Document Title

Summary of the residues in or on treated products, food and feed for Ethephon

Data Requirements

EU Regulation 1107/2009 & EU Regulation 283/2013
Document MCA
Section 6: Residues in or on treated products, food and feed

According to the guidance document SANCO 10181/2013 for preparing dossiers for the approval of a chemical active substance

Date

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Author(s)

[redacted]

Bayer AG
Crop Science Division

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Version history

Date	Data points containing amendments or additions[1] and brief description	Document identifier and version number
2016-01-16	Initial document submitted for Annex I renewal Ethephon	M-544719-02-1
2017-07-24	Statement included for acceptability of the lactating goat metabolism study (CA 6.2.3; p.27). Change of legal entity from Bayer CropScience AG to Bayer AG – Crop Science Division	M-544719-03-1

[1] It is suggested that applicants adopt a similar approach to showing revisions and version history as outlined in SANCO/10180/2013 Chapter 4 How to revise an Assessment Report

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INTRODUCTION

Ethephon is a plant growth regulator and was included into Annex I of Directive 91/414 in 2006 (Directive 2006/85/EC, dated 23rd of October 2006, Entry into Force 1st of August 2007).

This dossier contains only summaries of studies, which were not available at the time of the first Annex I inclusion of ethephon and were, therefore, not evaluated during the first EU review of this compound. All other studies, which were already submitted by Bayer AG (formerly Bayer CropScience AG) for the first Annex I inclusion, are contained in the Monograph and in the baseline dossier (D-012067-01). Where applicable, such studies are indicated by grey typeface in the summary dossier(s).

The here presented and submitted studies used different synonyms and codes for the active substance ethephon, its metabolites and reference compounds. In order to present a common basis for the evaluation the following list summarizes all names used.

Formula Report name used in summaries Codes used IUPAC index name / Other names / codes.

Formula Report name used in summaries	**Codes used** *IUPAC index name* / Other names / codes
Ethephon	AE F016382 Ethephon technical concentrate Ethephon Base 250
Ethephon-2-hepa	HEPA, 2-HEPA (2-hydroxyethyl)phosphonic acid

In addition, a list of metabolites, which contains the structures, the synonyms and code numbers attributed to the compound, is presented in Document N3 of this dossier. The matrices in which the metabolites were identified are also included in this list.

CA 6 RESIDUES IN OR ON TREATED PRODUCTS, FOOD AND FEED

The active substance ethephon (2-chloroethylphosphonic acid) is a plant growth regulator which acts in plants by releasing ethylene. It is used on various crops, e.g. to control flowering (fruit trees), increase resistance to lodging (cereals), promote maturation and coloration (tomatoes, apples), or facilitate harvest (cotton).

An Annex II Dossier for the inclusion of Ethephon in the Annex I of Directive 91/414 was submitted to EU authorities in April 2002. After in-depth evaluation of the data, the Netherlands (acting as Rapporteur Member State) issued a Draft Assessment Report in June 2004. This report served as the basis for the EU Peer Review, the conclusions of which were published by EFSA in April 2006 [EFSA Scientific Report (2006) 67, 1-61]. Eventually ethephon was included in the Annex I of Directive 91/414 on 1 August 2007. The toxicity endpoints were up-dated in September 2008 [EFSA Scientific Report (2008) 174, 1-65] while the residue definition for dietary risk assessment was modified in the context of the review of the existing EU MRLs according to article 12 of Regulation 396/2005 [EFSA Journal 2009; 7(10):1347].

Extensive residue and metabolism data for ethephon were submitted to EU authorities and EU Member States in the context of the EU Dossier for the Annex I inclusion of the active substance under Directive 91/414/EEC (Baseline Dossier). The present Supplemental Dossier for the renewal of the approval of ethephon only includes studies which were not part of the Baseline Dossier, either because they are new and were not available at the time when the Baseline Dossier was issued, or because they were not relevant to the uses supported in the Baseline Dossier. The studies of the Baseline Dossier, which were already evaluated during the previous EU review, are not summarised again in detail, but if these studies are still considered relevant, the main conclusions from the previous evaluations are provided. The representative use for the renewal of the approval of ethephon is the same as the representative use for the inclusion in Annex I of Directive 91/414, namely prevention of lodging and shortening of stems in wheat and barley. However, the Supplemental Dossier also includes some storage stability and metabolism data that are not directly relevant to the representative use but are necessary to support other uses of the active substance and should preferably be evaluated in the context of the upcoming EU review.

CA 6.1 Storage stability of residues

Table 6.1- 1 provides an overview of the storage stability data included in the Annex II dossier of 2002 and reviewed by the Rapporteur Member State in the Draft Assessment Report (DAR) of April 2004. In the following, detailed summaries are provided for supplementary storage stability studies that were not included in the Annex II dossier of 2002 and, therefore, not reviewed in the DAR.

Table 6.1- 1 Overview of the storage stability data for ethephon and its metabolite HEPA in plant matrices submitted in the Annex II dossier of 2002 and evaluated in the DAR of 2004

Document	Matrix	Category [rich in]	Analyte	Storage conditions	Stability demonstrated for up to
M-187521-01-1 (R013222)	Wheat grain	Starch	Ethephon	frozen at ca. -20°C	24 months
M-187519-01-1 (R013221)	Wheat straw	-	Ethephon	frozen at ca. -20°C	24 months
M-187533-01-1 (R013228)	Tomato fruit	Water	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187515-01-1 (R013219)	Apple fruit	Water	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187544-01-1 (R013233)	Grape berry	Acid	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187511-01-1 (R013217)	Blackberry fruit	Acid	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187525-01-1 (R013224)	Cottonseed	Oil	Ethephon	frozen at ca. -20°C	24 months
M-188009-01-1 (R013470)	Apple juice Cottonseed oil	- -	Ethephon	frozen at ca. -20°C frozen at ca. -20°C	12 months 12 months
M-210332-01-1 (C020900)	Wheat grain Tomato fruit	Starch Water	HEPA HEPA	frozen at ca. -18°C frozen at ca. -18°C	3 months 3 months

Report: KCA 6.1/11; [redacted]; 1992; M-187505-01-1
Title: Storage stability Study of Ethephon in/on whole Fresh Cherries
Report No.: R013214
Document No.: M-187505-01-1
Guideline(s): USEPA (=EPA): 171-4E
Guideline deviation(s): -
GLP/GEP: **yes**

Materials and methods

Untreated ground cherry samples (20 g) were fortified with ethephon at a concentration of 1.0 mg/kg and then either stored frozen at -15°C or freeze-dried and stored at room temperature. Ripe sweet cherries (variety Emperor) were used for this study to avoid the stabilising effects of the greater acid content of sour cherries. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether

and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD).

Findings

As shown in Table 6.1- 2, the procedural recoveries for ethephon were satisfactory at all storage intervals. The recoveries from the stored fortified samples were also satisfactory and did not evidence any degradation.

Conclusion

The residues of parent ethephon in cherry samples were shown to be stable for at least 24 months following storage at -15°C. The residues of ethephon in cherry samples were also stable for at least 24 months following storage at room temperature after freeze-drying.

Table 6.1- 2 Storage stability of ethephon in cherry

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Cherry	Ethephon	frozen at ca. -15°C	Day 0	91, 95	93	84	-
			1 month	112, 110	111	116	-
			2 months	105, 91	98	112	-
			6 months	91, 93	92	103	-
			9 months	93, 70	82	77	-
			12 months	86, 85	86	99	-
			18 months	97, 80	89	104	-
			24 months	102, 90	96	98	-
Cherry	Ethephon	freeze-dried at room temperature	Day 0	91, 95	93	84	-
			1 month	111, 97	104	108	-
			2 months	105, 95	100	80	-
			6 months	94, 110	102	105	-
			9 months	104, 89	97	104	-
			12 months	89, 89	89	82	-
			18 months	81, 70	76	96	-
			24 months	83, 85	84	101	-

Report:	KCA 6.1/12; [redacted]; 1991; M-187529-01-1
Title:	Storage stability of ethephon in/on walnut nutmeats
Report No.:	R013226
Document No.:	M-187529-01-1
Guideline(s):	USEPA (=EPA): 171-4(E)
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Untreated samples of ground walnut meat (20 g) were fortified with ethephon at a concentration of 0.2 mg/kg and then either stored frozen at ≤ -15°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 3, 5 and 6 months of storage (depending on the type of storage). At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed. On Day 0 and at the 5 month interval, the analysis was repeated with one or two additional sets of samples.

