processing factors

between 1.24 (fresh juice) and 1.57 (cold clarified juice). This result may be accounted for by the high water solubility of ethephon. A processing factor of almost 2 was observed in dried pomace as compared to whole fresh fruit. This indicates that part of the ethephon residues were eliminated during the drying process, probably due to co-sublimation with the water.

Table 71 Residues of ethephon in apple fruit and processed commodities

Commodities	Ethephon, mg/kg	Processing factor
Apple fruit (RAC)	0.37	1.0
Washed apple fruit	0.28	0.8
Wet pomace	0.24	0.6
Dry pomace	0.73	2.0
Fresh juice	0.46	1.2
Cold clarified juice	0.58	1.6
Hot clarified juice	0.56	1.5

The second study was conducted in Europe during 2003 on processing of apples harvested at a DALT of 14 days in a total of four trials in Europe (two in Italy, one in Portugal and one in Spain) into apple sauce, juice and wet and dry pomace (Bardel, Hoffmann & Eberhardt, 2005, RA-3610/03, [M-254102-01-1]). Apples were stored frozen prior to processing. Apples were partially defrosted and washed with tap water before processing.

The apples were then crushed and pressed into raw juice and wet pomace. The juice was filtered and subjected to ultrafiltration for 2–4 hours at room temperature. The resulting cleared juice was filtered to obtain clear apple juice, and pasteurised in glass bottles to give pasteurised juice.

The washed and thawed apples were cut into small pieces manually with a knife and then placed in a stainless steel pot. Water was added and the apples heated until all fruit parts were soft (cooking time 20 minutes at 96–99 °C). The apples were then crushed using a stainless steel food mill to remove cores and peel (pomace) and yield raw sauce. The pomace was discarded. The raw apple sauce was filled into a preserving bottle and pasteurised to give pasteurised sauce.

Residues of ethephon were determined by method 00903/E001 using LC-MS/MS. The LOQ was 0.05 mg/kg in apples and processed fractions. In the method validation, mean recoveries at fortification levels of 0.05–0.5 mg/kg were 104% in fruit, 104% in juice, 92% in pomace, 99% in washings and 96% in sauce/raw stewed fruit.

The samples were frozen after collection (< –14 °C) and stored frozen until extraction and analysis. The maximum period of storage was 462 days (< 16 months) for apple fruit and 71 days (2.3 months) for processed commodities.

Residues determined in apple fruit and processed fractions are shown in Table 72. At harvest, residues in apples were 0.06–0.63 mg/kg. Residues in the processed commodities were < 0.05–0.41 mg/kg in apple sauce, < 0.05–0.30 mg/kg in juice and < 0.05–0.71 mg/kg in wet pomace. Processing factors were calculated to be, 0.4–< 0.8, < 0.4–< 0.8 and 0.3–1.1, for apple sauce, juice and wet pomace, respectively.

Table 72 Residues of ethephon in apple fruit and processed commodities

Trial	Commodities	Ethephon, mg/kg	Processing factor
R2003 0153/7 Italy	Apple fruit (RAC)	0.14	
	Washed apple fruit	0.15	
	Washing water	0.07	
	Preparation of apple sauce		
	Raw sauce	0.08	
	Pasteurised sauce	0.07	0.5
	Preparation of apple juice		
	Wet pomace	0.06	0.4

Trial	Commodities	Ethephon, mg/kg	Processing factor
	Raw juice	< 0.05	
	Pasteurised juice	< 0.05	< 0.4
R2003 0423/4 Italy	Apple fruit (RAC)	0.06	
	Washed apple fruit	< 0.05	
	Washing water	< 0.05	
	Preparation of apple sauce		
	Raw sauce	< 0.05	
	Pasteurised sauce	< 0.05	< 0.8
	Preparation of apple juice		
	Wet pomace	< 0.05	< 0.8
	Raw juice	< 0.05	
	Pasteurised juice	< 0.05	< 0.8
R2003 0424/2 Portugal	Apple fruit (RAC)	0.63	
	Washed apple fruit	0.40	
	Washing water	0.18	
	Preparation of apple sauce		
	Raw sauce	0.26	
	Pasteurised sauce	0.24	0.4
	Preparation of apple juice		
	Wet pomace	0.71	1.1
	Raw juice	0.31	
	Pasteurised juice	0.30	0.5
R2003 0425/0 Spain	Apple fruit (RAC)	0.39	
	Washed apple fruit	0.32	
	Washing water	0.08	
	Preparation of apple sauce		
	Raw sauce	0.41	
	Pasteurised sauce	0.42	1.1
	Preparation of apple juice		
	Wet pomace	0.10	0.3
	Raw juice	0.16	
	Pasteurised juice	0.15	0.4

Grapes

The first study was conducted in the USA on processing of grapes harvested at a DALT of 42–47 days in six field trials in California during 1978 into dried grape and raisin waste (Harrison, 1979, 279C2, [M-188057-01-1]). Ethephon was applied as a foliar spray to Thompson seedless grapes at a rate of 0.56 kg ai/ha. The processing procedure is not reported.

The samples of grape berries, dried grapes and raisin waste were analysed according to the analytical method (AmChem Products Inc., 1975). The LOQ was 0.01 mg/kg. The mean recovery at a fortification level of 0.20 mg/kg in grapes was 107% (RSD 15.5%), at 0.40 mg/kg in dried grapes was 105% (RSD 4.6%), and at 10.0 mg/kg in raisin waste was 102% (RSD 8.9%).

The samples were stored frozen (–34 °C) until they were freeze dried, and the freeze-dried samples then stored frozen (–12 °C) or at ambient temperature. The maximum period of storage was 5 months.

Residues determined in grapes, dried grapes and raisin waste are shown in Table 73. Results give variable processing factors ranging between 0.79 and 8.5 for dried grapes and 19 and 82 for raisin waste. Considering the relationship of concentrations apple wet pomace and apple dry pomace, it is likely that the processing factor for dried raisin would be higher than 1.

Table 73 Residues of ethephon in grapes, dried grapes and raisin waste (Harrison, 1979)

Trial	Commodities	Ethephon, mg/kg	Processing factor

Trial	Commodities	Ethephon, mg/kg	Processing factor
Dinuba, CA, USA	Grapes (RAC)	0.46	
	Dried grape	0.46	1.0
	Raisin waste	9.28	20
Fresno, CA, USA	Grapes (RAC)	0.47	
	Dried grape	1.49	3.2
	Raisin waste	38.0	82
Parlier, CA, USA	Grapes (RAC)	0.15	
	Dried grape	0.21	1.4
	Raisin waste	3.27	22
Madeira [a], CA, USA	Grapes (RAC)	1.72	
	Dried grape	1.37	0.79
	Raisin waste	31.8	19
Kingsburg, CA, USA	Grapes (RAC)	0.24	
	Dried grape	0.22	0.89
	Raisin waste	4.72	19
Fresno, CA, USA	Grapes (RAC)	0.42	
	Dried grape	3.60	8.5
	Raisin waste	29.7	70

[a] Mite infested trial

Another study was conducted in 1995 on processing of grapes harvested at DALT of 35–38 days in two field trials in France to must and red wine (Grolleau, 1997, EA950185, [M-188232-01-1]).

The samples were shipped refrigerated (approximately 5 °C) to the processing facility on the day of collection in order to start immediately with the wine preparation procedure. The vinification procedure is shown below. Alcoholic fermentation takes about 4 weeks, malolactic fermentation about 3 weeks and clarification about 8 weeks. Several oenological additives were used in the process: potassium metabisulphite, yeast (*Saccharomyces cerevisiae*), sugar, lactic bacteria (*Leuconostoc oenos*), gelatine and metatartaric acid.

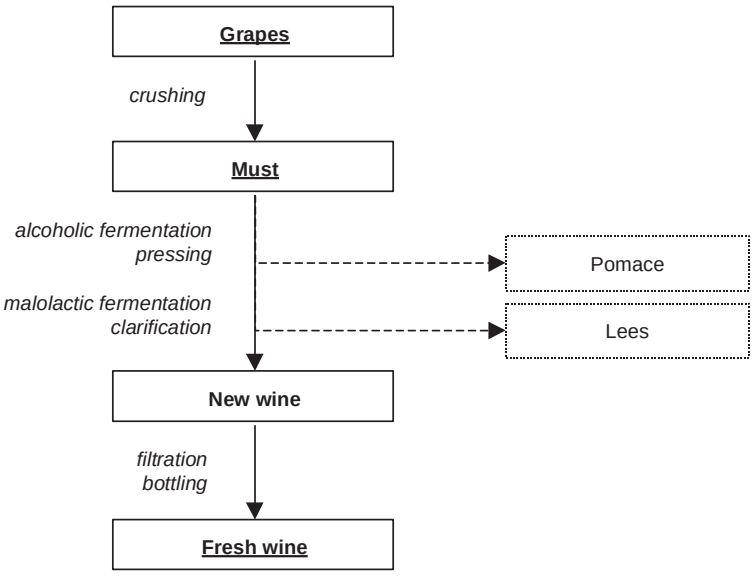


Figure 6 Processing of grapes to red wine

The samples of grape, must and red wine were analysed using the analytical method referenced in “Analytical Method for Residues of Pesticides” Part II-89, 5th Edition, SDU

Publishers, The Netherlands (1988). This method involves extraction with methanol, methylation with diazomethane and determination by GC/FPD and is similar to SOP 90070, and was validated on grapes prior to use. The LOQ was 0.10 mg/kg. Procedural recoveries at fortification levels of 0.10–2.0 mg/kg in grapes were 70–93% (mean 79%, RSD 9.9), at 0.10–0.25 mg/kg in must were 70–90%, and at 0.10–0.50 mg/kg in wine were 90–123%.

The samples were frozen after collection and stored frozen (< –18 ºC) until extraction and analysis. The maximum period of storage was 4 months for grapes and must, and 9 days for wine (after bottling).

Residues determined in grapes, must and red wine are shown in Table 74. The concentrations of ethephon in must were found to be comparable to or slightly lower than the concentrations in whole fruit. A concentration from fruit to wine was found, with processing factors of 1.4 and 2.1.

Table 74 Residues of ethephon in grapes, must and red wine (Grolleau, 1997)

Trial	Processed commodities	Ethephon, mg/kg	Processing factor
EA950185-FR01 France, 1995 (variety Syrah)	Grapes (RAC)	0.37	
	Must	0.34	0.9
	Wine	0.77	2.1
EA950185-FR02 France, 1995 (variety Grenache)	Grapes (RAC)	0.25	
	Must	0.17	0.7
	Wine	0.36	1.4

Two additional studies were conducted in 2003 in which processing of grapes from four trials in Europe (one in Germany, two in France and one in Greece) to raw juice and wine (Bardel & Hoffmann, 2005, RA-3680/03 and Amendment 1, [M-249278-02-1; Bardel & Hoffmann, 2005, RA-3681/03 and Amendment 1, [M-249332-02-1).

Juice was prepared through the following procedure: grapes were destemmed, washed and crushed, and the mash pressed to give raw juice and wet pomace. The raw juice was depectinised by heating for approximately 30 seconds at 80–85 °C, cooled and treated with pectolytic enzyme for 1 hour at room temperature. The cooled juice was filtered and pasteurised, and a juice sample collected.

Wine was prepared through the following procedure: grapes were crushed and destemmed, and the mash heated to 80 °C and then cooled down to fermentation temperature. The mash was pressed in a cloth press, and a sample of the resulting pomace collected. The must was filled into vessels and potassium hyposulphite and bentonite added. After clarifying, the must was decanted from the lees and a sample of must collected. Alcoholic fermentation was started by the addition of pure-culture yeast. After fermentation (approximately 6 weeks), the yeast was removed by decanting and filtration. The young wine was sulphited and finished for 2 months (trial R 2003 0468/4) and for 3 days (trials R 2003 0971/6, R 2003 0469/2 and R 2003 0973/2). The wine was filtered and bottled, and samples of bottled wine collected.

The samples of grapes and processed commodities were analysed using method 00903, which was validated prior to use. The LOQ was 0.05 mg/kg. Mean procedural recoveries at fortification levels of 0.05–0.5 mg/kg were 95% (RSD 5.9) in grapes, 99% (RSD 15.2%) in must, 103% (RDS 4.1%) in wine, 81% (RSD 5.7%) in pomace and 114% (RSD 4.2%) in juice.

The samples were frozen after collection and stored frozen (< –18 ºC) until extraction and analysis. The maximum period of storage was 14 months.

Residues determined in grape, juice, pomace, must and wine are shown in Table 75. The ethephon concentrations in juice, pomace and must were found to be comparable to or lower than those in whole fruit. The processing factors were in the range 0.5–1.1 for juice, 0.4–1.1 for wet pomace, 0.8–1.0 in must and 0.7–1.5 in wine.

Table 75 Residues of ethephon in grape, juice, pomace and wine

Trial	Commodities	Ethephon, mg/kg	Processing factor	Reference
R 2003 0468/4 Germany, 2003 (variety Spätburgunder)	Grapes bunch (RAC)	0.67		Bardel & Hoffmann, 2005, RA-3680/03 and Amendment 1 (M-249278-02-1)
	Grape berries	0.55		
	Juice	0.53	0.8	
	Pomace (wet)	0.76	1.1	
	Must	0.52	0.8	
	Wine (bottled)	0.98	1.5	
R 2003 0971/6 N France, 2003 (variety Gamay)	Grapes bunch (RAC)	0.19		
	Grape berries	0.22		
	Juice	0.21	1.1	
	Pomace (wet)	0.08	0.4	
	Must	0.19	1.0	
	Wine (bottled)	0.14	0.7	
R 2003 0469/2 Greece, 2003 (variety Roditis)	Grapes bunch (RAC)	0.22		Bardel & Hoffmann, 2005, RA-3681/03 and Amendment 1 (M-249332-02-1)
	Grape berries	0.20		
	Juice	0.12	0.5	
	Pomace (wet)	0.14	0.6	
	Must	0.21	1.0	
	Wine (bottled)	0.26	1.2	
R 2003 0973/2 S France, 2003 (variety Syrah)	Grapes bunch (RAC)	0.20		
	Grape berries	0.17		
	Juice	0.14	0.7	
	Pomace (wet)	0.18	0.9	
	Must	0.15	0.8	
	Wine (bottled)	0.19	1.0	

Olive

A study was conducted in 2007 on processing of olives harvested at a DALT of 11 days in four trials in Spain to table olives and olive oil (Fernandez, 2009, 07 D OL BY P/A, [M-352734-01-1]).

Table olives: Olives were placed into a 2–4% NaOH solution and oscillated for 5–8 hours. Afterwards, the olives were immersed in water for 12–20 hours to eliminate the NaOH from the fruit. After watering, the olives were put into a 10% NaCl solution to give table olives.

Olive oil: Olives were washed in tap water, and the washed olives then milled to a pulp. The pulp was mixed in a thermo-malaxer for approximately 30 minutes. Boiling water was added after the first 20 minutes of mixing, to give a water:pulp ratio of 1:1. The mixture was pressed into a liquid phase (oil and water) and solid phase (press cake). The liquid phase was decanted and centrifuged and the raw oil separated. Filtration of the raw oil yielded virgin oil. Soda was added to raw oil and the mixture heated to 60–70 °C for 30 minutes. The oil was separated from the sediment (soap) by filtration to give refined oil.

Residues of ethephon were determined using method 00918. The LOQ was 0.05 mg/kg. Procedural recoveries at fortification levels of 0.05–5.0 mg/kg in olives were within the acceptable range of 70–120%, RSD < 20%. Procedural recoveries at fortification levels of 0.05–0.50 mg/kg in oil were within the acceptable range of 70–120%, RSD < 20%.

The samples were frozen after collection and stored frozen (–18 ºC) until extraction and analysis. The maximum period of storage was 7 months for olives RAC and 7 months for table olives.

Residues determined in olives, table olives and oil are shown in Table 76. Concentrations of ethephon were 1.6–4.3 mg/kg in olive RAC. There is no significant transfer of residues of ethephon into the processed commodities, and residues in table olives and virgin and refined oil were < 0.05 mg/kg in all trials.