The samples were analysed for ethephon using the method SOP 90069. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and frozen overnight at -10°C to solidify lipid materials. The remaining methanolic extract was concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD).

Findings

As shown in Table 6.1- 3, the study results were quite inconsistent since the first series analysed on day 0 showed an average recovery rate of only 36% while better recoveries were obtained from samples stored for up to 6 months. The variability of the results may be attributed to the lack of repeatability of the residue analytical method and the low recoveries from some of the stored samples do not necessarily indicate that the residues degraded during storage.

Conclusion

The study is considered to be inconclusive.

Table 6.1- 3 Storage stability of ethephon in meat of walnut

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Meat of walnut	Ethephon	frozen at ≤ -15°C	Day 0	31, 40	36	112	112
			Day 0*	107, 84, 126, 87	101	72, 70	71
			1 months	84, 93	89	81	81
			3 months	108, 105	107	64	64
			5 months	69, 74, 66, 83	73	87, 89	88
Meat of walnut	Ethephon	freeze-dried at room temperature	Day 0	31, 40	36	112	112
			Day 0*	107, 84, 126, 87	101	72, 70	71
			1 months	91, 74	83	88	88
			5 months	64, 51, 42, 77	59	67, 79	73
			6 months	73, 83	78	73	73

* Second set

Report: KCA 6.1/13; [redacted]; 1992; M-161841-01-1
Title: Determination of the Storage Stability of Ethephon in Pineapple Forage
Report No.: R013230
Document No.: M-161841-01-1
Guideline(s): USEPA (=EPA): 171-4c
Guideline deviation(s): --
GLP/GEP: **yes**

Materials and methods

Untreated ground samples of pineapple forage (20 g) were fortified with ethephon at a concentration of 0.5 mg/kg and then either stored frozen at about -20°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 4, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed. In two cases, the stored samples yielded low recoveries and the results were checked by analysing a second set of samples.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with flame photometric detection (GC/FPD). Since the method had not been used to analyse pineapple forage previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1- 4, the method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals (Table 6.1- 5). No degradation was observed in the samples stored at about -20°C, as evidenced by satisfactory recoveries at all storage intervals up to 24 months. The residues in the freeze-dried samples stored at ambient temperature seemed to be less stable since low recoveries were obtained at the 12 month and 24 month storage intervals (55% and 57%, respectively).

Conclusion

The residues of parent ethephon in pineapple forage samples were shown to be stable for at least 24 months following storage at about -20°C. However, the residues of ethephon in pineapple forage samples were shown to be stable for only 9 months following storage at room temperature after freeze-drying.

Table 6.1- 4 Validation of the method SOP 90070 for the determination of ethephon in pineapple forage

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-161841-01-1 (SOP 90070)	Pineapple forage	0.05 0.20 0.50 overall	6 6 6 18	77, 82, 89, 92, 101, 118 88, 89, 90, 95, 95, 96 77, 87, 87, 92, 92, 94 -	77 82 85 81	7.7 3.2 5.2 6.7

Table 6.1- 5 Storage stability of ethephon in pineapple forage

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Pineapple forage	Ethephon	frozen at ca. -20°C	Day 0	82, 79	81	76	-
			1 month	95, 85	90	79	-
			2 months	90, 86	88	90	-
			4 months	106, 82	94	100	-
			6 months	81, 72	76	92	-
			9 months	85, 88	87	85	-
			12 months	82, 89	85	89	-
			18 months	84, 95	89	93	-
			24 months	86, 98	92	83	-

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Pineapple forage	Ethephon	freeze-dried at room temperature	Day 0	82, 79	81	76	-
			1 month	73, 86	79	74	
			2 months	92, 99	95	85	-
			4 months	92, 90	91	90	-
			6 months	87, 88	88	85	-
			9 months	76, 74	75	90	-
			12 months	49, 70, 51, 53	55	81, 85	83
			18 months	77, 77	77	96	-
			24 months	52, 59, 56, 63	57	89, 83	86

* The recoveries shown in this table were not corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-calculated based on the corrected values and the procedural recoveries.

Report: KCA 6.1/14; [redacted] 1992; M-187540-01-1
Title: Determination of the Storage Stability of Ethephon in Pineapple Fruit
Report No.: R013231
Document No.: M-187540-01-1
Guideline(s): USEPA (=EPA): 171-4e
Guideline deviation(s): --
GLP/GEP: **yes**

Materials and methods

Untreated ground samples of pineapple fruit (20 g) were fortified with ethephon at a concentration of 0.5 mg/kg and then either stored frozen at about -20°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 4, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with flame photometric detection (GC/FPD). Since the method had not been used to analyse pineapple fruit previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1- 6, the method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals (Table 6.1- 7). The recoveries from the stored fortified samples were equally satisfactory at all storage intervals and for both types of storage conditions. Therefore, no degradation was observed.

Conclusion

The residues of parent ethephon in pineapple fruit samples were shown to be stable for at least 24 months following storage at -20°C. The residues of ethephon in pineapple fruit samples were also stable for at least 24 months following storage at room temperature after freeze-drying.

Table 6.1- 6 Validation of the method SOP 90070 for the determination of ethephon in pineapple fruit

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-187540-01-1 (SOP 90070)	Pineapple fruit	0.05	6	77, 82, 89, 92, 103, 118	93	15.8
		0.20	6	88, 89, 90, 95, 95, 96	92	3.8
		0.50	6	77, 87, 87, 92, 92, 94	88	7.0
		overall	18	-	91	10.0

Table 6.1- 7 Storage stability of ethephon in pineapple fruit

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)*		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Pineapple fruit	Ethephon	frozen at ca. -20°C	Day 0	86, 86	86	83	-
			1 month	88, 93	91	79	-
			2 months	95, 95	95	93	-
			4 months	96, 117	106	94	-
			6 months	108, 106	107	98	-
			9 months	90, 90	90	102	-
			12 months	87, 79	83	99	-
			18 months	117, 112	114	110	-
			24 months	77, 98	88	86	-

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)*		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Pineapple fruit	Ethephon	freeze-dried at room temperature	Day 0	86, 86	86	83	-
			1 month	89, 86	88	73	-
			2 months	100, 93	96	89	-
			4 months	90, 99	95	90	-
			6 months	92, 102	97	82	-
			9 months	103, 91	97	89	-
			12 months	98, 94	96	104	-
			18 months	106, 86	96	102	-
			24 months	75, 84	79	87	-

* The recoveries shown in this table were not corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-calculated based on the corrected values and the procedural recoveries.

Report: KCA 6.1/15; [redacted]; 1992; M-187542-01-1
Title: Storage Stability Study of Ethephon in/on whole fresh Peppers
Report No.: R013232
Document No.: M-187542-01-1
Guideline(s): USEPA (=EPA): 171-4E
Guideline deviation(s): --
GLP/GEP: **yes**

Materials and methods

Untreated ground samples of green bell pepper (20 g) were fortified with ethephon at a concentration of 1.0 mg/kg and then either stored frozen at -15°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 2, 4, 6, 9, 12, 18 and 24 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070, which was slightly adapted. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with 05% tartaric acid in methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with nitrogen phosphorus detection (GC/NPD).

Findings

As shown in Table 6.1- 8, the procedural recoveries for ethephon were usually in the guideline range of 70-110% but frequently exceeded the upper limit of 110% with a maximum of 130% (which was

found at several storage intervals). However, the recoveries from the fortified samples stored at -15°C also exceeded the upper limit of 110% frequently and actually were very comparable to the procedural recoveries. It may be concluded that parent ethephon remained stable in green bell pepper upon storage at about -15°C for at least 24 months. Quite different results were obtained for the fortified samples of green bell pepper which were first freeze dried before storage at room temperature. For these samples satisfactory recoveries (similar to the procedural recoveries) were obtained at the three first storage intervals (day 0, 2 months, 4 months) while at the next intervals the recoveries were found to decrease progressively down to about 37% at the 24 month storage interval.

Conclusion

The residues of parent ethephon in pepper samples were shown to be stable for at least 24 months following storage at -15°C. However, these residues were found to be stable for only 4 months following storage at room temperature after freeze-drying.

Table 6.1- 8 Storage stability of ethephon in green bell pepper

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Bell pepper	Ethephon	frozen at ca. -15°C	Day 0	120, 110	115	130	-
			2 months	120, 110	115	110	-
			4 months	100, 100	100	98	-
			6 months	100, 87	94	110	-
			9 months	92, 78	85	100	-
			12 months	88, 96	92	85	-
			18 months	110, 120	115	110	-
			24 months	120, 130	125	130	-
Bell pepper	Ethephon	freeze-dried at room temperature	Day 0	120, 110	115	130	-
			2 months	110, 100	105	130	-
			4 months	92, 93	93	82	-
			6 months	62, 83 97*, 85*	73 91*	120 110*	-
			9 months	47, 57 70*, 60*	52 65*	96 98*	-
			12 months	42, 46	44	87	-
			18 months	37, 36	37	130	-

* Result obtained during re-analysis.
Note : In the report, the results are provided in mg/kg. However, the recovery rates can be calculated easily based on the fortification level of 1.0 mg/kg

Report:	KCA 6.1/16; [redacted]; 1993; M-187507-01-1
Title:	Determination of the Storage Stability of Ethephon in Cantaloupe Fruit
Report No.:	R013215
Document No.:	M-187507-01-1
Guideline(s):	USEPA (=EPA): 171-4e
Guideline deviation(s):	--
GLP/GEP:	**yes**

Materials and methods

Untreated ground melon samples (20 g) were fortified with ethephon at a concentration of 0.5 mg/kg and then either stored frozen at about -20°C or freeze-dried and stored at room temperature. In order to monitor any potential degradation of ethephon upon storage, analyses were conducted on day 0 and after 1, 2, 4, 6, 9, 12, 18, 24, 30 and 36 months of storage. At each interval, two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method SOP 90070. The hard-frozen samples were ground with dry ice and freeze-dried to a constant weight. The dry samples were Soxhlet extracted with methanol. Thereafter, the extract was acidified by addition of 10% HCl in methanol and concentrated under a stream of nitrogen. Solid materials were precipitated by addition of diethyl ether and separated by centrifugation. The resulting extract was concentrated and the residues of ethephon methylated with diazomethane. The ethephon dimethyl ester was analysed by gas chromatography with flame photometric detection (GC/FPD). Since the method had not been used to analyse melon fruit previously it was validated before the storage stability analyses.

Findings

As shown in Table 6.1- 9, the method validation results were satisfactory and the limit of quantification was established at 0.05 mg/kg. The procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals (Table 6.1- 10). The recoveries from the fortified samples stored at about -20°C were equally satisfactory at all storage intervals. Therefore, no degradation was observed up to 36 months of storage. Quite different results were obtained for the fortified samples of melon which were first freeze dried before storage at room temperature. For these samples satisfactory recoveries (similar to the procedural recoveries) were obtained at the first four storage intervals (day 0, 1 month, 2 months, 4 months) while at the next intervals the recoveries were found to decrease progressively down to 12% at the 18 month storage interval.

Conclusion

The residues of parent ethephon in melon samples were shown to be stable for at least 36 months following storage at about -20°C. However, these residues were found to be stable for only 4 months following storage at room temperature after freeze-drying.

Table 6.1- 9 Validation of the method SOP 90070 for the determination of ethephon in melon

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-187507-01-1 (SOP 90070)	Melon fruit	0.05 0.20 0.50 overall	6 6 6 18	74, 74, 67, 76, 77, 71 71, 80, 82, 81, 70, 84 79, 78, 76, 69, 74, 80	73 78 73 73	5.0 7.6 5.3 6.4

Table 6.1- 10 Storage stability of ethephon in melon

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)*		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Melon	Ethephon	frozen at ca. -20°C	Day 0	79 ,89	84	104	-
			1 month	79 ,90	84	76	-
			2 months	96 ,86	91	83	-
			4 months	97 ,97	97	105	-
			6 months	107 ,99	103	99	-
			9 months	103 ,92	97	90	-
			12 months	84 ,84	84	93	-
			18 months	75 ,80	78	80	-
			24 months	82 ,82	82	77	-
			30 months	113 ,111	112	105	-
			36 months	98 ,98	98	104	-
Melon	Ethephon	freeze-dried at room temperature	Day 0	79 ,89	84	104	-
			1 month	80 ,76	78	83	-
			2 months	76 ,64	70	73	-
			4 months	102 ,95	99	88	-
			6 months	59 ,37	48	89	-
			6 months**	47 ,38	42	106	-
			18 months	12 ,12	12	81	-

* The recoveries shown in this table were not corrected for the procedural recoveries from freshly fortified samples. In the study report the recoveries in stored samples were corrected for the procedural recoveries. The uncorrected recoveries were back-calculated based on the corrected values and the procedural recoveries.

** A second set of samples was analysed at this storage interval.

Report:	KCA 6.1/17; [redacted]; 2015; M-537340-01-1
Title:	Short-term storage stability of ethephon in/on cereals (grain) and the processed fractions (wholemeal bread, starch, malt sprouts and beer)
Report No.:	MR-15/138
Document No.:	M-537340-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market OECD Guidelines for the Testing of Chemicals. Stability of Pesticide Residues in Stored Commodities. 506. 2007-10-16. US EPA OCSPP 860.1380, Storage Stability Data
Guideline deviation(s):	none
GLP/GEP:	**yes**

During the barley and wheat processing studies 14-3400 and 14-3401 the examination samples intended for the analysis of parent ethephon residues were stored in a freezer room at a nominal temperature ≤ -18°C. However, for 15 hours and 15 minutes the actual temperature in this freezer room exceeded the tolerance of -18°C, with an average of -6.0°C; during this time the temperature was higher than -10°C for about 12 hours and 35 minutes with an average of -4.6°C. The maximum temperature was -1.2°C. The purpose of the study P642151808 was to investigate the impact of this temperature deviation.

Materials and methods

Control samples (5 g) of cereal grain and cereal processed commodities (wholemeal bread, starch, malt sprouts and beer) were fortified with ethephon at the 10-fold LOQ level of 0.10 mg/kg and first stored in a freezer at ≤ -18°C. After a few days the samples were taken out of the freezer and stored in a refrigerator for 24 hours. The temperature in the refrigerator ranged between -0.5°C and 5.9°C for the samples of grain, wholemeal bread, starch and malt sprouts, and between 0°C and 5.7°C for the samples of beer. Afterwards the samples were stored again at ≤ -18°C in a freezer until analysis. For each sample material and storage interval (immediate analysis on day 0 or analysis after storage) the analytical series consisted of one control sample, two freshly fortified sample for procedural recovery determination and three stored fortified samples.