Table 76 Residues of ethephon in olives, table olives and olive oil

Trial	Commodities	Ethephon, mg/kg	Processing factor
07 D OL BY P01 Spain, 2007 (variety Manzanillo)	Olives (RAC)	4.3	
	Table olives	< 0.05	< 0.01
07 D OL BY P02 Spain, 2007 (variety Manzanillo)	Olives (RAC)	2.2	
	Table olives	< 0.05	< 0.02
07 D OL BY P03 Spain, 2007 (variety Hojiblanca)	Olives (RAC)	2.5	
	Table olives	< 0.05	< 0.02
	Virgin oil	< 0.05	< 0.02
	Refined oil	< 0.05	< 0.02
07 D OL BY P04 Spain, 2007 (variety Hojiblanca)	Olives (RAC)	1.6	
	Table olives	< 0.05	< 0.03
	Virgin oil	< 0.05	< 0.03
	Refined oil	< 0.05	< 0.03

Tomato

A study was conducted in 1989 on processing of tomatoes harvested at a DALT in 3 days of trials in the USA (California) to juice, paste and puree (Nygren, 1991, USA89E30, [M-187599-01-1]).

The processing was performed using commercial equipment and each of the processed fractions generated was to industry specifications. A simplified flow chart of the processing is shown in the following Figure. The tomato processed fractions collected were fresh whole tomatoes, washed whole tomatoes, wet pomace, dry pomace, canned fresh juice, canned puree, canned paste and canned juice reconstituted from tomato concentrate.

Residues of ethephon were determined using method SOP 90070. The LOQ was 0.02 mg/kg and the method was validated prior to use. The mean procedural recovery at a fortification level of 0.2 mg/kg in tomatoes was 109% (n=9), and recoveries at 0.5 mg/kg in processed commodities were 70–105%.

The samples were frozen after collection (–15 °C) and stored frozen until extraction and analysis. The maximum period of storage was 17 months.

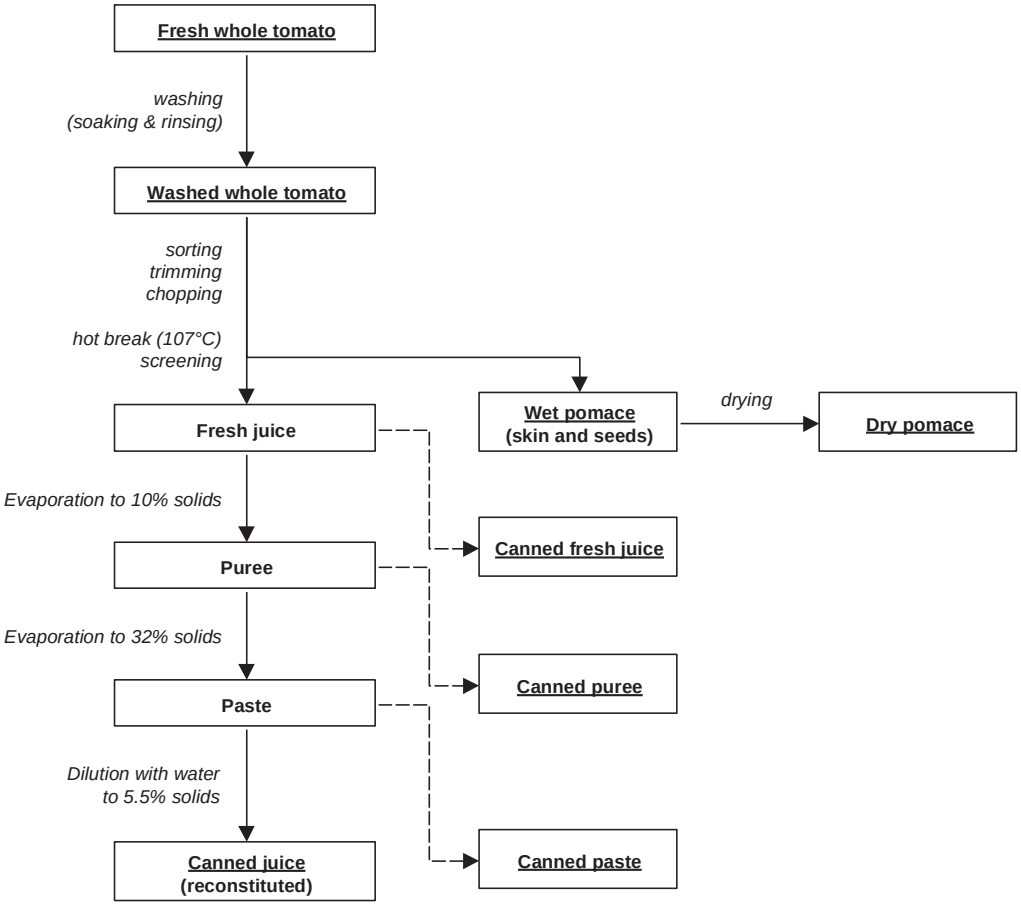


Figure 7 Tomato processing

Residues determined in fresh whole tomato and the tomato processed commodities are shown in Table 77. Ethephon did not concentrate in tomato processed commodities except in dry pomace which has a processing factor of 1.9. The data indicate that ethephon was lost during the preliminary processing, probably by heating.

Table 77 Residues of ethephon in processed tomato commodities (Nygren, 1991)

Trial	Commodities	Ethephon, mg/kg	Processing factor
89-138 CA, USA, 1989 (variety 1643)	Tomatoes (RAC)	0.73	1.0
	Washed fruit	0.68	0.93
	Wet pomace	0.38	0.52
	Dry pomace	1.39	1.9
	Canned fresh juice	0.25	0.34
	Canned puree	0.44	0.60
	Canned paste	0.55	0.75
	Canned juice from concentrate	0.29	0.40

In a published paper, processing of tomato into tomato paste was studied in Italy (Bolzuni & Leoni, Industria Conserve, *60*, 1985, pp 183, [M-188387-01-1). In this study, two lots of tomatoes (approximately 100 kg) containing incurred residues were processed using a procedure commonly used in industrial facilities. Following washing and chopping, the tomatoes were heated to 90 °C and passed through a sieve (opening Ø 0.6 mm) in order to remove seeds and skin. The juice obtained was concentrated into paste by heating at 55 °C under reduced pressure.

Finally, the paste was heated at 90 °C, canned and pasteurised. The samples of canned paste were stored for 9 months prior to analysis.

Analysis was by a method involving freeze drying, extraction with methanol, methylation using diazomethane and determination by means of GC/NPD. Mean procedural recoveries at fortification levels of 0.4 and 2.0 mg/kg in tomatoes were 86–95%, and at 0.2 and 1.0 mg/kg in tomato paste were 75–86%.

Residues determined in fresh whole tomatoes and tomato paste are shown in Table 78. The initial concentrations in the two lots of tomato were 0.27 and 0.36 mg/kg decreasing to 0.13 and 0.21 mg/kg, respectively, in paste with processing factor of 0.5 and 0.6 respectively.

Table 78 Residues of ethephon in tomato paste

Trial	Commodities	Ethephon, mg/kg	Processing factor
Trial 1 (variety UC 82)	Tomatoes (RAC)	0.27	
	Tomato paste	0.13	0.5
Trial 2 (variety UC 82)	Tomatoes (RAC)	0.36	
	Tomato paste	0.21	0.6

A study was conducted in 2004 on processing of tomato from three trials (Spain, Portugal and Italy) to juice, puree and preserve (Bardel, 2005, RA-3065/04, [M-262300-01-1]).

Preparation of juice: Tomatoes were washed in water, and samples of the washing water and washed tomato fruits collected. The washed tomatoes were cut into small pieces and heated with water (100 mL water/kg tomatoes) to 98–100 °C for 15–30 minutes. After this blanching process, the tomato pulp was passed through a strainer to separate raw juice and wet pomace. Sodium chloride was added to the raw juice, and sample of raw juice collected. One part of the raw juice was used for the processing into preserves. The rest of the raw juice was filled into preserving cans and pasteurised. After pasteurisation, a sample of juice was collected.

Preserves: Frozen tomatoes were washed in water and the peel removed. Samples of peel, peeling water and peeled fruits were collected. The peeled tomatoes were filled into preserving cans and raw juice added. The tomato preserves were pasteurised and a sample of tomato preserves collected.

Purée: Tomatoes were washed and then cut into small pieces. The cut tomatoes were heated with water (100 mL water/kg tomatoes) to 98–100 °C for 25–35 minutes. After this blanching process, the tomato pulp was passed through a strainer to separate raw juice and wet pomace. After the addition of sodium chloride, the raw juice was separated into raw purée and tomato liquid by centrifugation. The raw puree was filled into preserving cans and pasteurised. After pasteurisation, a sample of purée was collected.

Residues of ethephon were determined using method 00903, supplement E001. The LOQ was 0.05 mg/kg. The mean procedural recovery at fortification levels of 0.05–5.0 mg/kg in tomatoes was 103% (RSD 3.9%, n=10), at 0.05–0.5 mg/kg in juice was 103% (RSD 2.9%, n=8), at 0.05–0.5 mg/kg in puree was 98% (RSD 3.3%, n=8) and at 0.05–5.0 mg/kg in wet pomace was 90% (RSD 3.5%, n=7).

The samples were frozen after collection (–15 °C) and stored frozen until extraction and analysis. The maximum period of storage was 225 days (7.4 months).

Residues determined in fresh whole tomato and the tomato processed commodities are shown in Table 79. Ethephon did not concentrate in juice, preserves or puree. Residues were 0.30–0.57 mg/kg in fresh tomatoes, and decreased after processing to < 0.05–0.06 mg/kg in juice, < 0.05 mg/kg in puree and < 0.05–0.12 mg/kg in preserve.

Table 79 Residues of ethephon in processed tomato commodities

Trial	Commodities	Ethephon, mg/kg	Processing factor
R 2004 0468/9 Spain, 2004 (variety Malpica)	Tomatoes (RAC)	0.30	
	Fruit, peeled	0.09	
	Fruit, washed	0.13	0.4
	Washings	0.06	
	Juice	< 0.05	< 0.2
	Puree	< 0.05	< 0.2
	Raw juice	< 0.05	
	Preserve	< 0.05	< 0.2
	Wet pomace	< 0.05	< 0.2
	Raw puree	< 0.05	
	Peel, washed	0.11	
	Peeling water	0.08	
R 2004 0469/7 Portugal, 2004 (variety H-9661)	Tomatoes (RAC)	0.57	
	Fruit, peeled	0.09	
	Fruit, washed	0.11	0.2
	Washings	0.28	
	Juice	< 0.05	< 0.1
	Puree	< 0.05	< 0.1
	Raw juice	< 0.05	
	Preserve	< 0.05	< 0.1
	Wet pomace	< 0.05	< 0.1
	Raw puree	< 0.05	
	Peel, washed	0.23	
	Peeling water	0.24	
R 2004 0470/0 Italy, 2004 (variety Missouri)	Tomatoes (RAC)	0.55	
	Fruit, peeled	0.50	
	Fruit, washed	0.51	0.9
	Washings	< 0.05	
	Juice	0.06	0.1
	Puree	< 0.05	< 0.1
	Raw juice	0.48	
	Preserve	0.12	0.2
	Wet pomace	< 0.05	< 0.1
	Raw puree	< 0.05	
	Peel, washed	0.10	
	Peeling water	0.07	

Barley

A study was conducted on processing of barley grains obtained at a DALT of 49 days from a trial in Canada during 1981 to hulls and pearl barley (Harrison, 1981, 10223, [M-187972-01-1]).

Barley grain was milled into pearls as a batch operation. After pearling, the hulls and pearls were separated by sifting. Pearls were ground on a small plate grinder prior to analysis.

Residues of ethephon were determined using a method similar to SOP 90074. The LOQ was 0.05 mg/kg. The average recovery rate in wheat and barley grain at 0.2 mg/kg was 102% (RSD 17%, n=14). The recovery at 0.2 mg/kg in barley hulls was 114%, and in pearls was 99%.

The samples were frozen after collection at approximately –20 °C and stored frozen for 4 months.

Residues determined in barley processed commodities are shown in Table 80. In barley pearls, the ethephon concentration was slightly lower than in the corresponding raw agricultural commodity, while ethephon concentration in hulls was higher with a processing factor of 1.6.

Table 80 Residues of ethephon in barley grain and processed commodities

Trial	Commodities	Ethephon, mg/kg	Processing factor
Canada (variety Bruce)	Barley grain (RAC)	0.62	
	Barley pearls	0.54	0.9
	Barley hulls	1.01	1.6

Wheat

A study was conducted on processing of wheat grains harvested at a DALT of 65 days from one field trial in the USA (Texas) during 1989–1990 to dust, middlings, bran, flour, red dog and germ and shorts (Conn, 1992, SARS-90-24P, [M-187550-01-1]).

Wheat grain samples were processed to simulate industrial practice as closely as possible. The total quantity processed was approximately 81 kg. A simplified flow chart of the processing is shown in the following Figure.

Residues of ethephon were determined using a method similar to SOP 90074. The method involved Soxhlet extraction with methanol, precipitation of interfering materials, methylation using diazomethane and determination by means of GC/FPD. The LOQ was 0.1 mg/kg in red dog and 0.05 mg/kg for wheat grain and all other processed fractions. The average recovery rate at fortification levels of 0.05–1.0 mg/kg was 80% in wheat grain, 97% in dust, 73% in bran, 104% in low grade flour, 66% in patent flour, 60% in shorts and germ, and 74% in red dog. The overall average recovery was 79% (n=15).

Samples were in frozen storage for less than 1 month between harvest and processing and for no longer than 5 months between processing and analysis.

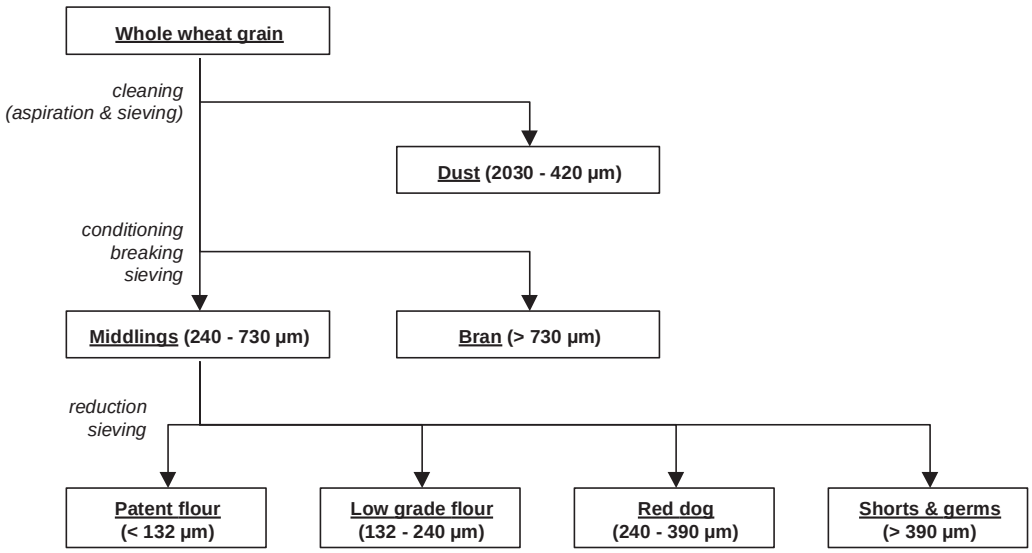


Figure 8 Wheat grain processing

Residues determined in wheat grain and the processed commodities are shown in Table 81. In middlings, low grade flour and patent flour, the residue levels were less than the LOQ (0.05 mg/kg). Measurable residues were found in unprocessed grain, grain dust, bran, shorts and germ and in red dog. Limited concentrations of ethephon residues occurred in bran, shorts and germs, and in red dog, with processing factors of less than 1.5.

Table 81 Residues of ethephon in wheat grain and processed products (Conn, 1992)

Trial	Commodities	Ethephon, mg/kg	Processing factor
USA (Texas) (variety Mitt)	Wheat grain (RAC)	0.17	
	Grain dust	0.10	0.6
	Bran	0.23	1.4
	Middlings	< 0.05	< 0.3
	Low grade flour	< 0.05	< 0.3
	Patent flour	< 0.05	< 0.3
	Shorts and germ	0.25	1.5
	Red dog	0.20	1.2

A second study was conducted on processing of wheat from a trial in Canada during 1981 to bran, flour, germ and shorts (Harrison, 1981, 10223, [M-187972-01-1]). Wheat grain was harvested at a PHI of 53 days.

The wheat grain sample was first brought to 15% moisture content and then milled using an automatic laboratory mill, which separated the ground grain into bran, flour, and a mixture of shorts and germ. The shorts and germ fraction was then manually separated into shorts and germ.