The residues of ethephon in/on cereals (grain) and the processed fractions (wholemeal bread, starch, malt sprouts and beer) were determined according to the method 01429. For beer the residues were extracted once with methanol. For cereal grain and all other processing materials the residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of isotopically labelled internal standard the extracts were analysed by HPLC-MS/MS. The procedure was validated for cereal grain as part of the initial validation. Further validation for the wheat and barley processed commodities was performed during the processing studies 13-3406 and 14-3400, respectively. The limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain and the cereal processing fractions (including beer).

Findings

As shown in Table 6.1- 11, the procedural recoveries determined alongside the storage stability analyses were also satisfactory at all storage intervals. The average recoveries from the fortified samples stored for 24 h at between -0.5°C and 5.9°C and about one month at ≤ -18°C ranged between 91% and 104%. These values were very comparable to the average recoveries determined on the day of fortification. Therefore, the residues of ethephon in cereal grain, wholemeal bread, starch, malt sprouts and beer remained stable upon storage for 24 h between -0.5°C and 5.9°C.

Conclusion

The residues of ethephon in cereal grain, wholemeal bread, starch, malt sprouts and beer were shown to be stable for at least 24 h under refrigerated storage between -0.5°C and 5.9°C.

Table 6.1- 11 Storage stability of ethephon in cereal grain and cereal processed commodities

Sample material	Compound	Storage period and conditions	Recoveries from stored samples (%)*		Procedural recoveries from freshly fortified samples (%)	
			Individual values	Average	Individual values	Average
Barley grain	Ethephon	Day 0	98, 93, 91	94	100, 94	97
		28 days frozen & 1 day refrigerated	100, 102, 104	102	106, 99	103
Wheat wholemeal bread	Ethephon	Day 0	95, 98, 95	96	96, 94	95
		28 days frozen & 1 day refrigerated	88, 88, 94	90	99, 92	96
Barley malt sprouts	Ethephon	Day 0	100, 90, 91	94	96, 95	96
		31 days frozen & 1 day refrigerated	96, 93, 96	95	102, 106	104
Wheat starch	Ethephon	Day 0	100, 90, 85	92	76, 100	88
		31 days frozen & 1 day refrigerated	89, 94, 94	92	91, 90	91
Barley beer	Ethephon	Day 0	105, 101, 102	102	100, 104	102
		23 days frozen & 1 day refrigerated	98, 102, 96	99	98, 105	102

* For the samples that were not analysed on day 0, storage was performed at ≤ -18°C, except for 24 h during which the samples were stored refrigerated between -0.5°C and 5.9°C (except for beer : between 0°C and 5.7°C).

Report: KCA 6.1/18; [redacted]; 2003; M-234800-01-1
Title: Storage stability of AE F020271 in wheat grain and tomatoes
Report No.: C034370
Document No.: M-234800-01-1
Guideline(s): --
Guideline deviation(s): --
GLP/GEP: **yes**

In many residue studies the samples were analysed for the metabolite HEPA in addition to parent ethephon. The storage stability of HEPA was investigated in wheat grain and tomato fruit. At the time when the previous dossier was submitted results were only available for storage periods up to 3 months (refer to the document M-210332-01-1 in Table 6.1- 1). However, the study was continued for up to 18 months of storage and the final results are reported in the document M-234800-01-1. It is important to note that, due to its favourable toxicological profile, HEPA is not part of the existing and

proposed residue definitions for dietary risk assessment or MRL setting. Therefore, no storage stability data on HEPA are needed to demonstrate consumer safety.

Materials and methods

Untreated ground samples of wheat grain and tomatoes (10 g) were fortified with HEPA at a concentration of 0.5 mg/kg and then stored frozen at less than -18°C. In order to monitor any potential degradation of HEPA upon storage, analyses were conducted on day 0 and after 1, 3, 6, 12 and 18 months of storage. At each interval (except on day 0), two stored fortified samples, one stored control sample and one freshly fortified sample were analysed.

The samples were analysed for ethephon using the method ISOP HYA 10071. The residues were extracted from the samples with methanol. After liquid/liquid partitioning with diethyl ether, the residues were methylated with diazomethane. The HEPA derivative was analysed by gas chromatography with flame photometric detection (GC/FPD).

Findings

As shown in Table 6.1- 12, the procedural recoveries for HEPA were in the guideline range of 70-110%. The average recoveries from stored fortified samples ranged between 73% and 102% in wheat grain and between 83% and 108% in tomato fruit. The somewhat low recoveries of 73% and 74% determined in wheat grain at the 6 month and 12 month storage intervals were not confirmed at the last storage interval of 18 months (recovery of 102%). It may be concluded that the residues of HEPA are stable for at least 18 months in wheat grain and tomato fruit samples stored at or below -18°C.

Conclusion

The residues of HEPA in samples of wheat grain and tomato fruit were shown to be stable for at least 18 months at or below -18°C.

Table 6.1- 12 Storage stability of HEPA in wheat grain and tomato fruit

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Wheat grain	Ethephon	frozen at ≤ -18°C	Day 0	93, 83	88	-	-
			1 month	95, 95	95	85	-
			3 months	88, 92	90	97	-
			6 months	66, 80	73	103	-
			12 months	78, 69	74	81	-
			18 months	98, 106	102	102	-

Sample material	Compound	Storage conditions	Storage period	Recoveries from stored samples (%)		Procedural recoveries from freshly fortified samples (%)	
				Individual values	Average	Individual values	Average
Tomato fruit	Ethephon	frozen at ≤ -18°C	Day 0	85, 85	85	-	-
			1 month	111, 95	103	95	
			3 months	92, 105	99	97	-
			6 months	80, 85	83	92	-
			12 months	81, 97	89	88	-
			18 months	110, 106	108	102	-

- Conclusion on the stability of residues during the storage of samples

Table 6.1- 13 provides an overview of the previously submitted storage stability data and herein provided supplementary storage stability data. The storage stability study in nutmeat, which was not conclusive, is not listed. Overall, the storage stability of ethephon was established for at least 24 months in deep frozen samples of 5 matrices with a high water content, 3 matrices with a high acid content, 1 matrix with a high starch content and one matrix with a high oil content.

Table 6.1- 13 Overview of the storage stability data for ethephon and its metabolite HEPA in plant matrices (compilation of previously submitted and supplementary data)

Document	Matrix	Category [rich in]	Analyte	Storage conditions	Stability demonstrated for up to
M-187521-01-1 (R013222)	Wheat grain	Starch	Ethephon	frozen at ca. -20°C	24 months
M-187519-01-1 (R013221)	Wheat straw	-	Ethephon	frozen at ca. -20°C	24 months
M-187533-01-1 (R013228)	Tomato fruit	Water	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187515-01-1 (R013219)	Apple fruit	Water	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187505-01-1	Cherry	Water	Ethephon	frozen at ca. -15°C freeze-dried at room temperature	24 months 24 months
M-187542-01-1	Bell pepper	Water	Ethephon	frozen at ca. -15°C freeze-dried at room temperature	24 months 4 months
M-187507-01-1	Melon	Water	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	36 months 4 months
M-187544-01-1 (R013233)	Grape berry	Acid	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187511-01-1 (R013217)	Blackberry fruit	Acid	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-187540-01-1	Pineapple fruit	Acid	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 24 months
M-161841-01-1	Pineapple forage	-	Ethephon	frozen at ca. -20°C freeze-dried at room temperature	24 months 9 months
M-187525-01-1 (R013224)	Cottonseed	Oil	Ethephon	frozen at ca. -20°C	24 months
M-188009-01-1 (R013470)	Apple juice Cottonseed oil	- -	Ethephon Ethephon	frozen at ca. -20°C frozen at ca. -20°C	12 months 12 months
M-234800-01-1	Wheat grain Tomato fruit	Starch Water	HEPA HEPA	frozen at ca. -18°C frozen at ca. -18°C	18 months 18 months

CA 6.2 Metabolism, distribution and expression of residues

CA 6.2.1 Plants

The Annex II dossier of ethephon submitted in 2002 includes two GLP metabolism studies for foliar application of ethephon in wheat and tomato, respectively. In all studies the main degradation route of ethephon was shown to involve decomposition to ethylene and phosphates. 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 (2-hydroxyethyl)phosphonic acid (abbreviated HEPA). HEPA is further metabolized by incorporation of the two carbon atoms in natural bio-molecules. In the wheat study ^{14}C-ethephon was foliar sprayed at the rate of 360 g as/ha when the

plants had reached the ligule stage (BBCH 39). At mature harvest, grain showed similar levels of parent ethephon and HEPA (0.47 mg/kg and 0.51 mg/kg, representing 43.5% and 47.7% of TRR, respectively) whereas straw was found to contain higher levels of ethephon than of HEPA (1.47 mg/kg and 0.62 mg/kg, representing 62.3% and 26.1% of TRR, respectively). In the tomato study the plants were foliar-treated with 1440 g a.s/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 (96.1% of TRR on day 0 and 47.1% of TRR on day 12). HEPA represented up to 15% of the total radioactive residue.