Residues of ethephon were determined using the same method as in the study above. The LOQ was 0.05 mg/kg. The average recovery rate in wheat and barley grain at 0.2 mg/kg was 102% (RSD 17%, n=14). The recovery at 0.2 mg/kg was 98% in shorts, 112% in germ, 84% in flour and 96% in bran.

The samples were frozen after collection at approximately –20 °C and stored frozen for less than 2 months.

Residues determined in wheat processed commodities are shown in Table 82. In wheat flour the residue level of ethephon was lower than in the corresponding raw agricultural commodity. Concentration of ethephon residues occurred in bran, shorts and germ with processing factors in the range of 2.0 to 3.5.

Table 82 Residues of ethephon in wheat grain and processed products (Harrison, 1981)

Trial	Commodities	Ethephon, mg/kg	Processing factor
Canada (variety Frederick)	Wheat grain (RAC)	0.35	
	Wheat bran	1.21	3.5
	Wheat flour	0.02	0.1
	Wheat shorts	0.78	2.2
	Wheat germ	0.71	2.0

A third study was conducted on processing of wheat from a trial in Canada during 1984 into bran and flour (Nygren, 1985, 866R11, [M-187977-01-1]). Three separate grain samples were processed into bran and flour. The shorts and germ fractions were combined during processing to a whole wheat flour fraction.

Residues of ethephon were determined using the same method as above. The method was validated by determination of the recovery rates for control samples fortified at 0.20 mg/kg. The recovery rates were good: 74% in grain, 79% in bran, 85% in flour and 84% in shorts and germ.

The samples were stored frozen (< –34 °C) for less than 12 months.

Residues determined in wheat processed commodities are shown in Table 83. Ethephon concentrations were lower in wheat flour in unprocessed grain. Ethephon residues occurred in bran as well as in shorts and germs (combined to whole wheat flour) with average processing factors of 3.1 and 2.7, respectively. These results compare well with those obtained in the previous study. A material balance is provided in the report which shows that the residues

measured in the milled fractions accounted for 78 to 86% of the residues determined in the corresponding unprocessed wheat grain samples.

Table 83 Residues of ethephon in wheat grain and processed products (Nygren, 1985)

Trial	Commodities	Ethephon, mg/kg	Mean processing factor
Canada (variety Augusta)	Wheat grain (RAC)	0.07, 0.10, 0.07 (mean 0.08)	
	Wheat bran	0.20, 0.22, 0.30 (mean 0.24)	3.1
	Wheat flour	0.02, 0.03, 0.02 (mean 0.02)	0.2
	Whole wheat flour (germ + shorts)	0.25, 0.18, 0.19 (mean 0.21)	2.7

Cotton seed

A study was conducted on processing of cotton seed from a trial in the USA (Louisiana) in 1993–1994 to oil and pomace (Lee, 1994, USA93I04R, [M-203874-01-2]). Three replicate samples (approximately 72 kg each) were harvested by hand 7 days after treatment.

The cotton was processed in such a way as to simulate industrial practice as closely as possible. However, due to the sample size, a batch process was adopted (as opposed to a continuous operation). A simplified flow chart of the processing is shown in the following Figure with analysed fractions underlined. The kernel (with some hull material) was heated (66–76 °C), flaked (82–114 °C) and then exposed to hexane (49–60 °C) to remove the crude oil from the flakes. After the crude oil and the hexane mixture was adjusted to the proper ratio, the crude oil was refined by heating up to 49 °C with sodium hydroxide. Thereafter the soapstock was separated by centrifugation and heated to about 70 °C in order to remove solvent. The refined oil was obtained from the liquid phase by evaporating the hexane. As the refined oil had a dark colour, it was refined again.

Residues of ethephon were analysed by ethylene release with method EC-92-228. The LOQ was 0.07 mg/kg for seed and processed commodities. Procedural recoveries at fortification levels of 0.07–6.0 mg/kg were 95% (RSD 3.2%, n=7) for seed, 108% (RSD 14.6%, n=5) for hulls, 101% (RSD 10.3%, n=5) for meal, 99% (RD 6.7%, n=7) for crude oil, 93% (RSD 14.1%, n=8) for soapstock and refined soapstock) and 100% (RSD 6.0%, n=8) for refined and re-refined oil.

The samples were frozen after collection at < -10 °C and stored frozen until extraction and analysis. The maximum period of storage was 12 months.

Residues determined in the ginned cottonseed and the cottonseed processed fractions are shown in Table 84. The mean ethephon residue level in ginned cottonseed amounted to 4.96 mg/kg. There was no concentration in any of the analysed processed fractions. Mean ethephon concentrations amounted to 0.35 mg/kg in hulls, 0.12 mg/kg in meal and 0.13 mg/kg in soapstock. Ethephon concentrations in crude and refined oil were less than the limit of quantification of 0.07 mg/kg. The data suggest that a significant part of the ethephon residue decomposes during processing.

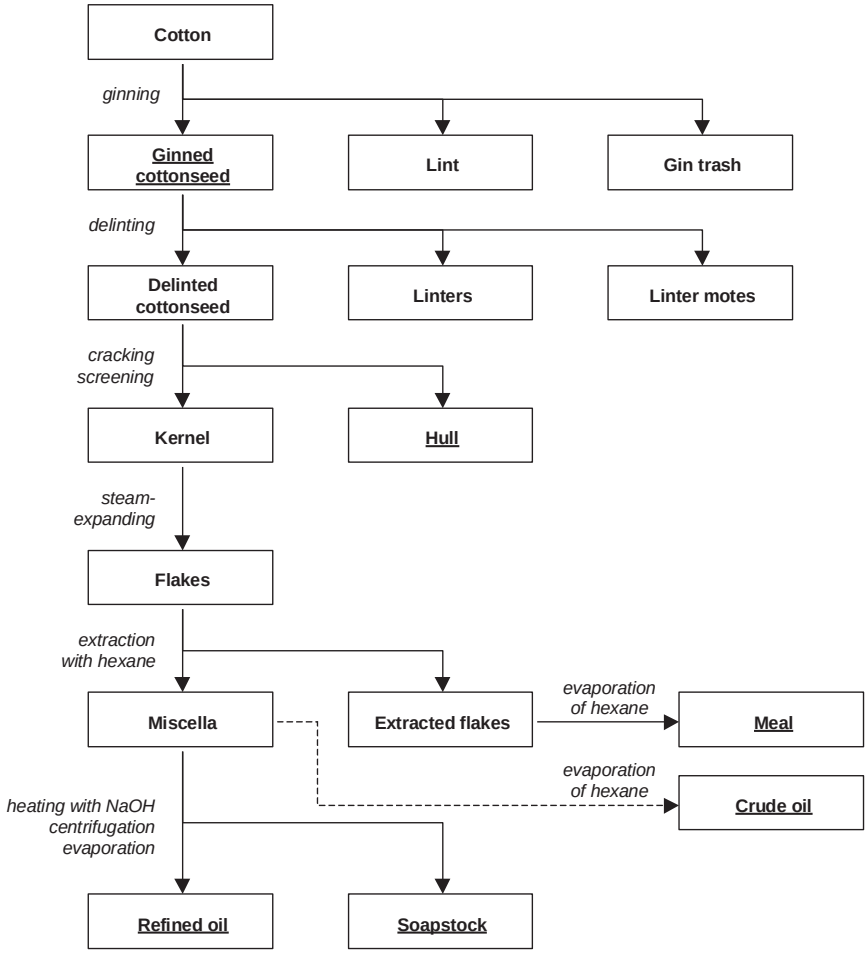


Figure 9 Cotton seed processing

Table 84 Residues of ethephon in cotton seed and processed products (Lee, 1994)

Trial	Commodities	Ethephon, mg/kg	Processing factor
USA (Louisiana) (variety DPL 41)	Cottonseed	5.84, 3.75, 5.30 (mean 4.96)	
	Hulls	0.22, 0.29, 0.55 (mean 0.35)	0.07
	Meal	0.15, 0.07, 0.14 (mean 0.12)	0.02
	Crude oil	< 0.07, < 0.07, < 0.07 (mean < 0.07)	< 0.02
	Soapstock	0.13, 0.15, 0.11 (mean 0.13)	0.03
	Refined oil	< 0.07, < 0.07, < 0.07 (mean < 0.07)	< 0.02
	Refined soapstock	< 0.07, < 0.07, < 0.07 (mean < 0.07)	< 0.02
	Re-refined oil	< 0.07, < 0.07, < 0.07 (mean < 0.07)	< 0.02

Another study was conducted on processing of cotton seed from two field trials in Greece and Spain in 2008 to oil (Billian & Krusell, 2010, 08-3401, [M-367885-01-1]).

The processing included the following steps: conditioning, extraction and refining. Initially pressing was planned, but it was not carried out because the oil content of the cotton seeds was < 25%. Instead, the oil was separated by solvent extraction.

The seeds were defrosted and crushed using a roller mill. After conditioning (adjusting the content of moisture for < 5%), the crushed cotton seeds extracted with n-hexane (2 hours at 60 °C) in a small technical extraction plant. The solvent-oil-mixture (miscella) was pumped into a distillation vessel and the hexane removed by distillation. The hexane was recycled back to the seed for a second hexane extraction step. After distillation, the rest of the solvent was removed from the extracted by rotary evaporation at 50 °C to give solvent extracted oil. The solvent-extracted crushed seed was sampled as meal after storing at room temperature for approximately one day.

The solvent extracted oil was filtered to give pre-clarified crude oil. Refining consisted of hydration, desliming (degumming), neutralization, washing, drying, bleaching, filtration and deodorization

Residues of ethephon were determined using method 00918. The LOQ was 0.05 mg/kg. Mean procedural recoveries at fortification levels of 0.05–15.0 mg/kg were 98% (RSD 6.5%, n=4) in bolls, 88% (RSD 6.4%, n=3) in meal, 91% (RSD 5.5%, n=4) in seed and 94% (RSD 3.2%, n=6) in oil.

The samples were frozen after collection at < –10 °C and stored frozen until extraction and analysis. The maximum period of storage for bolls was 452 days (14.9 months), for seed was 439 days (14.4 months) and for oil and meal was 437 days (14.4 months).

Residues determined in the cottonseed and processed fractions are shown in Table 85. Ethephon concentrations in bolls were 12.7–13.4 mg/kg. Residues in seed were 1.48–2.0 mg/kg. There was no concentration in any of the analysed processed fractions and little transfer of residues into the oil. Residues in all oil fractions were < 0.05 mg/kg and in meal were 0.05–0.14 mg/kg. The mean processing factors are < 0.03 for oil and 0.05 for meal.

Table 85 Residues of ethephon in cotton seed, oil and meal (Billian & Krusell, 2010)

Trial	Commodities	Ethephon, mg/kg	Processing factor
Trial 08-3401-01 Greece (variety Carmen)	Bolls (0 day PHI)	12.7	
	Cotton seed (7 day PHI)	2.0	
	Meal	0.14	0.07
	Solvent extracted oil	< 0.05	< 0.03
	Preclarified crude oil	< 0.05	< 0.03
	Neutralised crude oil	< 0.05	< 0.03
	Refined oil	< 0.05	< 0.03
Trial 08-3401-02 Spain (variety Alexandro)	Bolls (0 day PHI)	13.4	
	Cotton seed (7 day PHI)	1.48	
	Meal	0.05	0.03
	Solvent extracted oil	< 0.05	< 0.03
	Preclarified crude oil	< 0.05	< 0.03
	Neutralised crude oil	< 0.05	< 0.03
	Refined oil	< 0.05	< 0.03

Summary of processing factors

Based on the available processing studies, the processing factors that have been calculated are summarized in Table 86.

Table 86 Summary of processing factors

Commodity	Processed commodities	Processing factor	
		Individual value	Best estimate
Apple	Wet pomace	0.3, 0.4, 0.6, < 0.8, 1.1	0.60

Commodity	Processed commodities	Processing factor	
		Individual value	Best estimate
	Dry pomace	2.0	2.0
	Apple juice	< 0.4, 0.4, 0.5, < 0.8, 1.5	0. 5
	Apple sauce	0.4, 0.5, < 0.8, 1.1	0.5
Grape	Dried grapes	0.79, 0.89, 1.0, 1.4, 3.2, 8.5	1.2
	Grape juice	0.5, 0.7, 0.8, 1.1	0.75
	Wet pomace	0.4, 0.6, 0.9, 1.1	0.75
	Must	0.7, 0.8, 0.8, 0.9, 1.0, 1.0	0.85
	Wine	0.7, 1.0, 1.2, 1.4, 1.5, 2.1,	1.3
Olives	Olive oil (virgin and refined)	< 0.02, < 0.03	< 0.02
	Table olives	< 0.01, < 0.02, < 0.02, < 0.03	< 0.01
Tomato	Wet pomace	< 0.1, < 0.1, < 0.2, 0.52	0.52
	Dry pomace	1.9	1.9
	Tomato juice	< 0.1, 0.1, < 0.2, 0.34	0.22
	Tomato puree	< 0.1, < 0.1, < 0.2, 0.60	0.60
	Tomato paste	0.5, 0.6, 0.75	0.6
	Tomato preserves	< 0.1, < 0.2, 0.2	0.2
Barley	Pearl barley	0.9	0.9
	Barley hulls	1.6	1.6
Wheat	Flour	0.1, 0.2, < 0.3,	0.15
	Wheat germ	2.0	2.0
	Wholemeal flour (germ + shorts)	2.7	2.7
	Wheat bran	1.4, , 3.1, 3.5	3.1
Cotton	Cottonseed refined oil	< 0.02,< 0.03, < 0.03	< 0.02
	Meal	0.02, 0.03, 0.07	0.03

RESIDUES ON ANIMAL PRODUCTS

Livestock feeding studies

Dairy cattle feeding study

As the goat metabolism studies conducted at exaggerated dose rate suggested that residues of ethephon may transfer to edible tissues and mil, a cattle feeding study was conducted (Wells-Knecht, 1996, 96E08334, [M-188195-01-1]). Three groups of three Holstein dairy cows were orally dosed once daily with ethephon in gelatine capsules for 28 consecutive days. One additional cow was maintained as control and received no test compound. One group received an amount of ethephon equivalent to nominally 43 ppm diet (1×, actual mean level = 44 ppm), another was fed 129 ppm diet (3×, actual mean level = 128 ppm), and the last group received 430 ppm diet (10×, actual mean level = 415 ppm).

Milk samples were collected twice daily and, the p.m. milk and the a.m. milk of the following day were combined. Milk samples for each animal were retained for analysis on study days 0, 1, 4, 8, 11, 15, 18, 22, 25 and 27. All cows were sacrificed after 28 days of dosing, within 6 hours after receiving the final dose. Tissues collected were: kidney, liver, fat (composite of omental and peri-renal fat), and muscle (composite of thigh and loin muscle). All samples were frozen at –20 ºC until analysis.

Ethephon was measured in the homogenised tissue samples using analytical method 11-94 (Nygren, 1994, 11-94). The LOQ was 0.01 mg/kg for tissues and 0.002 mg/kg for milk. The concurrent mean recovery in milk was 99±6% (n=17) at fortification levels of 0.002–0.10 mg/kg. The mean recovery in liver was 105±7% (n=3) at fortification levels of 0.01–2.0 mg/kg, in kidney was 94±14% (n=5) at fortification levels of 0.01–12 mg/kg, in fat was 70% (n=2) at fortification levels of 0.01 and 4 mg/kg and in muscle was 98% (n=2) at fortification levels of 0.01 and 0.4 mg/kg.

All milk and tissue samples were analysed within 30 days of sampling, except for the reanalysis of the Day 8 milk samples, which were analysed after 34 days of storage. The results of the reanalysis corresponded with the results of the initial analysis conducted within 30 days of collection. The storage stability study showed that ethephon residues are stable in milk for at least 4 months, and in meat for at least 12 months when stored frozen.

A summary of the residues found in milk is given in in the table below. All milk samples from the control cow did not contain ethephon (ND). Following oral administration to lactating cows for 28 consecutive days, the residues of ethephon in whole milk appeared to plateau after Day 4. At the dose level of 43 ppm diet, residues of ethephon in milk were less than 0.01 mg/kg. Maximum residue concentrations in milk were 0.007 mg/kg at the low dose level, 0.019 mg/kg at the mid dose level and 0.033 mg/kg at the high dose level.

Table 87 Mean residues of ethephon in whole milk during 28 days oral administration to dairy cows

Day sampled [a]	Ethephon in individual cow, mg/kg (Mean ethepon, mg/kg)		
	43 ppm diet	129 ppm diet	430 ppm diet
0	ND, ND, ND	ND, ND, ND	ND, ND, ND
1	0.0068, 0.0074, 0.0074 (mean 0.072)	0.0178, 0.0116, 0.0142 (0.0145)	0.0331, -, 0.0275 (0.0303)
4	0.065, 0.0054, 0.0066 (0.0062)	0.0147, 0.0122, 0.0186 (0.0152)	0.0263, 0.0307, 0.0274 (0.0281)
11	0.0034, 0.0020, 0.0041 (0.0032)	0.0149, 0.0116, 0.0122 (0.0129)	0.0308, 0.0244, 0.0243(0.0265)
15	0.025, 0.025, 0.041 (0.0030)	0.0119, 0.0094, 0.0113 (0.0109)	0.0269, 0.0283, 0.0261 (0.0271)
18	< 0.002, < 0.002, 0.0023 (< 0.002)	0.0110, 0.0077, 0.0112 (0.0100)	0.0322, 0.0179, 0.0249 (0.0250)
22	0.0020, < 0.002, 0.0025 (< 0.002)	0.0108, 0.0067, 0.102 (0.0092)	0.0276, 0.0180, 0.0271 (0.0242)
25	0.0022, < 0.002, 0.0023 (0.002)	0.0149, 0.0050, 0.0084 (0.0094)	0.0267, 0.0197, 0.0251 (0.0238)
27	< 0.002, < 0.002, 0.0023(< 0.002)	0.0069, 0.0095, 0.0138 (0.0101)	0.0251, 0.0257, 0.0323 (0.0277)

[a] Day 8 milk not included in table because of suspect untreated control

A summary of the residues of ethephon in tissue samples from cows fed 43 ppm, 129 ppm, and 430 ppm in the diet of ethephon for 28 days are summarized in the table below. The results show that residues are very low in tissues except in kidney. The residue levels in kidney are up to 7 times higher than the residue level in liver. Residue levels of ethephon in tissue and milk samples are proportional to dose level.

Table 88 Residues of ethephon in tissues from dairy cattle following dosing with ethephon for 28 days

Tissue	Ethephon in individual cow, mg/kg (Mean ethephon, mg/kg)			
	0 ppm diet	43 ppm diet	129 ppm diet	430 ppm diet
Fat	< 0.01	< 0.01, < 0.01, < 0.01 (< 0.01)	0.016, 0.069, 0.037 (0.04)	0.038, 0.029, 0.13 (0.06)
Kidney	0.03	0.64, 0.24, 0.58 (0.49)	2.8, 3.2, 3.5 (3.2)	8.0, 4.6, 10.9 (7.8)
Liver	0.05	0.095, 0.066, 0.085 (0.08)	0.39, 0.65, 0.50 (0.51)	0.85, 0.63, 1.5 (0.99)
Muscle	< 0.01	0.014, < 0.01, 0.016 (0.01)	0.043, 0.061, 0.049 (0.05)	0.11, 0.074, 0.17 (0.12)

Poultry feeding study

A poultry feeding study was conducted (Wells-Knecht, 1996, 96E08335, [M-188192-01-1]). Three groups of ten Leg Horn laying hens were orally dosed once daily with ethephon in gelatine capsules for 28 consecutive days. Each group was sub-divided into three subgroups of three or four hens. One additional group of ten hens was maintained as a control and received no test compound. One group received ethephon at a dose level equivalent to nominally 2.3 ppm diet (1×), another was fed 6.9 ppm diet (3×), and the last group received 23 ppm diet (10×).

Eggs were collected twice daily. Egg samples from study days 0, 1, 4, 8, 11, 15, 18, 22, 25 and 27 were pooled by sub-group. All hens were sacrificed after 28 days of dosing, within 4 hours after receiving the final dose. Tissue samples collected were liver, skin with adhering fat, and muscle (breast and leg). All samples were frozen at –20 ºC until analysis.

Ethephon was measured in the homogenised egg and tissue samples using analytical method 11-94. The LOQ was 0.01 mg/kg for tissues and 0.002 mg/kg for eggs. The concurrent mean recovery in egg was 99 ± 4% (n=17) at fortification levels of 0.002–0.10 mg/kg. The mean recovery in liver was 104 ± 10% (n=4) at fortification levels of 0.01–2.0 mg/kg, in skin with fat was 89 ± 3% (n=5) at fortification levels of 0.004–0.20 mg/kg and in muscle was 98 ± 9% (n=5) at fortification levels of 0.04–0.10 mg/kg.

All egg and tissue samples were analysed within 30 days of sampling.

A summary of the residues found in eggs is given in in the table below. Following oral administration to laying hens for 28 consecutive days, the residues of ethephon in whole eggs from the highest dose group were slightly above or below the LOQ of 0.002 mg/kg with the highest concentration of 0.0036 mg/kg in eggs from sub-group C of the high dose group on Day 8 (mean residue on Day 8 was 0.0029 mg/kg). Eggs from the low and mid dose groups were not analysed.

Table 89 Residues of ethephon in whole egg during 28 days oral administration to laying hens

Day sampled	Ethephon in subgroup, mg/kg (Mean ethephon, mg/kg)			
	0 ppm diet	2.3 ppm diet	6.9 ppm diet	23 ppm diet
0	< 0.002	< 0.002, < 0.002, < 0.002 (< 0.002)	0.002, < 0.002, < 0.002 (< 0.002)	0.002, < 0.002, < 0.002 (< 0.002)
1	< 0.002	Not analysed	Not analysed	0.002, < 0.002, < 0.002 (< 0.002)
4	0.002	Not analysed	Not analysed	0.0023, 0.0027, 0.0028 (0.0026)
8	< 0.002	Not analysed	Not analysed	0.0025, 0.0027, 0.0036 (0.0029)
11	< 0.002	Not analysed	Not analysed	0.002, < 0.002, < 0.002 (< 0.002)
15	< 0.002	Not analysed	Not analysed	0.002, < 0.002, < 0.002 (< 0.002)
18	< 0.002	Not analysed	Not analysed	0.002, < 0.002, < 0.002 (< 0.002)
22	< 0.002	Not analysed	Not analysed	0.0023, 0.0028, < 0.002 (0.0024)
25	< 0.002	Not analysed	Not analysed	0.0023, 0.0023, 0.0024 (0.0023)
27	< 0.002	Not analysed	Not analysed	< 0.002, 0.0024, 0.0024 (0.0023)

A summary of the residues of ethephon in tissue samples from hens fed 2.3 ppm, 6.9 ppm, and 23 ppm in the diet of ethephon for 28 days are summarized in the table below. The results show that residues are very low in tissues from the low dose group. The highest residue level was found in liver at 0.033 mg/kg in the low dose level. Residue levels of ethephon in egg and tissue samples increased proportionally with dose level. At the highest dose level, the maximum residue in liver was 0.29 mg/kg.

Table 90 Residues of ethephon in tissues from laying hens following dosing with ethephon for 28 days

Tissue	Ethephon in subgroup, mg/kg (Mean ethephone, mg/kg)			
	0 ppm diet	2.3 ppm diet	6.9 ppm diet	23 ppm diet
Liver	0.01	0.0028, 0.0033 (0.031)	0.059, 0.058, 0.068 (0.062)	0.29, 0.19, 0.20 (0.23)
Skin + fat	< 0.01	0.011, 0.014 (0.013)	0.024, 0.017, 0.032 (0.024)	0.117, 0.075, 0.087 (0.093)
Muscle	< 0.01	< 0.01, < 0.01 (< 0.01)	< 0.01, < 0.01, 0.015 (0.012)	0.060, 0.023, 0.027 (0.037)

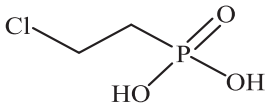
APPRAISAL

Ethephon, 2-chloroethylphosphonic acid, is a systemic plant growth regulator belonging to the phosphonate family. It is readily absorbed by the plant and releases ethylene, a natural plant hormone. Ethylene not only influences directly several physiological processes such as ripening and maturation, but also stimulates the endogenous ethylene production. It has been registered in many countries for a variety of crops, including fruits, vegetables, cereals and oilseed crops.

Ethephon was first evaluated by JMPR in 1977 as a new compound, and then reviewed several times for residues. It was evaluated under the periodic review programme in 1994. The compound was listed in the Priority List by the Forty-sixth Session of CCPR in 2014 for toxicological and residue evaluation by the current Meeting in the CCPR periodic review programme.

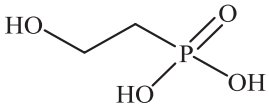
The Meeting received information on identity, metabolism and environmental fate, residue analysis, use pattern, supervised trials (on apples, cherries, grapes, figs, olives, pineapples, tomatoes, cereals, and cotton), processing, and animal feeding studies.

In this Appraisal, the following names were used for referred compounds.



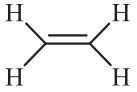
Ethephon

2-Chloroethylphosphonic acid



HEPA

(2-hydroxyethyl)-phosphonic acid



Ethylene

Plant metabolism

The Meeting received information on plant metabolism studies conducted on a variety of plants including information from the published scientific literature. The information dated from 1962 to 2003 and covered peaches, grapes, pineapples, cucumbers, squash, melons, tomatoes, wheat, hazelnuts, walnuts and cotton.

Many studies conducted on various plants indicate the release of ethylene after treatment with ethephon. In several of such studies, methanol, acidified methanol or water was used to extract ethephon from fruits and/or leaves and, where data are available, significant amount of the applied radioactivity (> 60%) or TRR (> 80%) was recovered in the surface wash and solvent extract combined.

The studies involving characterization and identification of other metabolites are described below.

Tomato plants grown outdoor were treated with a foliar spray of uniformly labelled [^{14}C]ethephon at a rate approximating 1.46 kg ai/ha at the "green mature" or "colour break" growth stage and fruits were harvested 0, 5 and 12 days after the treatment (DAT). The majority of the radioactivity was recovered from the methanol surface wash on 0 DAT but 96% (including surface wash) and 98% of the TRR was recovered in methanol extracts of 5 DAT and 12 DAT samples respectively.

The predominant radioactive residue in methanol extract of tomato fruit was ethephon, 70% and 59% of the TRR corresponding to 1.2 mg/kg and 0.68 mg/kg in 5 DAT and 12 DAT was found in fruits, respectively. The concentration of ethephon decreased over the time period in the study from 7.5 mg/kg at 0 DAT to 0.68 mg/kg at 12 DAT. The only significant metabolite found was HEPA accounting for 15% TRR (0.26 mg/kg) on 5 DAT and 13% TRR (0.15 mg/kg) on 12 DAT. No other metabolites exceeded 5% TRR in the methanol extract.

Wheat plants grown outdoor were treated with a foliar spray of [^{14}C]ethephon at a rate of 0.36 kg ai/ha and 3.6 kg ai/ha at the forage stage (BBCH 39) and forage samples were collected on 0 DAT, hay on 14 DAT and grain and straw on 34 DAT. The majority of radioactivity was recovered in methanol extracts of plant parts (hay and straw) on 14 and 34 DAT regardless of the dose used (94% TRR including 1% in surface wash in hay of both doses and 58% and 74% TRR in straw respectively) while radioactivity was similarly distributed in the methanol surface wash and methanol extract (45–46% and 54–55% TRR) of forage on 0 DAT. Unextracted residues were about 5% in 14 DAT for hay and 10% (1×) and 26% (10×) in 34 DAT for straw.

Methanol extraction recovered only 28 and 22% TRR from grain samples after the low and high doses. Acid hydrolysis of the remaining solid released a further 56 and 71% TRR; extraction of the post-hydrolysis solids released a total of 9.9% and 4.3% TRR, respectively. This indicates the presence of significant conjugates in grains. Unextracted residues were 1.8–6.0% TRR.

Most of the TRR was attributed to the sum of ethephon and HEPA. The major radioactive residue in 14 DAT hay was HEPA (72% TRR and 3.7 mg/kg) followed by ethephon (20% TRR and 1.0 mg/kg). In the 34 DAT straw, the major radioactive residue was ethephon (62% TRR and 1.5 mg/kg).

In 34 DAT grain, HEPA was found at a similar level as ethephon after the low dose (HEPA 48% TRR and 0.51 mg/kg and ethephon, 44% and 0.47 mg/kg). After the higher dose, approximately two times larger amount of HEPA was found than ethephon (HEPA, total of 60% TRR and 2.0 mg/kg; and ethephon, total of 32% TRR and 1.1 mg/kg). No other metabolites exceeded 3% of TRR.

Cotton plants grown outdoor were treated with a foliar spray at a rate of 1.4 kg ai/ha seven days before harvest. Plants were harvested at 7 DAT. The majority of radioactivity was recovered in methanol/water (9:1) for gin trash (89% TRR) and in methanol extract for seeds (82% TRR).

The predominant radioactive residue in gin trash was ethephon at 93% TRR and 30 mg/kg; and 78% TRR and 0.64 mg/kg in seeds. HEPA was low, 1.7% TRR and 0.52 mg/kg in gin trash and 9.6% TRR and 0.08 mg/kg in seeds. No other metabolites exceeded 2% of TRR.

In summary, plant metabolism studies conducted on tomatoes, wheat and cotton indicate that the metabolism of ethephon in these plants was qualitatively similar and indicate that radioactivity penetrated into plants after a foliar application and translocated to edible matrices of plants.

After foliar application to plants, ethephon was metabolized to ethylene and phosphates and HEPA which would be either metabolized to carbon dioxide and phosphate or incorporated into biomolecules such as proteins, carbohydrates and lipids after further metabolism.

In tomatoes, cotton, and wheat hay, most radioactivity was recovered from methanol extracts whilst in wheat grains and straw a significant amount of radioactivity was recovered in the acid hydrolysate, suggesting ethephon is present in conjugated forms.

In tomato and cotton, ethephon was the predominant residue with little HEPA present. However, in wheat grains, HEPA and its conjugates were present at a similar concentration as that of ethephon and its conjugates after the 1× dose and approximately two times higher concentration than ethephon after the 10× exaggerated rate in grain. In wheat hay, HEPA was present at 3.5 times higher than ethephon.

Ethephon would be an appropriate marker for plants except cereal grains and straw in which ethephon was significantly metabolised to HEPA and to conjugates of ethephon and HEPA.

Animal metabolism

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

Metabolism studies on laboratory animals including rats were reviewed in the framework of toxicological evaluation by the current JMPR.

After oral administration of ethephon to rats, absorption was rapid with a Tmax of 1.0–1.3 hours and 1.9–2.5 hours after a single oral dose of 50 or 1000 mg/kg bw, respectively. Six days after a single dose tissue, and carcass contained only 0.08% or less of administered radioactivity. Highest concentrations were found in liver and kidney. Radioactivity was excreted in urine (47–60%), expired air (18–21%, mainly ethylene) and faeces (4–6.5%), indicating that at least 65% of the administered dose was absorbed. Ethephon was mainly metabolized to ethylene and to a small extent to HEPA.

Two lactating goats were orally administered [^{14}C]ethephon twice daily after am and pm milking in capsules for seven consecutive days at 0.37 and 0.46 mg/kg bw/day (approximately 10 ppm in the diet). The goats were sacrificed approximately 16 hours after the last dose.

A significant portion of the administered dose was released as ethylene (29%) and carbon dioxide (2.0%). Radioactivity was also excreted in urine (19%) and faeces (6.7%). In total, milk contained 3.3% of the administered dose, tissues 3.0%, and content of gastro ontestinatl (GI) tract, 0.84%. Amongst tissues, kidney contained the highest radioactivity at 1.2 mg eq/kg followed by liver at 1.0 mg eq/kg. Fat contained 0.50 mg eq/kg, heart 0.16 mg eq/kg and muscle 0.10 mg eq/kg. Over the study period, average TRR in milk increased from 0.081 mg/kg on day 0.5 to a plateau level of 0.42 mg/kg at day 3.5. The fat fraction of milk contained 45% of the TRR in milk; skimmed milk contained 0.15–0.20 mg eq/kg; and milk fat, 3.0–4.2 mg eq/kg.