The Annex II dossier also includes non-GLP studies and publications on the metabolism of ethephon in pineapple, summer squash, cucumber, apple, cherries and grape. Despite many limitations, these non-GLP data were consistent with the results of the two GLP studies since hydrolysis of ethephon to ethylene was shown to be the main metabolic pathway and HEPA was sometimes identified as a minor residue component. They also provided information on the formation and incorporation of phosphates.

Besides the wheat and tomato metabolism studies a GLP cotton metabolism study is also available. This study is reviewed below since it was still on-going at the time when the Annex II dossier of ethephon was issued.

Report:	KCA 6.2.1/08; [redacted]; [redacted]; 2006; M-240888-01-2
Title:	Metabolism of [U-14C]-Ethephon in cotton
Report No.:	B003904
Document No.:	M-240888-01-2
Guideline(s):	USEPA (=EPA): 860.1300 and EU 91/414/EEC
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Cotton plants growing in an outdoor plot (1.28 m^2) were foliar-treated with ^{14}C-ethephon (specific activity 36 µCi/mg). The application rate was 1400 g as/ha, which approximately corresponds to the maximum application rate of 1440 g as/ha for the use of ethephon in cotton in the field. Samples for analysis were taken at day 0 just after treatment (foliage), and 7 days after treatment at harvest maturity (gin trash and bolls). The bolls were separated into lint (which was not analyzed further) and seed.

The day 0 foliage samples were first washed with acetonitrile to recover surface residues. The washed foliage was then extracted with acetonitrile. The final harvest (mature) samples were frozen and ground prior to being analyzed further. Sample aliquots were combusted to determine the total radioactive residues. Thereafter, the gin trash samples (principally leaves and boll husks) were extracted with methanol/water (9/1, v/v) while the seed samples were extracted with methanol. Fibers were separated from the extracts by filtration. In order to remove oil, the seed extracts were repeatedly partitioned with hexane prior to analysis. The radioactivity in washes and extracts was measured by LSC. The radioactivity remaining in the fiber was determined by combustion. Extracted fibers from the gin trash and seed were hydrolyzed with a mixture of concentrated hydrochloric acid and water (1/7, v/v). The samples were incubated for 20 hours at room temperature, then filtered and washed with methanol. The radioactivity extracted in the acid hydrolysate (filtrate plus methanol wash) was measured by LSC. The residual fiber was dried and the radioactivity remaining unextracted quantified by combustion.

The individual radioactive residues in the extracts were identified and quantified by high performance liquid chromatography (HPLC) against a mixture of analytical reference standards. Identification was confirmed by thin layer chromatography (TLC).

Findings

The total residues in foliage at day 0 averaged 237.3 mg/kg ethephon equivalents (average of two samples) while 7 day later analysis at final harvest showed 31.4 mg/kg ethephon equivalents in the gin trash and 0.8 mg/kg ethephon equivalents in the cotton seed. The residue levels and extraction profiles at each time point are presented in Table 6.2.1- 1.

There was significant variability between the two samples at day 0 as might be expected given the small sample size at this time point. The total residue (as determined by extraction and combustion) in the day 0 samples ranged from 113.7 mg/kg to 360.8 mg/kg ethephon equivalents. The recovery of the residue at Day 0 by acetonitrile wash and extraction was relatively inefficient, but this was used only to establish the residue levels at day 0 and to develop extraction methodology for the final harvest.

At final harvest, the residue levels and extraction profiles for the replicate samples were comparable. Methanol extraction of mature gin trash and seed proved very effective recovering over 80% of the total radioactive residue. Acid hydrolysis recovered the majority of the remainder of the residue (11-17% TRR), leaving only 0.2% TRR fiber bound in the gin trash and 1.2% bound in the cotton seed.

Table 6.2.1- 1 Total Radioactive Residues (TRR) and extractability of residues in cotton samples

Sample type	Sample ID	TRR		Surface Wash		Matrix Extract		Acid hydrolysate		Non extractable residue	
		ppm	% TRR	ppm	% TRR	ppm		% TRR	ppm	% TRR	ppm
Day 0 Leaves	1P	113.7	50.2	57.0	1.5	1.7		na	na	48.3	54.9
	2P	360.8	73.0	263.3	0.3	1.0		na	na	26.8	96.6
	Mean	237.3	61.6	160.1	0.9	1.4		na	na	37.6	75.8
Day 7 Gin Trash	3P	30.0	na	na	89.5	26.8		10.4	3.1	0.1	0.04
	4P	32.8	na	na	87.7	28.8		12.0	3.9	0.3	0.11
	Mean	31.4	na	na	88.6	27.8		11.2	3.5	0.2	0.08
Day 7 Seeds	7PA	0.82	na	na	84.1	0.69		14.9	0.12	1.0	0.008
	7PB	0.82	na	na	80.0	0.66		18.6	0.15	1.4	0.011
	Mean	0.82	na	na	82.1	0.67		16.8	0.14	1.2	0.010

Notes :
- ppm = mg equivalents of ethephon per kg of sample.
- na = not applicable.
- The total radioactive residue (TRR) in the day 0 samples was calculated by summation of the radioactive residues determined in the various fractions (wash, extract and fiber). The TRR at Day 7 was determined by combustion.

Chromatography of the day 0 surface washes confirmed that they were primarily composed of parent ethephon (mean of 59.2% TRR). A further 0.2% of the radioactivity was identified as

(2-hydroxyethyl)phosphonic acid (HEPA), with no other single metabolite representing more than 1.5% TRR. The remainder of the radioactivity was not extracted from the fiber.

Chromatography results of the individual extracts at final harvest showed excellent correlation. The majority of the residue in the gin trash and cotton seed (93.0 and 78.3%, respectively) consisted of unchanged parent. The only significant metabolite was HEPA representing 1.7% TRR in the gin trash and 9.6% TRR in the cotton seed. 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. The mean results are shown in Table 6.2.1- 2. Identification by HPLC was confirmed by TLC.

Table 6.2.1- 2 Identification of ethephon residues in cotton samples

Sample type	Extract Type	Total Extractable Residue		Ethephon		HEPA		Largest Single Unknown		Total Identified	
		% TRR	ppm	% TRR	ppm	% TRR	ppm	% TRR	ppm	% TRR	ppm
Day 0 Leaves	Acetonitrile wash	61.6	160.1	59.2	156.3	0.2	0.2	0.9	2.1	59.4	156.5
Day 7 Gin Trash	Methanol/Water extract	88.6	27.8	83.7	26.7	1.3	0.4	1.3	0.4	85.0	27.1
	Acid hydrolysate	11.2	3.5	9.3	2.9	0.4	0.1	1.0	0.3	9.7	3.1
	Combined total	99.8	31.3	93.0	29.7	1.7	0.5	na	na	94.7	30.2
Day 7 Seed	Methanol extract	81.7	0.7	66.1	0.5	7.7	0.06	1.9	0.02	73.7	0.60
	Acid hydrolysate	16.8	0.1	12.2	0.1	1.9	0.02	1.8	0.01	14.1	0.11
	Combined total	98.5	0.8	78.3	0.6	9.6	0.08	na	na	87.8	0.72

Notes :
- All results are means from duplicate samples.
- ppm = mg equivalents of ethephon per kg of sample.
- The total radioactive residue (TRR) in the day 0 samples was calculated by summation of the radioactive residues determined in the various fractions (wash, extract and fiber). The TRR at Day 7 was determined by combustion.