In order to estimate ethephon, portions of tissues were hydrolyzed by shaking at 40 °C at pH 11 for one hour to transform ethephon to ethylene. Ethylene released by this hydrolysis was 0.4% TRR in kidney corresponding to 0.008 mg/kg ethephon, 0.05% TRR in fat, and 0% TRR in muscle, liver and milk. Radioactivity in the remaining solids were 0.3%, 2.1%, 71% and 35% of the respective TRR in kidney, liver, muscle and fat.

Extraction of a portion of liver with ether released 5.3% TRR, methanol, a further 64% TRR leaving 27% TRR unextracted. Precipitation with trichloroacetic acid resulted in 12% TRR in liver which is associated with proteins. Glycogen was isolated at a concentration of 0.9 mg/kg.

Two studies were provided on metabolism of ethephon in laying hens. In both studies, hens were orally administered either by capsule or gavage [^{14}C]ethephon at a rate equivalent to 53–67 ppm in the diet for five consecutive days. Hens in the first study were sacrificed 22–23 hours after the last dose and those in the second 9–10 hours after the last treatment.

In the first study, the majority of the administered dose (58%) was recovered as expired ethylene while expired carbon dioxide was negligible. In the excreta, 26–30% of the

administered dose was recovered. Liver contained 0.31 mg eq/kg (average), followed by kidney with 0.20 mg eq/kg and fat with 0.15 mg eq/kg. Radioactive residues in the eggs and tissues accounted for less than 1% of the administered dose. Muscle contained 0.023 mg eq/kg showing lower levels than other tissues. Radioactive residues in eggs reached a plateau on Day 4. No identification of metabolites was carried out in this study.

In the second study, approximately one third of the administered dose was recovered in excreta. About 3% of the administered dose was recovered as ethylene but this percentage is not reliable due to the leakage in the experiment. Radioactive residues in the eggs and tissues accounted for less than 1% of the administered dose. Kidneys contained 0.71–1.1 mg eq/kg, liver 0.63–0.90 mg eq/kg, and fat 0.051–0.091 mg eq/kg and muscle, 0.051–0.058 mg eq/kg. Radioactive residues in eggs did not reach a plateau within the study period of 5 days. Higher radioactivity was found in eggs in this study than the first study reaching the level of approximately 0.40 mg eq/kg on Day 5. In eggs, egg yolk contained much higher radioactivity than egg white (1.02 mg eq/kg egg yolk and 0.092 mg eq/kg in egg white).

Ethephon and HEPA were identified in methanol/water extracts of muscle, liver and kidney but not in the hexane/tetrahydrofuran extracts of fat or eggs (both yolk and white). Ethephon was the major residue in kidney accounting for 42% of TRR (0.30 mg/kg) but at a similar level as HEPA in liver (ethephon, 0.11 mg/kg; HEPA, 0.10 mg/kg) and muscle (ethephon, 0.006 mg/kg; HEPA, 0.009 mg/kg). Significant radioactivity was incorporated into amino acids (3–35% of TRR) in these tissues and in fatty acids (around 40% TRR) in fat. Significant amounts of radioactive residues (23 or 40% TRR for liver and 42 or 71% TRR for fat) remain unidentified. In eggs, radioactivity was incorporated into peptides (93% TRR in egg white) and fatty acids/cholesterol/glycerol (77–79% in egg yolk).

In summary, ethephon, when administered orally, was rapidly eliminated either in the excreta or expired as ethylene. Ethephon and HEPA were identified in kidney, liver and muscle in hens. Ethephon was found in kidneys of goats at very low concentrations. Ethephon was metabolized through two routes: metabolized to ethylene and/or to carbon dioxide through HEPA. A similar metabolic pattern was observed in rats, goats and hens. In livestock, radioactivity was found in fatty acids, proteins and glycogen.

Environmental fate

Hydrolysis

Ethephon degrades rapidly at pH 7 and 9 with the half-life of 2.4 and 1.0 day, respectively. At pH 5, it degrades more slowly with a half-life of 73.5 days. Ethylene gas and methylated phosphoric acid were the only degradation products found.

Photochemical degradation

Ethephon showed degradation under continuous irradiation for 360 hours at pH 5 at 25 °C. The half-life was 29 days under irradiation and 51 days without irradiation. Ethephon and ethylene were the only major compounds found. Ethylene was the only degradate of ethephon in the headspace.

Aerobic soil metabolism

The studies on aerobic soil degradation of ethephon in five different soils at 20–25 °C indicate that ethephon applied on soil degraded over time with different rates with the formation of ethylene. DT_{50} values ranged from 2.7–38 days for the five soils tested.

Photolysis on soil surface

Photolysis of ethephon on soil was found to be insignificant. Only ethylene and carbon dioxide were formed.

Field dissipation

Field dissipation studies were conducted at three sites in the USA. In all cases ethephon declined with time. DT_{50} values were 6.8–2 5 days.

Residues in succeeding crops

A confined rotational crop study was conducted to examine the nature and level of residues of ethephon in three succeeding crops (radish, collard and wheat) under outdoor conditions. A single application of radio-labelled ethephon was made on bare plots in plastic containers at a rate of 2.36 kg ai/ha (approximating the highest single application rate for cotton in the USA among approved label rates available to the Meeting). After plant back intervals (PBI) of 30, 120 and 379 days, collard, radish and wheat were planted into the treated soil. Mature radish, collard and wheat were harvested 54–62 days, 68–91 days and 110–158 days after planting. Immature wheat foliage was harvested 47–68 days after planting.

Ethephon declined steadily in soil. Radioactivity in mature plant samples declined in parallel with or faster than the decline in soil. The total extracted radioactive residues were at or lower than 0.07 mg eq/kg in any sample analysed. The solvent extraction recovered 34–37% TRR in 30 day PBI collards, 120 day PBI radish top and 30 day PBI and 120 day PBI wheat forage. As observed in the metabolism study on wheat, only 7.3–24% TRR were extracted by solvents from 30 day PBI and 120 PBI wheat grains and straw.

In the HPLC analysis of plant extracts, where radioactivity was sufficient for characterization, ethephon and HEPA were detected at or below 0.01 mg/kg in the extracts of radish, collard and wheat. No unknown peaks were observed. Sequential treatments of the unextracted radioactive residues for natural components indicated that most of the radioactivity in the plant samples were incorporated into biomolecules, such as starch, proteins, and cellulose fractions.

Overall, ethephon was shown to degrade relatively fast in soil with half-lives around or shorter than the plant back interval of 30 days. The confined succeeding crop study indicated the presence of very low levels of ethephon and HEPA in rotational crops. Therefore, no significant residues of ethephon or HEPA would be expected in rotational crops.

Methods of analysis

Analytical methods for determination of residues of ethephon and its metabolite HEPA were developed for a wide range of matrices of plant and animal origin.

There are three different principles for these analytical methods:

- Ethylene-release by heating in alkaline solution (headspace GC-FID)
- Derivatization to methyl ester using diazomethane (GC-FPD or GC-NPD)
- Extraction: mostly by methanol, acidified methanol or 0.01% formic acid
- LC-MS/MS (m/z 143→ 107 or 145-> 107 and HEPA 125→ 95)
- Extraction: mostly by a mixture of methanol, water and formic acid. Clean-up: mostly with SPE column.

The LC-MS/MS methods were used in the more recent studies.

The methods for plant matrices were validated for ethephon resulting in acceptable mean recoveries and relative standard deviations (RSDs) with the LOQ of 0.01–0.05 mg/kg. They are suitable for determining ethephon in a free form (some methods also for free HEPA).

An LC-MS/MS method was recently developed to determine ethephon and HEPA in both free and conjugated forms in cereal grains, straw and green materials. For the extraction of these compounds, grains and straw were extracted first with methanol and then by a mixture of

concentrated hydrochloric acid and water at 50 °C overnight and the extract and hydrolysate were combined for analysis. For green materials, this acid hydrolysis step was not included. This method was validated for ethephon and HEPA in these matrices resulting in acceptable mean recoveries and RSDs with the LOQ of 0.01 mg/kg for grains and 0.05 mg/kg for straw and green materials.

Methods for animal matrices were validated for ethephon resulting in acceptable mean recoveries and RSDs. The LOQ was 0.002–0.01 mg/kg. They are suitable for determining ethephon in a free form.

A multi-residue method DFG S19 (two variants) was examined for analysis of ethephon in plants for enforcement. However, due to low extraction (30%), this method does not seem appropriate for analysis of ethephon.

Stability of pesticide residues in stored analytical samples

The stability of ethephon was investigated in homogenates of various FROZEN plant and animal matrices at –20–15 °C, at fortification levels 0.2–1.0 mg/kg (plant matrices) or 0.1 mg/kg (animal matrices).

Ethephon was stable when stored frozen for at least 24 months in apples, cherries, grapes, blackberries, pineapples (fruit and forage), melons (36 months), peppers, tomatoes, wheat (grain and straw) and cotton seed (25 months). It was also stable for at least 12 months in apple juice and cotton seed oil.

Ethephon was stable when stored frozen for at least 4 months, the longest period tested, in bovine milk, bovine meat and egg.

Definition of the residue

Plant metabolism studies indicate that ethephon is metabolised in a qualitatively similar pattern in plants. Ethephon penetrates into plants after foliar application and residues of ethephon were found in edible commodities. Ethephon was metabolized to ethylene, which is naturally occurring in plants (but at levels not relevant to MRL setting). Ethephon was metabolized to form HEPA and further metabolized to be incorporated in many biomolecules, such as proteins, carbohydrates and lipids.

In the plants studied, ethephon was the major residue. Except for cereal grains, hay and straw, HEPA was found at much lower concentrations than the parent. In wheat plant fractions, HEPA was present at similar concentrations or higher concentrations than those of ethephon in grain and in hay.

In wheat grains and straw, radioactive residues were recovered at a significant proportion from acid hydrolysate and most of this radioactivity was attributed to ethephon and HEPA. This indicates that ethephon and HEPA were also present in these commodities in the form of conjugates.

The current Meeting considered that HEPA is not a toxicologically relevant metabolite as it does not inhibit cholinesterase activity and the NOAEL for HEPA in a 28-day gavage study in animals is at least two orders of magnitude higher than the NOAEL in humans that formed the basis of the ADI and ARfD.

Residues of ethephon were not expected to occur in significant concentrations in rotational crops.

In summary, the Meeting noted that in cereal grains and straw, presence of ethephon in the form of conjugates is significant. In other plant commodities, the Meeting considered that ethephon would be a good marker for enforcement and for estimation of dietary intake.

One recently developed and validated method, involving methanol extraction and acid hydrolysis/extraction of post methanol-extraction solids is capable of determining total ethephon

in free and conjugated forms in cereal matrices. There are other validated methods suitable for determining ethephon in its free form in plant matrices.

In animal metabolism studies, ethephon was rapidly eliminated either in the excreta or exhaled as ethylene. Ethephon was found at low levels in tissues. No metabolites were significant. The Meeting considered that ethephon is a suitable marker for enforcement and for estimation of dietary intake.

There are validated methods available for the determination of ethephon in its free form in animal matrices.

The log K_{ow} (–1.8 to –0.6 at 20 °C) indicates that ethephon is highly water-soluble. Although radioactive residues were found at higher levels in milk fat and egg yolk than skimmed milk or egg white, they were attributed to radioactivity incorporated into fatty acids. The Meeting concluded that the residue is not fat-soluble.

Based on the above, the Meeting recommended the following residue definitions for plant and animal commodities.

Definition of the residue for plant commodities except cereal grains and straw (for compliance with the MRL and for estimation of dietary intake): *Ethephon.*

Definition of the residue for cereal grains and straw (for compliance with the MRL and for estimation of dietary intake*): Ethephon and its conjugates, expressed as ethephon*.

Definition of the residue for animal commodities (for compliance with the MRL and for estimation of dietary intake): *Ethephon.*

The residue is not fat-soluble.

Results of supervised residue trials on crops

The Meeting received supervised trial data for ethephon on apples, cherries, grapes, figs, olives, pineapples, tomatoes (outdoor and indoor), barley, rye, wheat and cotton using foliar sprays of mostly SL formulations containing various concentrations of ethephon.

As ethephon is reviewed under the periodic review programme, the Meeting decided to withdraw its previous recommendations for blueberries, cantaloupes, peppers, dried chilli peppers, hazelnuts and walnuts due to the lack of data.

Apple

A total of 18 supervised trials were conducted on apples in Europe in 2000, 2002, 2006 and 2007, eight in France, two in Germany, one in the UK, two in Italy, two in Spain, one in Portugal and two in Greece.

Residues of ethephon from 13 trials matching critical GAP for apple in France (0.036 kg ai/hL, one to two applications, and PHI 10 days) were: < 0.05, 0.06, 0.07, 0.08, 0.08, 0.14, 0.15, 0.15, 0.24, 0.26, 0.27, 0.40 and 0.49 mg/kg.

The trials matching GAP in France were appropriate for estimating a maximum residue level. The Meeting estimated a maximum residue level of 0.8 mg/kg for apples to replace the previous recommendation. The Meeting also estimated an STMR of 0.15 mg/kg and an HR of 0.49 mg/kg.

Cherries

A total of 15 supervised trials were conducted on cherries in Europe in 2000, 2002 and 2009, ten in France, one in Italy, one in Spain, one in Greece, one in Belgium and one in the Netherlands.

Residues of ethephon from 13 trials matching GAP in Austria for cherries and in the Netherlands for sour cherries (0.36 kg ai/ha, one application, PHI 7 days) were: 0.28, 0.30, 0.33, 0.37, 0.44, 0.52, 0.65, 0.67, 0.91, 1.4, 2.0, 2.3 and 2.7 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg for cherries to replace the previous recommendation and an STMR of 0.65 mg/kg and an HR of 2.7 mg/kg.

Grapes

A total of ten supervised trials were conducted on grapes in France in 1995, 2006 and 2009. The GAP in France for grapes allows one application at a maximum rate of 0.45 kg ai/ha with a PHI of 28 days.

Residues from ten trials matching GAP in France were: 0.05, 0.07, 0.14, 0.18, 0.18, 0.20, 0.21, 0.25, 0.37 and 0.52 mg/kg.

The Meeting estimated a maximum residue level of 0.8 mg/kg for grapes to replace the previous recommendation, an STMR of 0.19 mg/kg and an HR of 0.52 mg/kg.

Fig

Six supervised trials were conducted on figs in Brazil in 2004–2005. GAP in Brazil for figs allows one application of 0.94 kg ai/hL with a PHI of 5 days. Ethephon should be applied directly to fruits using brushes with sponge tips or other equipment for even distribution.

Residues from three trials matching GAP in Brazil were, 0.71, 0.73 and 0.75 mg/kg. The Meeting estimated a maximum residue level of 3 mg/kg, an STMR of 0.73 mg/kg and an HR of 0.75 mg/kg for fig.

Olives

Eight supervised trials were conducted on olives in Spain in 2007–2008. GAP in Italy allows two applications (1st application 18 days before harvest at a rate of 0.45 kg ai/ha and 2nd application 11 days before harvest at 0.60 kg ai/ha) with a PHI of 11 days.

Residues from eight trials matching GAP in Italy were, 0.85, 0.90, 0.98, 1.6, 2.2, 2.5, 2.6 and 4.3 mg/kg.

The Meeting estimated a maximum residue level of 7 mg/kg, an STMR of 1.9 mg/kg and an HR of 4.3 mg/kg for olives.

Pineapple

A total of 15 supervised trials were conducted. Five in Brazil in 1994, 1995 and 2005, two in Costa Rica in 1998, two in Côte d'Ivoire in 1997 and 1998, and six in the USA in 1989.

GAP in Kenya for pineapple allows one application at the maximum rate of 1.92 kg ai/ha with a PHI of 7 days. Residues from trial conducted in Côte d'Ivoire matching this GAP were (n=2): 0.11 and 0.97 mg/kg.

Residues from five trials in Brazil matching GAP in Brazil for pineapple (one application at a maximum rate of 0.94 kg ai/ha with a PHI of 14 days) were: < 0.05, 0.11, 0.15, 0.19 and 0.20 mg/kg.

The trials conducted in the USA involved two applications of ethephon and the rate of the first application was two times higher than GAP in Costa Rica (up to two applications at the maximum rate of 1.2 kg ai/ha with a PHI of 1 day; first one 5–7 months before harvest and second 1–2 weeks before harvest) but it was made six months earlier than the expected harvest time with little impact on the residues at harvest.

In the trial in Costa Rica, pineapple was harvested on 0 DALA but as the decline trials indicated that there was no significant decline from 0 to 1 DALA, the Meeting agreed to use the data from 0 DALA.

Residues from trials conducted in the USA and Costa Rica matching GAP in Costa Rica were (n=4), 0.19, 0.22, 0.42 and 0.72 mg/kg. One trial conducted in Brazil matched GAP in

Costa Rica and residues were (n=1), 0.47 mg/kg. Combined residue dataset was (n=5), 0.19, 0.22, 0.42, 0.47 and 0.72 mg/kg.

As the dataset from five trials matching GAP in Costa Rica would lead to a higher maximum residue level than the dataset from five trials matching GAP in Brazil, the Meeting decided to use the dataset associated with GAP in Costa Rica. The Meeting estimated a maximum residue level of 1.5 mg/kg to replace its previous recommendation.

The Meeting calculated a mean pulp/whole fruit ratio to be 0.29 using residue levels higher than LOQ. Using the mean and highest residue in whole fruit and this ratio, the Meeting estimated an STMR of 0.12 mg/kg and an HR of 0.21 mg/kg for pineapple.

Tomato

A total of 33 supervised trials on tomatoes were conducted. Twenty-one trials were in Europe in 1999, 2000, 2001 and 2004 and 15 in the USA in 1989–1991 and 2005. As the labels provided to the Meeting do not specify outdoor or indoor uses, the Meeting considered both trials conducted outdoor and indoor.

The critical GAP for the European trials was GAP in Italy which allows the maximum rate of 1.92 kg ai/ha which can be divided into two applications with a PHI of 7 days. Residues from 12 outdoor trials in Europe matching GAP in Italy were 0.24, 0.30, 0.40, 0.45, 0.46, 0.5, 0.55, 0.57, 0.62, 0.68, 0.78, and 0.78 mg/kg.

Residues from nine indoor trials matching GAP in Italy were 0.31, 0.36, 0.45, 0.51, 0.52, 0.66, 0.68, 0.69 and 0.79 mg/kg.

Residues from five independent outdoor trials in the USA matching GAP in Canada (one application of 1.54 kg ai/ha, PHI 14–21 days) were 0.05, 0.06, 0.09, 0.67 and 0.69 mg/kg.

As the outdoor and indoor trials conducted in Europe were in compliance with the same GAP of Italy and they were not significantly different according to Mann-Whitney U test, they could be combined to estimate a maximum residue level. Residues in the combined data set were 0.24, 0.30, 0.31, 0.36, 0.40, 0.45, 0.45, 0.46, 0.5, 0.51, 0.52, 0.55, 0.57, 0.62, 0.66, 0.68, 0.68, 0.69, 0.78, 0.78 and 0.79 mg/kg.

The Meeting confirmed the pervious recommendation of 2 mg/kg for tomato and estimated an STMR of 0.52 mg/kg and an HR of 0.79 mg/kg.

Cereal grains

As the residue definition for cereal grains was recommended to be “ethephon and its conjugates, expressed as ethephon”, the Meeting used only those trial data obtained with the recently developed analytical method involving acid hydrolysis to convert ethephon conjugates to free ethephon.

Barley

A total of 53 trials were conducted in Europe in 2000, 2001, 2004, 2007, 2008, 2013 and 2014 on barley.

There are several different groups of GAP in Europe. Critical GAP is either GAP in the UK allowing a maximum single rate of 0.48 kg ai/ha, maximum total rate of 0.48 kg ai/ha, and application timing up to BBCH 49, or GAP in Germany allowing one application at a maximum rate of 0.46 kg ai/ha up to BBCH 49.

Residues from seven trials matching GAP in the UK or Germany were 0.03, 0.07, 0.09, 0.13, 0.23, 0.41, 0.73 mg/kg.

The Meeting estimated, using the dataset matching GAP in the UK or Germany, a maximum residue level of 1.5 mg/kg for barley grains to replace the previous recommendation, and an STMR of 0.13 mg/kg.

Rye

Nine supervised trials were conducted in 2006–2007 in Europe. No data were available on the sum of free and conjugated ethephon in rye grains. (See "Wheat" section below.)

Wheat

A total of 43 supervised trials were conducted on wheat in Europe in 2000, 2001, 2004, 2006, 2007, 2013 and 2014.

There are several different groups of GAP in Europe. Critical GAP is that in Austria and Germany allowing one application at a maximum rate of 0.46 kg ai/ha with application timing up to BBCH 51.

Residues from eight supervised trials matching these GAP were 0.05, 0.06, 0.06, 0.08, 0.11, 0.14, 0.23 and 0.31 mg/kg.

The Meeting estimated, using the dataset from trials matching GAP in Austria and Germany, a maximum residue level of 0.5 mg/kg for wheat grains to replace the previous recommendation, and an STMR of 0.095 mg/kg.

As there are similar GAPs existing for wheat, rye and triticale in countries in Europe, the Meeting decided to extrapolate the maximum residue level and STMR for wheat to rye and triticale.

Cotton seed

A total of ten trials were conducted in Europe in 1993, 1994, 1995 and 2008 on cotton, 41 trials in the USA in 1989, 1993 and 1994, and seven trials in Brazil in 1996 and 2006.

Residues from ten trials conducted in Europe matching GAP in Greece for cotton (one application at a maximum rate of 1.44 kg ai/ha with a PHI of 7 days) were 0.07, < 0.10, < 0.10, < 0.10, 0.10, 0.19, 0.30, 0.35, 0.59 and 1.13 mg/kg.

Residues from six independent trials conducted in Brazil matching GAP in Brazil for cotton (one application at a maximum rate of 1.2 kg ai/ha with a PHI of 7 days) were all below the LOQ: < 0.10 (4) and < 0.20 (2) mg/kg.

Residues from 30 trials matching GAP in the USA for cotton (one application at a maximum rate of 2.24 kg ai/ha with a PHI of 7 days) were 0.06, 0.09, 0.10, 0.11, 0.16, 0.18, 0.23, 0.24, 0.26, 0.26, 0.34, 0.35, 0.36, 0.41, 0.54, 0.55, 0.59, 0.61, 0.65, 0.69, 0.75, 0.86, 1.18, 1.42, 1.50, 2.40, 2.42, 2.73, 2.88 and 4.93 mg/kg.

As the residues from US trials would lead to a higher maximum residue level, the Meeting used the results of the US trials to estimate a maximum residue level. The Meeting estimated a maximum residue level of 6 mg/kg for cotton seed to replace the previous recommendation, and an STMR of 0.545 mg/kg.

Animal feed

Cereal forage

As there is no restriction on feed uses of treated cereal plants, the Meeting used residues in forage samples collected on 0 DALA for cereal forage. Since the determination of ethephon in green materials do not require acid hydrolysis, the Meeting used all available data on barley green material.

Barley forage

Residues in forage collected on 0 DAT from 19 trials matching GAP in the UK or GAP in Germany (a maximum single rate of 0.48 kg ai/ha, maximum total rate of 0.48 kg ai/ha, and application timing up to BBCH 49, or one application at a maximum rate of 0.46 kg ai/ha up to BBCH 49) were 2.6, 3.0, 3.2, 4.2, 4.8, 5.1, 5.7, 6.2, 6.2, 6.2, 6.6, 6.6, 7.7, 7.9, 8.1, 8.4, 9.4, 10 and 11 mg/kg.

Residues from 15 trials matching GAP in France (one application at a maximum application rate of 0.48 kg ai/ha and application timing up to BBCH 39 with a PHI of 56 days) in forage were 3.3, 3.5, 4.2, 4.6, 5.2, 5,6, 5.6, 5.9, 6.0, 6.2, 6.7, 8.1, 8.2, 8.3 and 9.5 mg/kg.

Residues from five trials matching GAP in Poland (one application at a maximum application rate of 0.72 kg ai/ha and application timing up to BBCH 39 were 6.0, 7.1, 8.9, 9.6 and 13 mg/kg.

Residues from seven trials matching another GAP in France (one application at a maximum rate of 0.23 kg ai/ha and application timing up to BBCH 39) were 3.0, 3.7, 4.1, 4.5, 5.2, 5.4, 5.9 and 7.5 mg/kg.

Residues arising from five trials using the application rate of 0.72 kg ai/ha showed higher median and highest residues. Based on this dataset, the Meeting estimated a median residue of 8.9 mg/kg and a highest residue of 13 mg/kg ("as received" basis) for barley forage for animal dietary burden calculation.

Rye forage

Residues in forage collected on 0 DAT from nine trials matching GAP in Germany and Austria (one application at a max rate of 0.73 kg ai/ha, application timing up to BBCH 49) were 4.4, 6.4, 7.2, 7.7, 9.1, 9.2, 9.4, 9.6 and 13 mg/kg.

The Meeting estimated a median and highest residue of 9.1 mg/kg and 13 mg/kg for rye forage on an "as received" basis.

Wheat forage

Residues in forage collected 0 DAT from 17 trials matching GAP in Austria and Germany (one application at a maximum rate of 0.46 kg ai/ha, application timing up to BBCH 51) were 3.1, 3.3, 3.5, 4.0, 4.9, 5.2, 5.9, 6.2, 6.4, 6.5, 7.0, 7.0, 7.1, 7.2, 7.5, 10 and 16 mg/kg.

Residues from 18 trials matching GAP in France (one application at a maximum rate of 0.48 kg ai/ha and application timing up to BBCH 39) were 3.1, 4.5, 4.9, 5.6, 5.7, 6.0, 6.1, 6.9, 7.0, 7.2, 7.4, 7.7, 8.3, 12, 14, 14, 17 and 18 mg/kg

Using the dataset from trials matching GAP in France, the Meeting estimated a median residue of 7.1 mg/kg and a highest residue of 18 mg/kg for wheat forage ("as received" basis).

Cereal straw and fodder, dry

As the residue definition for cereal straw was recommended to be "ethephon and its conjugates, expressed as ethephon", the Meeting used only those trial data obtained using the recently developed analytical method involving acid hydrolysis to convert ethephon conjugates to free ethephon.

Barley straw and fodder, dry

Residues from seven trials matching GAP in the UK or Germany (a maximum single rate of 0.48 kg ai/ha, maximum total rate of 0.48 kg ai/ha, and application timing up to BBCH 49, or one application at a maximum rate of 0.46 kg ai/ha up to BBCH 49) in straw were 0.35, 0.43, 0.51, 0.64, 1.2, 1.5 and 3.6 mg/kg.

Using the data set from the trials matching GAP in the UK or Germany, the Meeting estimated a maximum residue level of 7 mg/kg on a dry weight basis (moisture content of 89%) to replace the previous recommendation. For the purpose of calculation of animal dietary burden, the Meeting estimated a median residue and highest residue of 0.64 mg/kg and 3.6 mg/kg ("as received" basis).

Rye straw and fodder, dry

No data were available on the sum of free and conjugated ethephon in rye straw. (See "Summary of cereal straw and fodder, dry" section below.)

Wheat straw and fodder

Residues from eight trials matching GAP in Austria and Germany (one application at a maximum rate of 0.46 kg ai/ha and application timing up to BBCH 51) in straw were 0.36, 0.44, 0.57, 0.66, 1.2, 1.2, 1.3 and 1.5 mg/kg.

Residues from eight trials matching GAP in France (one application at a maximum rate of 0.48 kg ai/ha and application timing up to BBCH 39 with a PHI of 70 days) in straw were 0.21, 0.29, 0.30, 0.44, 0.84, 0.86, 1.2 and 1.7 mg/kg.

Using the data set from the trials matching GAP in France, the Meeting estimated a median residue of 0.64 mg/kg and a highest residue of 1.7 mg/kg ("as received" basis).

Summary

The Meeting noted that it is not always possible to distinguish straw and fodder of barley, rye, triticale and wheat moving in trade, due to their similarity in appearance. It also noted that there are common or similar GAPs existing for wheat, rye and triticale in countries in Europe. The Meeting decided to extend the maximum residue level recommended for barley straw and fodder at 7 mg/kg on a dry weight basis to straw and fodder of wheat, rye and triticale. The new maximum residue levels for rye and wheat straw and fodder, dry replaces the respective previous recommendations.

The median residue and highest residue estimated for wheat straw and fodder should also apply to rye and triticale straw and fodder, dry.

Cotton gin trash

In 12 US trials, residues in cotton gin trash were analysed and reported. Residues in cotton gin trash from ten trials matching GAP in the USA were: 8.41, 11.1, 13.5, 17.1, 25.1, 28.9, 40.5, 45.5, 54.2 and 55.7 mg/kg. The Meeting estimated a median residue of 27 mg/kg. From the highest residue concentration of individual samples, the Meeting estimated a highest residue of 67 mg/kg.

Fate of residues during processing

High temperature hydrolysis

To simulate the degradation of ethephon during pasteurization, baking, brewing, boiling and sterilisation, the hydrolysis of radio-labelled ethephon was investigated in sterile buffered aqueous solutions.

After incubation at 90 °C (pH 4) for 20 minutes, about 80% of ethephon remained and about 10% was recovered as ethylene. The majority of ethephon was converted to ethylene (76–78%) after incubation at 100 °C (pH 5) for 60 minutes or 120 °C (pH 6) for 20 minutes. Only a minor amount of HEPA was formed.

Processing

The Meeting received information on processing of apple, grapes, olives, tomato, barley, wheat, and cotton seed.

Processing factors calculated for the processed commodities of the above raw agricultural commodities are shown in the table below. STMR-Ps were calculated for processed commodities of apples, grapes, tomatoes, barley, wheat and cotton seed for which maximum residue levels were estimated. Where residues concentrate in processed commodities the Meeting estimated maximum residues levels for these processed commodities using the maximum residue levels for the respective raw agricultural commodities and processing factors.

As no data were available on the processing of fig to dried or dried and candied figs, the Meeting withdrew its previous recommendation on figs, dried and dried and candied.

The processing factor of grape to dried grapes was estimated at 1.2 and therefore a maximum residue level for dried grapes was unnecessary. The Meeting decided to withdraw its previous recommendation on dried grapes.

RAC or Processed commodities	Processing factor		STMR-P	Maximum residue level
	Individual value	Best estimate		
Apple			0.15 (STMR)	0.8
Apple juice	< 0.4, 0.4, 0.5, < 0.8, 1.5	0.5	0.075	–
Apple sauce	0.4, 0.5, < 0.8, 1.1	0.5	0.075	–
Grape			0.19(STMR)	0.8
Dried grapes	0.79, 0.89, 1.0, 1.4, 3.2, 8.5	1.2	0.23	–
Grape juice	0.5, 0.7, 0.8, 1.1	0.75	0.14	–
Must	0.7, 0.8, 0.8, 0.9, 1.0, 1.0	0.85	0.16	–
Wine	0.7, 1.0, 1.2, 1.4, 1.5, 2.1,	1.3	0.25	–
Olives			1.9	–
Olive oil (virgin and refined)	< 0.02, < 0.03	< 0.02	0.038	–
Table olives	< 0.01, < 0.02, < 0.02, < 0.03	< 0.01	0.019	–
Tomato			0.52(STMR)	2
Tomato juice	< 0.1, 0.1, < 0.2, 0.34	0.22	0.18	–
Tomato puree	< 0.1, < 0.1, < 0.2, 0.60	0.60	0.31	–
Tomato paste	0.5, 0.6, 0.75	0.6	0.31	–
Tomato preserves	< 0.1, < 0.2, 0.2	0.2	0.10	–
Barley			0.13(STMR)	1.5
Pearl barley	0.9	0.9	0.12	–
Wheat			0.095 (STMR)	0.5
Flour	0.1, 0.2, < 0.3,	0.15	0.014	–
Wheat germ	2.0	2.0	0.19	1
Wheat bran	1.4, 3.1, 3.5	3.1	0.29	1.5
Cotton seed			0.545 (STMR)	6
Cottonseed refined oil	< 0.02,< 0.03, < 0.03	< 0.02	0.011	–

For the purpose of calculating animal dietary burden, the Meeting estimated the following median residues for feed items.