Conclusion

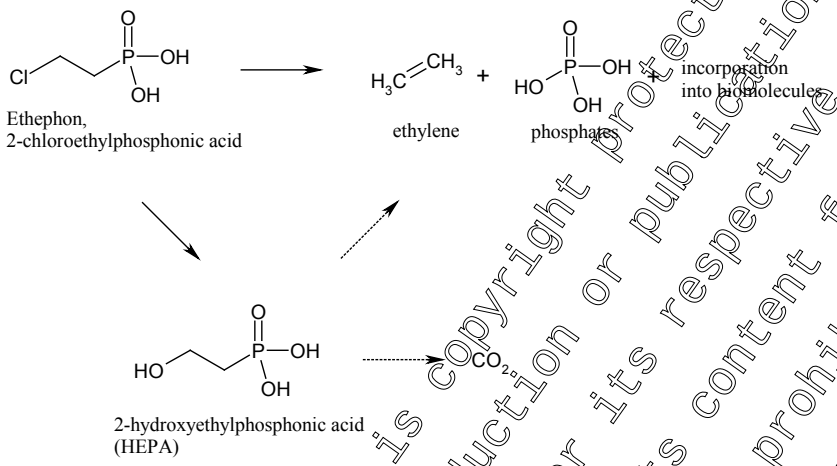
The metabolism of ^{14}C-ethephon in cotton was investigated after a single application at the rate of 1400 g as/ha when the plants had reached a growth stage approaching maturity. The radioactive residues in the mature gin trash and seed taken on day 7 after application were principally recovered by extraction with methanol. The remaining radioactivity was recovered by acid hydrolysis, leaving very little radioactive residues bound to fiber. Parent ethephon comprised the main part of the residue in both the gin trash and cotton seed (93.0% and 78.3%, respectively). The metabolite (2-hydroxyethyl)phosphonic acid (HEPA) was present at lower levels representing 1.7% TRR in gin trash and 9.6% TRR in cotton seed.

- General conclusion on the metabolism in crops

The results of the cotton metabolism study are consistent with those of the wheat and tomato metabolism studies. Since wheat, tomato and cotton belong to three different groups in the sense of

the OECD Guideline on metabolism in crops, the results may be generalized to other crop groups, as appropriate. Hence it is concluded that the main degradation route of ethephon in plants involves decomposition to ethylene and phosphates. Ethylene is rapidly released into the atmosphere while the phosphates are taken up in the natural phosphate cycle of the plant. Part of the applied ethephon is metabolized according to a different metabolic pathway that results in the formation of the metabolite (2-hydroxyethyl)phosphonic acid (abbreviated HEPA). HEPA is further metabolized by incorporation of the two carbon atoms in natural bio-molecules.

Figure 6.2.1- 1 Metabolism of ethephon in plants



CA 6.2.2 Poultry

The Annex II dossier of ethephon submitted in 2002 includes two hen metabolism studies in which 8-10 birds per study were dosed orally for 5 consecutive days with ^{14}C-ethephon in gelatine capsules at levels equivalent to 53-67 mg/kg in the feed (about 2.6-4.1 mg/kg bw/day). The compound was found to be rapidly and efficiently eliminated in expired air (mainly as ethylene) and excreta. Less than 1% of the administered radioactivity was recovered in eggs and hen edible tissues.
Characterization of residue constituents in hen tissues indicated that besides hydrolysis to ethylene, a competitive degradation pathway results in the formation of the metabolite HEPA, which is likely to be further metabolized via dissociation of the phosphonic acid moiety and incorporation of the carbon atoms into natural tissue constituents such as lipids and proteins. Parent ethephon and HEPA accounted for 42% and 14%, respectively, of the total radioactive residue (TRR) in kidney, 17% and 16% in liver, and 12% and 18% in muscle. No ethephon or HEPA residues were identified in fat, egg yolk or egg white.
In the EFSA Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347) the study was not considered to be necessary since the dietary burden of poultry was estimated to be below the trigger value of 0.1 mg/kg. However, the following conclusions were drawn :
"This study demonstrates that metabolic pathways of ethephon in ruminants and poultry are very similar […]. It is therefore concluded that the relevant residue in poultry could also be defined as ethephon."

CA 6.2.3 Lactating ruminants

The Annex II dossier of ethephon submitted in 2002 includes a goat metabolism study in which two animals were dosed orally for 7 successive days with ^{14}C-ethephon in gelatine capsules at a level equivalent to 10 mg/kg in the feed (about 0.37-0.46 mg/kg bw/day). In the EFSA Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347) the main study results are summarised as follows :

"This study demonstrates that the parent compound is hydrolysed to lose its chlorine and phosphate groups and that the carbon units are taken up into the tricarboxylic acid cycle to yield natural products like fat, protein, carbohydrate and CO_2. Ethephon and HEPA are expected to be the only toxicologically relevant compounds and the highest radioactive residue level was found in liver (1 mg/kg) of which 0.15% was considered ethephon and/or HEPA (max. 0.0015 mg/kg). […] Based on these data and the fact that residues in all ruminant commodities were expected to be very low, no residue definition was proposed in the framework of the peer review (EFSA, 2008a). In the framework of this review, however, additional crops contribute to the dietary burden of livestock resulting in a higher exposure of livestock to ethephon residues and the necessity to establish a residue definition in pigs and ruminants. Also in contrast to the peer review, data are now available indicating that HEPA is expected to result in adverse effects at much higher exposure levels than ethephon […]. Therefore, the relevant residue in […] ruminants is now defined as ethephon, both for enforcement and risk assessment purposes."

In the initial peer review process (EFSA Conclusion, 2008), the goat metabolism study was considered sufficient. To stress the acceptability of this study, the following information is additionally provided.

Residues of ethephon found in all animal matrices were <0.01 mg/kg.
The dose administered in goat metabolism study was 10 mg/kg feed (DM) which corresponds to approximately 11 times the maximum concentration taken up through feed items derived from cereals, apples and cotton seed treated according to cGAP of current uses (see EFSA RO, 2009: max. 0.92 mg/kg feed DM). When the maximum residue of 1.18 mg /kg measured in kidney in the goat study is normalised to this feed burden, a maximum residue of 0.11 mg/kg results. Of the 0.11 mg/kg radioactive residue only 0.15% is considered to be ethephon and/or HEPA (max. 0.00016 mg/kg). Since ethephon residues of less than 0.01 mg/kg in animal edible products are expected with the current GAP no new metabolism studies are deemed necessary. The existing goat ADME study is providing sufficient data regarding the evaluation of the current uses.
In the argumentation (Bayer paper M-223288-02-1(3), [redacted], P, 2005; KCA 6.2.3/01) further (raw) data from the goat ADME study are presented. 31% of daily dose measured as volatiles on study day 7 is considered representative for the percentage of volatiles in total dose. Characterisation and identification was not considered necessary because residues in tissues and milk were <10% TRR (2.95% and 3.28%, respectively).
The metabolism of ethephon has been demonstrated to be both extensive and rapid in goat, hen and rat. The metabolic fate of radiolabelled ethephon was, in majority, to be hydrolysed to ethylene and expired via respiration but there was also an additional pathway that lead to the release of $^{14}CO_2$ which was then either be expired or entered the natural biochemical pathways leading to the biosynthesis of amino acids, proteins, carbohydrates and lipids that contain radioactive residues. There was also evidence that glutathione conjugation was an active pathway. It appears that performing an additional goat metabolism study would be very unlikely to add any significant new data to the understanding of the fate of ethephon in ruminants. Thus, acceptance of the existing goat ADME study should be carefully reconsidered, also with regards to animal welfare.