RAC or Processed commodities	Processing factor		median residue
	Individual value	Best estimate	
Apple			0.15 (STMR)
Wet pomace	0.3, 0.4, 0.6, < 0.8, 1.1	0.5	0.075
Dry pomace	2.0	2.0	0.30
Grape			0.19(STMR)
Wet pomace	0.4, 0.6, 0.9, 1.1	0.75	0.14
Tomato			0.52(STMR)
Wet pomace	< 0.1, < 0.1, < 0.2, 0.52	0.52	0.27
Dry pomace	1.9	1.9	0.99
Barley			0.13(STMR)
Barley hulls	1.6	1.6	0.21
Cotton seed			0.55 (STMR)
Meal	0.02, 0.03, 0.07	0.03	0.016

Residues in animal products

Farm animal feeding studies

Lactating cows received oral administration of ethephon at dose rates equivalent to 44, 128 and 415 ppm in the diet once daily for 28 consecutive days. The residues of ethephon in whole milk appeared to reach plateau after Day 4. Ethephon in milk was 0.007 mg/kg at 44 ppm dose, 0.02 mg/kg at 128 ppm dose, and 0.03 mg/kg at the 415 ppm dose. After a 28 day-administration, the highest concentration of ethephon in kidney was 0.58, 3.2 and 7.8 mg/kg respectively after 44, 128 and 415 ppm dose. In liver, it was 0.08, 0.51 and 0.99 mg/kg. In muscle, the ethephon concentration was much lower at 0.01, 0.05 and 0.12 mg/kg for these dose groups. In fat, at the highest dose, ethephon was present at only 0.06 mg/kg.

Laying hens were orally administered with ethephon at rates equivalent to 2.3, 6.9 and 23 ppm in the diet once daily for 28 consecutive days. The residues of ethephon in whole eggs were very low and those from the highest dose group contained at a maximum 0.0036 mg/kg. Therefore, eggs from the 2.3 ppm and 6.9 diets were not analysed. After 28-day administration, liver contained the highest concentration of ethephon, 0.033 mg/kg at the 2.3 ppm dose, 0.068 at the 6.9 ppm dose and 0.29 ppm at the 23 ppm dose. In skin + fat, it was 0.014, 0.032 and 0.117 mg/kg. In muscle, it was 0.060 at 23 ppm diet.

Estimation of dietary burdens

The maximum and mean dietary burdens were calculated using the highest and median residues of ethephon estimated at the current Meeting on a basis of the OECD Animal Feeding Table. In Australia, use of ethephon-treated cereal green materials as feed is not allowed and cereal forage is not in trade. Residues arising from use of ethephon in barley, rye and wheat forages were not used for calculating animal dietary burden for the Australian diets.

Summary of livestock dietary burdens (ppm of dry matter diet)

	US-Canada		EU		Australia		Japan	
	Max	Mean	max	Mean	Max	Mean	Max	mean
Beef cattle	4.19	1.65	18.8	9.14	4.04	0.81	0.13	0.13
Dairy cattle	14.5	6.22	18.9 [a]	9.17 [b]	1.46	0.79	0.059	0.059
Broilers	0.11	0.11	0.10	0.10	0.024	0.024	0.015	0.015
Layers	0.11	0.11	7.33 [c]	3.17 [d]	0.024	0.024	0.012	0.012

[a] Suitable for estimating maximum residue levels for milk, meat, fat and edible offal of cattle

[b] Suitable for estimating STMRs for milk, meat, fat and edible offal of cattle

[c] Suitable for estimating maximum residue levels for eggs, meat, fat and edible offal of poultry

[d] Suitable for estimating STMRs for eggs, meat, fat and edible offal of poultry

Residues in milk and cattle tissues

The maximum and mean dietary burdens in cattle were 18.9 and 9.17 ppm of dry matter diet respectively for estimating a maximum residue level and STMR for milk and edible tissues. The maximum residue levels, STMRs and HRs for relevant commodities of mammal origin were estimated using the residue levels in tissues and milk at 0 and 44 ppm feeding groups.

	Feed level (ppm) for milk residues	Ethephon (mg/kg) in milk	Feed level (ppm) for tissue residues	Ethephon (mg/kg) in			
				Muscle	Liver	Kidney	Fat
Maximum residue level beef or dairy cattle							
Feeding study [a]	0 44	– 0.002	0 44	< 0.01 0.016	0.05 0.095	0.03 0.64	< 0.01 < 0.01
Dietary burden and highest residue	18.9	0.0009	18.8	0.007	0.069	0.29	0.004
STMR beef or dairy cattle							

Feeding study [b]	0 44	– 0.002	0 44	< 0.01 0.01	0.05 0.08	0.03 0.49	< 0.01 < 0.01
Dietary burden and mean residue	9.17	0.0004	8.25	0.002	0.056	0.13	0.002

[a] Highest residues for tissues and mean residue for milk

[b] Mean residues for tissues and mean residue for milk

The level < LOQ at 0 ppm dose is assumed to be 0 mg/kg residue.

The Meeting estimated STMRs of 0.0004, 0.002, 0.056, 0.13 and 0.002 mg/kg, and HRs of 0.0009, 0.007, 0.069, 0.29 and 0.004 mg/kg for milk, meat, liver and kidney respectively.

On a basis of highest residues above, the Meeting estimated maximum residue levels of 0.01*, 0.01*, 0.4 and 0.01* mg/kg for milks mammalian meat, edible offal and fat, respectively.

The previous recommendations for milk of cattle, goats and sheep, meat of cattle, goats, houses, pigs and sheep, and edible offal of cattle, goats, horses, pigs and sheep were withdrawn.

Residues in eggs and chicken tissues

The maximum and mean dietary burdens in poultry were 7.33 and 3.17 ppm of dry matter diet respectively for estimating a maximum residue level and STMR for eggs and edible tissues. The maximum residue levels, STMRs and HRs for relevant commodities of poultry origin were estimated using the residue levels in tissues and eggs at 2.3, 6.9 and 23 ppm feeding groups.

	Feed level (ppm) for egg residues	Ethephon (mg/kg) in			
		Eggs	Muscle	Liver	Fat [a]
Maximum residue level broiler or layer hens					
Feeding study	6.9 23	na 0.0023	0.015 0.060	0.068 0.23	0.032 0.117
Dietary burden and highest residue	7.33	0.00005	0.016	0.072	0.034
STMR broiler or layer hens					
Feeding study	2.3 6.9	na na	< 0.01 0.012	0.031 0.062	0.013 0.024
Dietary burden and mean residue	3.17	0 [b]	0.01	0.037	0.015

[a] From data in fat + skin

[b] At a dose of 23 ppm in the dry matter diet, residues were 0.0036 mg/kg

The Meeting estimated STMR of 0, 0.01, 0.037 and 0.015 mg/kg, and HR of 0.00005, 0.016, 0.072 and 0.034 mg/kg, respectively for poultry eggs, meat, edible offal and fat.

On a basis of HR, the Meeting estimated maximum residue levels of 0.01 *, 0.02, 0.08 and 0.04 mg/kg for eggs, poultry meat, edible offal and fat, respectively. The recommendations for poultry meat and edible offal replace the previous recommendations.

The Meeting withdrew its previous recommendation on chicken eggs.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed in Annex 1 are suitable for establishing maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue for plant commodities except cereal grains and straw (for compliance with the MRL and for estimation of dietary intake): *Ethephon.*

Definition of the residue for cereal grains and straw (for compliance with the MRL and for estimation of dietary intake): *Ethephon and its conjugates, expressed as ethephon*.

Definition of the residue for animal commodities (for compliance with the MRL and for estimation of dietary intake): *Ethephon.*

The residue is not fat-soluble.

CCN	Commodity	Recommended Maximum residue level (mg/kg)		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
FP 0226	Apple	0.8	5	0.15	0.49
GC 0640	Barley	1.5	1	0.13	
AS 0640	Barley straw and fodder, Dry	7 (dw)[b]	5	0.64[a]	3.6 [a]
FB 0020	Blueberries	W	20		
FC 4199	Cantaloupe	W	1		
FS 0013	Cherries	5	10	0.65	2.7
PE 0840	Chicken eggs	W	0.2*		
SO 0691	Cotton seed	6	2	0.55	
DF 0269	Dried grapes	W	5	0.23	
MO 0105	Edible offal (mammalian)	0.4		Kidney 0.056 Liver 0.12	Kidney 0.069 Liver 0.29
MO 0096	Edible offal of cattle, goats, horses, pigs and sheep	W	0.2*		
PE 0112	Eggs	0.01*		0	0.00005
FT 0297	Fig	3		0.73	0.75
DF 0297	Figs, Dried or dried and candied	W	10		
FB 0269	Grapes	0.8	1	0.19	0.52
TN 0666	Hazelnuts	W	0.2		
MF 0100	Mammalian fats (except milk fats)	0.01*		0.002	0.004
MM 0095	Meat (from mammals other than marine mammals)	0.01 *		0.002	0.007
MM 0096	Meat of cattle, goats, horses, pigs and sheep	W	0.1*		
ML 0106	Milks	0.01 *		0.0004	
ML 0107	Milk of cattle, goats and sheep	W	0.05*		
FT 0305	Olives	7		1.9	4.3
VO 0051	Peppers	W	5		
HS 0444	Peppers Chili, dried	W	50		
FI 0353	Pineapple	1.5	2	0.12	0.21
PM 0110	Poultry meat	0.02	0.1*	0.01	0.016
PO 0111	Poultry, Edible offal of	0.08	0.2*	0.037	0.072
PF 0111	Poultry fats	0.04		0.015	0.034
GC 0650	Rye	0.5	1	0.095	
AS 0650	Rye straw and fodder, Dry	7 (dw)	5	0.64 [a]	1.7 [a]
VO 0448	Tomato	2	2	0.52	0.79
GC 0651	Triticale	0.5		0.095	
	Triticale straw and fodder, Dry	7 (dw)		0.64 [a]	1.7 [a]
TN 0678	Walnut	W	0.5		
GC 0654	Wheat	0.5	1	0.095	
CM 0654	Wheat bran	1.5		0.29	
CF 1201	Wheat germ	1		0.19	
AS 0654	Wheat straw and fodder, Dry	7 (dw)	5	0.64 [a]	1.7 [a]
JF 0226	Apple juice			0.075	
	Apple sauce			0.075	
OC 0691	Cotton seed oil, edible			0.011	
DF 0269	Dried grapes (=currants, Raisins and Sultanas)			0.23	
JF 0269	Grape juice			0.14	
	Grape must			0.16	
	Olive oil, virgin and refined			0.038	
DM 0305	Olives, processed			0.019	
	Pearl barley			0.12	

CCN	Commodity	Recommended Maximum residue level (mg/kg)		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
JF 0048	Tomato juice			0.18	
VW 0448	Tomato paste			0.31	
	Tomato preserves			0.1	
MW 0448	Tomato puree			0.31	
CF 1211	Wheat four			0.014	
	Wine			0.25	
AB 1230	Apple pomace, wet			0.075	
	Barley forage			8.9	13
	Barley hulls			0.21	
OR 0691	Cotton seed meal			0.016	
AB 1204	Cotton gin trash			27	67
	Grape pomace wet			0.14	
AF 0650	Rye forage (green)			9.1	13
	Tomato pomace wet			0.27	
	Wheat forage			7.1	18

[a] as received basis

[b] dw – dry weight

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Dietary Intakes (IEDIs) of ethephon were calculated for the 17 GEMS/Food cluster diets using STMRs and STMRPs estimated by the current Meetings (see Annex 3 to the 2015 Report). The ADI is 0–0.05 mg/kg bw and the calculated IEDIs were 0–6% of the maximum ADI. The Meeting concluded that the long-term intake of residues of ethephon resulting from the uses considered by the current JMPR is unlikely to present a public health concern.

Short-term intake

The International Estimated Short-Term Intakes (IESTI) of ethephon were calculated for commodities using HRs/HR-Ps and STMRs/STMR-Ps estimated by the current Meeting (see Annex 4 to the 2015 Report). The ARfD is 0.05 mg/kg and the calculated IESTIs were 0–100% of the ARfD for the general population and 0–70% of the ARfD for children. The Meeting concluded that the short-term intake of residues of ethephon, when used in ways that have been considered by the JMPR, is unlikely to present a public health concern.

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EC-94-253 [M-188009-01-1]	Nygren, RE	1995	Storage Stability of Ethephon in Apple juice and Cottonseed Oil Spiked with Ethephon. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
EC-92-198	Leonard, MS	1993	Storage Stability of Ethephon in/on Frozen Bovine Meat, Bovine Milk and Chicken Eggs Spiked with Ethephon. Rhône-Poulenc Ag Company, NC 27709, USA. Report No. EC-92-198, File no. 44198 [M-187997-01-1] GLP, Unpublished
R&D/CRLD/ AN/0215010 [M-209123-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), North/France/2000—2 trials—Harvest study, Residues in apple (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished

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R&D/CRLD/ AN/0215012 [M-210409-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), North/France/2000—2 trials—Decline study, Residues in apple (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
02 R 792 [M-220915-01-1]	Sonder, KH	2004	Residue Behaviour in Apples European Union (Northern Zone) 2002. Bayer CropScience GmbH, D-65926 Frankfurt, Germany. GLP, Unpublished
RA-2514/06 [M-292470-01-1]	Billian, P	2007	Determination of the residues of ethephon in/on apple after spraying of AE F016382 00 SL40 A1 (480 SL) in the field in Southern France, Italy, Spain, Portugal and Greece. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2576/07 [M-311032-01-1]	Billian, P, Erler, S & Wolters, A	2008	Determination of the residues of ethephon in/on apple after spraying of AE F016382 00 SL40 A1 (480 SL) in the field in southern France, Italy, Spain and Greece. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
R&D/CRLD/ AN/mr/0115439 [M-208089-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), South/France/2000—2 trials—Decline study, Residues in cherry (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
R&D/CRLD/ AN/0115458 [M-208961-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), South/France/2000—2 trials—Harvest study, Residues in cherry (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
R&D/CRLD/ AN/0215009 [M-210351-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), North/France/2000—2 trials—Decline study, Residues in cherry (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
R&D/CRLD/ AN/0215013 [M-210352-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), North/France/2000—2 trials—Harvest study, Residues in cherry (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
02 R 795 [M-220921-01-1]	Sonder, KH	2004	Residue Behaviour in Cherries, European Union (Southern Zone) 2002. Bayer CropScience GmbH, D-65926 Frankfurt, Germany. GLP, Unpublished
09-2147 [M-403958-01-1]	Uceda, L & Meilland-Berthier, I	2011	Determination of the residues of ethephon in/on cherry, sweet after spraying of Ethephon SL 480 in the field in Belgium and Netherlands. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
EA950185 [M-188232-01-1]	Grolleau, G	1997	Magnitude of the Residue of Ethephon on RAC Grapes and processed Fractions after Application of CA1418 at colour-change stage. European Agricultural Services (EAS), F-69007 Lyon, France. GLP, Unpublished
RA-2562/06 [M-294217-01-1]	Billian, P, Lorenz, S & Telscher, M	2005	Determination of the residues of ethephon in/on grape after low-volume spraying of AE F016382 00 SL18 A1 (180 SL) in the field in Northern France. Bayer CropScience AG, D-40789 Monheim, Germany GLP, Unpublished
RA-2563/06 [M-294366-01-1]	Billian, P & Telscher, M	2005	Determination of the residues of ethephon in/on grape after low-volume spraying of AE F016382 00 SL18 A1 (180 SL) in the field in Southern France. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
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102/5373/04 [M-284626-01-2	Trevizan, LRP & de Baptista, GC	2004	Determinacao de Residuos de Ethrel em Figo 1(R04MA1)/Valinhos-SP. Laboratorio de Residues de Pesticidas e Analises Cromatograficas, 13418-900 Piracicaba-SP, Brazil. Non-GLP, Unpublished
102/5374/04 [M-284634-01-2	Trevizan, LRP & de Baptista, GC	2004	Determinacao de Residuos de Ethrel em Figo 2(R04MA01-P1)/Monte-Mor-SP. Laboratorio de Residues de Pesticidas e Analises Cromatograficas, 13418-900 Piracicaba-SP, Brazil. Non-GLP, Unpublished
102/5375/04 [M-284637-01-2	Trevizan, LRP & de Baptista, GC	2004	Determinacao de Residuos de Ethrel em Figo 3(R04MA01-P2)/Caldas-SP. Laboratorio de Residues de Pesticidas e Analises Cromatograficas, 13418-900 Piracicaba-SP, Brazil. Non-GLP, Unpublished

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RA-927/05 [M-284681-01-2	Galhiane, MS & Santos, L de S	2005	Relatorio de Estudo de Residuo de Ethrel 720 (Ethephon) em Figo (Analises Realizadas em Frutos). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
07 D OL BY P/A [M-352734-01-1]	Fernandez, E	2009	Residues of Ethephon in Olives and its Processed Products: Table Olives and Olive Oil (Virgin & Refined), Following Two Applications of Fruitel (480 g/L ethephon) in Tank Mix with Monopotassium Phosphate Under Field Conditions—Spain—Season 2007. Promo-Vert, E-41805 Sevilla, Spain. GLP, Unpublished
08-2053 [M-350265-02-1] (Amendment 1).	Billian, P	2009	Determination of the residues of ethephon in/on olive after spraying of Ethephon SL 480 G in the field in Spain. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
CP-1997 PA-081/94 [M-188144-02-1]	Garcia, M	1994	Residue Analysis of Ethephon on Pineapple. Rhodia S.A. Research Center of Paulinia, 13140 Paulinia-SP, Brazil. Non-GLP, Unpublished
4170 [M-421140-01-1]	Guimarães, GAR	1997	Determinação Analítica de Resíduo de Ethephon em Abacaxi. Universidade Federal do Paranã, Centro de Pesquisa e Processamento de Alimentos Convenio Funpar/CEPPA, 81531-970 Paranã, Brazil. Non-GLP, Unpublished
RA-966/05 [M-284613-02-1	Galhiane, MS & Santos, L de S	2005	Relatorio de Estudo de Residuo de Ethrel (Ethephon) em Abacaxi (Analises Realizadas em Fruto). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
RA-967/05 [M-284618-02-1	Galhiane, MS & Santos, L de S	2005	Relatorio de Estudo de Residuo de Ethrel (Ethephon) em Abacaxi (Analises Realizadas em Fruto). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
RA-968/05 [M-284623-02-1	Galhiane, MS & Santos, L de S	2005	Relatorio de Estudo de Residuo de Ethrel (Ethephon) em Abacaxi (Analises Realizadas em Fruto). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
R&D/CRLD/ AN/msa/ 9816197 [M-165714-01-1]	Maestracci, M	1998	Ethephon, Formulation EXP03149B (SL), Trials Costa Rica 1998, Residues in pineapple, Decline study. Rhône-Poulenc Agro, F-69009 Lyon, France. GLP (analytical), non-GLP (field), Unpublished
R&D/CRLD/ AN/msa/ 9816152 [M-165702-02-1]	Maestracci, M	1998	Ethephon, Formulation EXP03149B (SL), Trials Ivory Coast 1997–1998, Residues in pineapple, Decline study. Rhône-Poulenc Agro, F-69009 Lyon, France. GLP (analytical), non-GLP (field), Unpublished
R&D/CRLD/ AN/mr/9916533 [M-179309-01-1]	Baudet, L	1999	Ethephon, Formulation EXP03149B (SL), South/Ivory Coast /1998–1999–1 Decline study trial, Residues in pineapple (flesh and skin). Rhône-Poulenc Agro, F-69009 Lyon, France. GLP (analytical), non-GLP (field), Unpublished 10 November 1999
USA89E27 [M-187578-01-1]	Nygren, RE	1992	Ethrel/Pineapple/Residue. Non-GLP, Unpublished
DR 00 EUS 522 [M-203527-01-1]	Hees, M	2001	Residue Study in industrial field tomatoes European Union [southern zone] 2000, ethephon, AE F016382, water soluble concentrate (SL) 480 g/L. Aventis Cropscience, D-65926 Frankfurt, Germany GLP, Unpublished
01R773 [M-215341-01-1]	Davies, P	2002	Decline of residues in tomatoes, European Union Southern zone 2001, ethephon, AE F016382 watersoluble concentrate (SL) 39.67 % w/w (480 g/L). Bayer CropScience GmbH, D-65926 Frankfurt, Germany GLP, Unpublished
RA-2065/04 [M-261821-01-1]	Bardel, P	2005	Determination of the Residues of Ethephon and HEPA in/on Tomato after Spraying of AE F016382 00 SL40 A1 (480 SL) in the Field in Spain, Portugal and Italy. Bayer CropScience AG, D-40789 Monheim, Germany GLP, Unpublished

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R&D/CRLD/ AN/0215069 [M-210410-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03149B (SL), Greenhouse/The Netherlands/1999—2 trials—Harvest study, Residues in tomato (fruit). Aventis Cropscience, F-69009 Lyon, France. GLP, Unpublished
01R791 [M-210553-01-1]	Davies, P	2002	Decline of residues in protected tomatoes, European Union Indoors 2001, ethephon, AE F016382 watersoluble concentrate (SL) 39.67% w/w (480 g/L). Bayer CropScience GmbH, D-65926 Frankfurt, Germany. GLP, Unpublished
USA89E30 [M-187599-01-1]	Nygren, RE	1991	ETHREL/Tomato/Residues. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
USA90E16 [M-187596-01-1]	Nygren, RE	1992	ETHREL/Tomato/Magnitude of residue study. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
USA91E16 [M-187891-01-1]	Nygren, RE	1995	ETHREL® brand plant regulator/Tomato/magnitude of Residue. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
IR-4 PR No 00250 [M-301374-01-1]	Dorschner, K	2008	Ethephon: Magnitude of the Residue on Tomato (Greenhouse) IR-4 Project, Rutgers, The State University of New Jersey, NJ 08540, USA. GLP, Unpublished
DR 00 EUS 525 [M-199982-01-1]	Hees, M	2001	Residue Study in Barley, European Union [southern zone] 2000, Ethephon, Water soluble concentrate, 480 g/L. Aventis CropScience, D-65926 Frankfurt, Germany. GLP, Unpublished
R&D/CRLD/ AN/mr/0115430 [M-208093-01-1]	Ballesteros, C	2001	Ethephon and its metabolite (RPA732569), Formulation EXP03725B (SL), South/France/ 2000—2 Decline study trials, Residues in winter barley (plant, straw and grain). Aventis CropScience, F-69009 Lyon, France. GLP, Unpublished
01R761 [M-209901-01-1]	Davies, P	2002	Residue behaviour in barley, European Union Northern zone 2001, ethephon, AE F016382, water soluble concentrate (SL), 39.83 % w/w (480 g/L). Aventis CropScience, D-65926 Frankfurt, Germany. GLP, Unpublished
01R771 [M-210307-01-1]	Davies, P	2002	Residue behaviour in barley, European Union Southern zone 2001, ethephon, AE F016382, water soluble concentrate (SL), 39.83 % w/w (480 g/L). Aventis CropScience, D-65926 Frankfurt, Germany. GLP, Unpublished
RA-2094/04 [M-249305-02-1]	Report: Bardel, P & Wolters, A Amendment 1: Bardel, P	2005	Determination of the Residues of Ethephon and Chlormequat chloride in/on Spring Barley after Spraying of AE F080286 02 SL40 A1 in the Field in Northern France, Sweden and Germany. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2095/04 [M-251234-01-1]	Bardel, P & Wolters, A	2005	Determination of the Residues of Ethephon and Chlormequat chloride in/on Spring Barley after Spraying of AE F080286 02 SL40 A1 in the Field in Southern France, Italy and Portugal. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2093/04 [M-251235-01-1]	Bardel, P & Wolters, A	2005	Determination of the Residues of Ethephon and Chlormequat chloride in/on Winter Barley and Spring Barley after Spraying of AE F080286 02 SL40 A1 in the Field in Greece, Italy, Southern France and Spain. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2092/04 [M-251366-01-1]	Bardel, P & Wolters, A	2005	Determination of the Residues of Ethephon and Chlormequat Chloride in/on Winter Barley after Spraying of AE F080286 02 SL40 A1 in the Field in Sweden, Germany and Northern France. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2519/06 [M-290151-01-1]	Billian, P & Erler, S	2007	Determination of the residues of ethephon and chlormequat chloride in/on winter barley after spraying of Ethephon & AEF080286 (450 SL) in the field in Southern France. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2515/06 [M-294373-01-1]	Billian, P & Telscher, M	2007	Determination of the residues of ethephon in/on winter barley after spraying of AE F016382 00 SL40 A2 (480 SL) in the field in Northern France, the United Kingdom and Germany. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished

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RA-2516/06 [M-294780-02-1	Report: Billian, P & Telscher, M Amendment 1: Billian, P	Report: 2007 Amend-ment 1: 2010	Determination of the residues of ethephon in/on winter rye after spraying of AE F016382 00 SL40 A2 (480 SL) in the field in Northern France, the United Kingdom, Sweden and Germany. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2574/07 [M-318501-01-1]	Billian, P, Erler, S & Wolters, A	2008	Determination of the residues of Ethephon in/on winter rye after spraying of AE F016382 00 SL40 A2 (480 SL) in the field in northern France, Germany and the United Kingdom. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
R&D/CRLD/ AN/mr/0115433 [M-208087-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03725B (SL), South/France/2000—2 trials—Decline study, Residues in soft winter wheat (plant, straw and grain). Aventis CropScience, F-69009 Lyon, France. GLP, Unpublished
R&D/CRLD/ AN/mr/0115434 [M-208091-01-1]	Ballesteros, C	2002	Ethephon and its metabolite (RPA732569), Formulation EXP03725B (SL), South/France/2000—2 Harvest trials, Residues in soft winter wheat (straw and grain). Aventis CropScience, F-69009 Lyon, France. GLP, Unpublished
01R762 [M-210306-01-1]	Davies, P	2002	Residue behaviour in common wheat, European Union Northern zone 2001, ethephon, (AE F016382), water soluble concentrate (SL) 480 g/L. Aventis CropScience, D-65926 Frankfurt, Germany. GLP, Unpublished
01R772 [M-210308-01-1]	Davies, P	2002	Residue behaviour in wheat, European Union Southern zone 2001, ethephon, (AE F016382), water soluble concentrate (SL), 39.83 % w/w (480 g/L). Aventis CropScience, D-65926 Frankfurt, Germany. GLP, Unpublished
RA-2090/04 [M-251226-01-1]	Bardel, P	2005	Determination of the Residues of Ethephon and Chlormequat Chloride in/on Wheat after Spraying of AE F080286 02 SL40 A1 in the Field in Sweden, Germany and Northern France. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2091/04 [M-251236-02-1 (Amendment 2)	Bardel, P	2005	Determination of the Residues of Ethephon and Chlormequat Chloride in/on Wheat and Wheat, hard after Spraying of AE F080286 02 SL40 A1 in the Field in Greece, Southern France, Spain and Portugal. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2517/06 [M-294528-01-1]	Billian, P & Telscher, M	2007	Determination of the residues of ethephon in/on winter wheat after spraying of AE F016382 00 SL40 A2 (480 SL) in the field in Northern France, the United Kingdom and Germany. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
RA-2575/07 [M-312007-01-1]	Billian, P	2008	Determination of the residues of ethephon in/on winter wheat after spraying of AE F016382 00 SL40 A2 (480 SL) in the field in northern France and Germany. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
10223 [M-187972-01-1]	Harrison, SL	1981	Residues of Ethephon in wheat and barley resulting from applications of Ethrel® as an anti-lodging agent. Union Carbide Agricultural Products Company Inc., North Carolina, USA. Non-GLP, Unpublished
SARS-89-24 [M-187553-01-1]	Conn, RL	1992	Magnitude of the Residues of Ethephon and Monochloroacetic Acid (MCAA) in or on Wheat. Stewart Pesticide Registration Associates, Inc., Virginia 22202, USA. GLP, Unpublished
R&D/CRLD/ AN/bd/9515891 [M-163122-01-1]	Richard, M & Muller, MA	1995	RPA090946 or Cyclanilide Ethephon Formulation EXP31039A (SC) Greece 1993 Residues in Cotton (seed) Rhône-Poulenc Agrochimie, F-69263 Lyon, France. Non-GLP (field phase), GLP (analytical phase), Unpublished
R&D/CRLD/ AN/bd/9515911 [M-163133-01-1]	Richard, M & Muller, MA	1995	RPA090946 or Cyclanilide Ethephon Formulation EXP31039A (SC) Spain 1994 Residues in Cotton (fibre, seed) Decline study Rhône-Poulenc Agrochimie, F-69263 Lyon, France. GLP, Unpublished
R&D/CRLD/ AN/bd/9516706 [M-163236-01-1]	Muller, MA	1996	RPA090946 or Cyclanilide–Ethephon Formulation EXP31039A (SC) Trial Spain 1995 Residues in Cotton (seed and fibre) Rhône-Poulenc Secteur Agro, F-69009 Lyon, France. GLP, Unpublished

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R&D/CRLD/ AN/vg/9516705 [M-163240-01-1]	Muller, MA	1996	RPA090946 or Cyclanilide–Ethephon Formulation EXP31039A (SC) Trials Greece 1995 Residues in Cotton (seed) Rhône-Poulenc Secteur Agro, F-69009 Lyon, France. GLP, Unpublished
08-2023 [M-360139-01-1]	Billian, P, Reineke, A & Krusell, L	2009	Determination of the residues of cyclanilide and ethephon in/on cotton after spraying of FINISH SC 540 in the field in Greece and Spain. Bayer CropScience AG, D-40789 Monheim am Rhein, Germany. GLP, Unpublished
USA89I03 [M-187602-01-1]	Nygren, RE	1991	PREP/Cotton/Residues. Rhône-Poulenc Ag Company, NC 27709, USA. Non-GLP, Unpublished
USA93I03R [M-252199-01-1]	See, RM	1994	Magnitude of RPA-90946 and Ethephon Residues in/on Seed Cotton Resulting from Foliar Applications of 31039B, 1993. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
USA94I01R [M-253436-01-1]	See, RM	1995	Magnitude of RPA-90946 and Ethephon Residues in/on Seed Cotton Resulting from Foliar Application of 31039B, 1994. Rhône-Poulenc Ag Company, NC 27709, USA. GLP, Unpublished
CP-2466/97 [M-188222-01-1]	Garcia, M	1997	Residue Analysis of Ethephon on Cotton. Rhodia S.A. Research Center of Paulinia, 13.140.000 Paulinia-SP, Brazil. Non-GLP, Unpublished
CP-2435/97 [M-253467-02-1] and M-253467-02-1]	Garcia, M, & de Oliverira, NT	1997	Residue Analysis of Ethephon and Cyclanilide on Cotton. Rhodia S.A. Research Center of Paulinia, 13.140.000 Paulinia-SP, Brazil. Non-GLP, Unpublished
CP-2436/97 [M-253470-02-1] and M-253470-02-1]	Garcia, M & de Oliverira, NT	1997	Residue Analysis of Ethephon and Cyclanilide on Cotton. Rhodia S.A. Research Center of Paulinia, 13.140.000 Paulinia-SP, Brazil. Non-GLP, Unpublished
RA-218/06 [M-285068-01-2	Galhiane, MS & Santos, L de S	2006	Relatorio de Estudo de Resíduo de Finish (Etefon + Cyclanilide) em Algodao (Analises Realizadas em Sementes sem Fibras). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
RA-219/06 [M-285070-01-2]	Galhiane, MS & Santos, L de S	2006	Relatorio de Estudo de Resíduo de Finish (Etefon + Cyclanilide) em Algodao (Analises Realizadas em Sementes sem Fibras). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
RA-220/06 [M-285073-01-2]	Galhiane, MS & Santos, L de S	2006	Relatorio de Estudo de Resíduo de Finish (Etefon + Cyclanilide) em Algodao (Analises Realizadas em Sementes sem Fibras). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
RA-221/06 [M-285075-01-2]	Galhiane, MS & Santos, L de S	2006	Relatorio de Estudo de Resíduo de Finish (Etefon + Cyclanilide) em Algodao (Analises Realizadas em Sementes sem Fibras). Laboratorio de Quimica Analitica e Cromatografia, 17.033-360 Bauru/SP, Brazil. Non-GLP, Unpublished
CP02/001 [M-211072-01-1]	Selzer, J	2002	Ethephon: Investigation of the Nature of the Potential Residue in the Products of Industrial Processing or Household Preparation. Aventis Cropscience, D65629 Frankfurt am Main, Germany. GLP; Unpublished
USA89E32 [M-187583-01-1]	Nygren, RE	1990	Ethrel Apple 1989 Residue Program. Rhône-Poulenc Ag Company, NC 27709, USA. Non-GLP, Unpublished
RA-3610/03 [M-254102-01-1]	Bardel, P, Hoffmann, M & Eberhardt, R	2005	Determination of the Residues of Ethephon in/on Apple (Fruit, Juice, Sauce, Pomace) after Spraying of AE F016382 00 SL40 A1 (480 SL) in Italy, Portugal and Spain. Bayer CropScience AG, D-40789 Monheim, Germany. GLP, Unpublished
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