CA 6.2.4 Pigs

According to the EFSA Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347) : *"Since metabolism in rats and ruminants was demonstrated to be similar,*

the findings in ruminants can also be extrapolated to pigs. […] Therefore, the relevant residue in pigs […] is now defined as ethephon, both for enforcement and risk assessment purposes."

CA 6.2.5 Fish

No suitable test method for the conduct of metabolism studies on fish is listed in Commission Communication 2013/C 95/01 about the implementation of Regulation (EU) No 283/2013. Therefore, this point does not need to be addressed at the current stage.
However, according to the working document SANCO/11187/2013 rev. 3 it seems that metabolism studies to determine the nature of residues in fish will only be required for fat-soluble substances (log Pow ≥ 3). Since ethephon is not a fat-soluble substance (its log Pow is estimated to be -1.89 at pH 7) it is expected that no metabolism study to determine the nature of ethephon-derived residues in fish will be required.

CA 6.3 Magnitude of residue trials in plants

The representative uses for the renewal of the approval of ethephon in the EU are defined as a single broadcast spray application to cereals (barley and wheat) to prevent lodging. In the context of the renewal dossier the maximum application rate is 480 g as/ha. The latest time for application is BBCH 51 (Beginning of heading: tip of inflorescence emerged from sheath, first spikelet just visible) in the northern residue zone and BBCH 39 (Flag leaf stage: flag leaf fully unrolled, ligule just visible) in the southern residue zone. Since the application is conducted at an early growth stage, it is not deemed necessary to propose a pre-harvest interval (PHI). These representative uses are the same as the uses that were considered for the previous EU evaluation.

Table 6.3- 1: Representative uses of ethephon as an anti-lodging agent in cereals (barley and wheat)

Country	F, G, or I	Formu-lation	Application						PHI (days)	Remarks
			Method	Growth stage	Number	Interval (days)	Water (L/ha)	Rate (g as/ha)		
EU North	F	SL 480 g/L	Foliar spraying	BBCH 41-51	1	-	200-400	480	-	Since the application is conducted at an early stage, there is no need to set a PHI
EU South	F	SL 480 g/L	Foliar spraying	BBCH 37-39	1	-	200-400	480	-	Since the application is conducted at an early stage, there is no need to set a PHI

A sufficient number of residue trials to support these representative uses are included in the Annex II dossier submitted in 2002. However, in these trials all the straw and grain samples were extracted with methanol, which is not in line with the extraction procedure of the wheat metabolism study. In order to comply with new data requirements [Regulation (EU) No 283/2013) and new guidelines [OECD Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17] it was decided to conduct a new set of trials, in which the straw and grain samples were extracted in the same way as in the wheat metabolism study (i.e. first by blending with methanol and then by digestion with hydrochloric acid).

Since ethephon is applied to cereals at an early stage (i.e. before the edible part of the plant forms) and in accordance with the guideline SANCO 7525/VI/95 - rev.9 of March 2011, it possible to extrapolate between barley and wheat. However, as shown in Table 6.3- 2, a full set of new trials (8 trials per zone) was conducted for each of the two crops. The trials were distributed over two different growing seasons (2013 and 2014) and half of them were decline trials. Detailed summary tables for these trials may be found in Appendix 1.

Table 6.3- 2: Overview of the residue studies conducted to support the representative uses of ethephon as an anti-lodging agent in cereals (barley and wheat)

Crop	Document No.	Report & study No.	Year of trials	Zone	Number of trials	Remarks *
Barley	M-526906-01-1	13-2027	2013	North	4	2 harvest trials and 2 decline trials
Barley	M-533473-01-1	14-2022	2014	North	4	2 harvest trials and 2 decline trials
Barley	M-529491-01-1	13-2028	2013	South	4	2 harvest trials and 2 decline trials
Barley	M-533463-01-1	14-2020	2014	South	4	2 harvest trials and 2 decline trials
Wheat	M-529493-01-1	13-2029	2013	North	3	1 harvest trial and 2 decline trials
Wheat	M-532267-01-1	14-2018	2014	North	5	3 harvest trials and 2 decline trials
Wheat	M-529488-01-1	13-2030	2013	South	4	2 harvest trials and 2 decline trials
Wheat	M-532272-01-1	14-2019	2014	South	4	2 harvest trials and 2 decline trials

* In the harvest trials, green material was sampled on day 0 and at about growth stage BBCH 75 while grain and straw were sampled at normal harvest. In the decline trials, 3 supplementary samples of green material were taken on about day 7, day 14 and day 21.

In addition to the residues of parent ethephon, the samples from all the above studies were also analysed for the residues of the metabolite HEPA. However, the available storage stability data for HEPA do not fully cover the storage periods and matrix types of the studies. Furthermore, in several trials, the untreated control samples of grain and straw showed apparent residues of HEPA of about the same magnitude as the residues of HEPA found in the corresponding treated samples. For these reasons, the residue results for HEPA are only considered indicative. In the following summaries they are not commented in detail but nevertheless provided in the result tables next to the residue results for parent ethephon. It is important to note that, due to its favourable toxicological profile, HEPA is not part of the existing and proposed residue definitions for dietary risk assessment or MRL setting. The residue data for HEPA are not needed to demonstrate consumer safety.

CA 6.3.1 Barley

Report:	KCA 6.3.1/06; [redacted]; [redacted]; 2015; M-526906-01-1
Title:	Determination of the residues of ethephon in/on winter barley after spray application of Ethephon SL 480 in Germany, Belgium, the Netherlands and the United Kingdom
Report No.:	13-2027
Document No.:	M-526906-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1997-07-22) OECD 509 Adopted 2009-09-07, OECD GUIDELINE FOR THE TESTING OF CHEMICALS, Crop Field Trial US EPA OCSPP Guideline No. 860.1500
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in Germany, Belgium, the Netherlands and the United Kingdom. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of about 480 g as/ha after dilution in 200-300 L/ha of water. In one trial, however, the application was conducted at the slightly overdosed rate of 512 g as/ha. Samples of green material were taken on day 0 (shortly after application) and 24-43 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 55-68 days after application.

Details about the design and results of the trials are given in Table 6.3.1- 1.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 20 months (582 days) until analysis. In the Belgian trial (13-2027-02) the temperature rose above -18°C during the shipment of the green material field samples from the test site to the test facility. The average temperature during shipment was estimated at ca. -11°C. However, owing to the very short duration of the shipment (3 hours and 5 minutes) and since the samples remained frozen, this deviation is unlikely to have impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.2-7.9 mg/kg on day 0 and had decreased to < 0.05-0.43 mg/kg at the growth stage BBCH 75. At harvest, which was 55-68 days after application, the residues of parent ethephon were in the range of 0.067-0.73 mg/kg in grain and 0.35-3.6 mg/kg in straw.

Table 6.3.1- 1: Residue trials performed in the northern part of the EU in 2013 to support the use of ethephon as an anti-lodging agent in barley – overview of trial design and residue results [Study 13-2027]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ha	kg as/hL	Growth stage		ETP	HEPA	
M-526906-01-1 13-2027 13-2027-01	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 51	green material	6.2 0.61 0.55 0.26 0.43	0.091 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 24
								grain	0.13	0.019 (0.013)*	59
								straw	0.54	< 0.05	59
M-526906-01-1 13-2027 13-2027-02	[redacted] 2013	SL	480	1	0.51	0.19	BBCH 51	green material	3.2 < 0.05	< 0.05 < 0.05	0 33
								grain	0.067	< 0.01	55
								straw	0.35	< 0.05	55
M-526906-01-1 13-2027 13-2027-03	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 51	green material	7.9 3.8 0.85 0.57 0.27	0.094 0.088 0.085 0.076 0.059	0 7 14 21 43
								grain	0.73	0.086	56
								straw	1.5	< 0.05	56
M-526906-01-1 13-2027 13-2027-04	[redacted] 2013	SL	480	1	0.48	0.24	BBCH 51	green material	6.6 0.36	0.093 < 0.05	0 34
								grain	0.23	0.055	68
								straw	3.6	0.066	68

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Table 6.3.1- 2: Validation data and concurrent recoveries for the determination of ethephon-derived residues in cereal commodities from the 2013 season residue trials [Studies 13-2027, 13-2028, 13-2029 & 13-2030]

Report (Method)	Matrix	Compound	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1 (01429)	Green material	Ethephon	0.05	5	81; 108; 117; 87; 94	97	15.3
			0.5	4	78; 106; 78; 95	89	15.4
			5.0	1	100	100	-
			10	3	81; 89; 82	84	5.2
			20	1	80	80	-
			overall	14	-	91	13.8
		HEPA	0.05	5	93; 102; 112; 97; 113	103	8.6
			0.5	4	84; 105; 71; 98	90	16.9
			5.0	1	94	94	-
			10	3	82; 85; 84	84	1.8
			20	1	76	76	-
			overall	14	-	93	13.9
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1 (01429)	Grain	Ethephon	0.01	3	96; 110; 81	96	15.2
			0.1	2	95; 101	98	-
			1.0	2	90; 91	91	-
			overall	7	-	95	9.6
		HEPA	0.01	3	105; 93; 102	100	6.2
			0.1	2	81; 104	93	-
			1.0	2	80; 85	83	-
			overall	7	-	93	11.8
M-526906-01-1 M-529491-01-1 M-529493-01-1 M-529488-01-1 (01429)	Straw	Ethephon	0.05	2	92; 99	96	-
			0.5	2	86; 85	86	-
			5.0	2	89; 91	90	-
			overall	6	-	90	5.6
		HEPA	0.05	4	80; 86; 99; 103	92	11.7
			0.5	2	70; 77	74	-
			5.0	2	80; 78	79	-
			overall	8	-	84	13.5

The fortification levels are expressed as ethephon for parent ethephon and as HEPA for the metabolite HEPA.

Conclusion

Four residue trials were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. In each trial there was one foliar application at the rate of 480-512 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 55-68 days after application, the residues of parent ethephon were in the range of 0.067-0.73 mg/kg in grain and 0.35-3.6 mg/kg in straw.

Report:	KCA 6.3.1/07; [redacted]; [redacted]; 2015; M-533473-01-1
Title:	Determination of the residues of ethephon in/on winter barley after spray application of ethephon SL 480 in Germany, northern France and the United Kingdom
Report No.:	14-2022
Document No.:	M-533473-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market; OECD Guideline for the Testing of Chemicals on Crop Field Trial (TG 509 published in September 2009); US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial
Guideline deviation(s):	none
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in Germany, France and the United Kingdom. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray, usually when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of about 480 g as/ha after dilution in 200-336 L/ha of water. In one trial, however, the application was delayed until the growth stage BBCH 55, while in an other trial the application was conducted at the slightly overdosed rate of 537 g as/ha. Samples of green material were taken on day 0 (shortly after application) and 21-36 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 56-78 days after application.

Details about the design and results of the trials are given in Table 6.3.1- 3.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 14 months (414 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 6.2-7.7 mg/kg on day 0 and had decreased to < 0.05-0.37 mg/kg at the growth stage BBCH 75. At harvest, which was 56-78 days after application, the residues of parent ethephon were in the range of 0.031-0.41 mg/kg in grain and 0.43-1.2 mg/kg in straw.

Table 6.3.1- 3: Residue trials performed in the northern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in barley – overview of trial design and residue results [Study 14-2022]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ha	kg as/hL	Growth stage		ETP	HEPA	
M-533473-01-1 14-2022 14-2022-01	[redacted] 2014	SL	480	1	0.54	0.16	BBCH 51	green material	6.2 0.50 0.29 0.17 0.086	0.12 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 36
								grain	0.031	0.016	78
								straw	0.64	0.055	78
M-533473-01-1 14-2022 14-2022-02	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 51	green material	7.7 0.37	0.12 < 0.05	0 21
								grain	0.41	0.055 (0.054)*	64
								straw	1.2	0.063 (0.061)*	64
M-533473-01-1 14-2022 14-2022-03	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 81	green material	6.6 0.34 0.15 0.10 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 28
								grain	0.090	0.021	56
								straw	0.43	< 0.05	56
M-533473-01-1 14-2022 14-2022-04	[redacted] 2014	SL	480	1	0.48	0.24	BBCH 55	green material	7.3 0.13	0.072 0.050	0 34
								grain	0.16	0.047 (0.011)*	73
								straw	0.78 (0.088)*	< 0.05	73

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Table 6.3.1- 4: Validation data and concurrent recoveries for the determination of ethephon-derived residues in cereal commodities from the 2014 season residue trials [Studies 14-2018, 14-2019, 14-2020 & 14-2022]

Report (Method)	Matrix	Compound	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Green material	Ethephon	0.05	6	99; 100; 100; 87; 94; 101	97	5.6
			0.50	4	89; 97; 90; 94	93	4.0
			5.0	1	89	89	-
			10	3	92; 87; 88	89	3.0
			20	1	98	98	-
			overall	15	-	94	5.5
		HEPA	0.05	6	91*; 96; 100; 85; 85; 104	94	8.4
			0.50	4	86; 90; 79; 86	85	5.4
			5.0	1	96	96	-
			10	3	91; 76; 90	86	9.8
			20	1	100	100	-
			overall	15	-	90	8.7
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Grain	Ethephon	0.01	4	105; 109; 100; 109	106	4.0
			0.10	2	89; 106	98	-
			1.0	2	98; 90	94	-
			overall	8	-	101	7.9
		HEPA	0.01	3	85; 96; 90	90	6.1
			0.10	2	85; 82	84	-
			1.0	2	79; 82	81	-
			overall	7	-	86	6.7
M-532267-01-1 M-532272-01-1 M-533463-01-1 M-533473-01-1 (01429)	Straw	Ethephon	0.05	5	93; 108; 113; 83; 104	100	12.1
			0.50	4	90; 100; 103; 106	100	7.0
			1.5	3	70; 70; 80	73	7.9
			5.0	1	71	-	-
			overall	13	-	92	16.8
		HEPA	0.05	4	73; 82; 106; 77	85	17.5
			0.50	4	63; 71; 83; 70	72	11.6
			1.5	3	66; 68; 77	70	8.3
			5.0	1	66	-	-
			overall	12	-	75	15.4

The fortification levels are expressed as ethephon for parent ethephon and as HEPA for the metabolite HEPA.

* This recovery was corrected for the apparent residue of 0.0165 mg/kg in the control sample used for fortification. Before correction the recovery was 122%.

Conclusion

Four residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. In each trial there was one foliar application at the rate of 480-537 g as/ha when the crop had reached the growth stage BBCH 51, except in one trial, in which the application was delayed until the growth stage BBCH 55. At harvest, which was 56-78 days after application, the residues of parent ethephon were in the range of 0.031-0.41 mg/kg in grain and 0.43-1.2 mg/kg in straw.

Report:	KCA 6.3.1/08; [redacted]; [redacted]; 2015; M-529491-01-1
Title:	Determination of the residues of ethephon in/on winter barley after spray application of ethephon SL 480 in southern France, Spain and Italy
Report No.:	13-2028
Document No.:	M-529491-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1997-07-22) OECD 509 Adopted 2009-09-07, OECD Guideline for the testing of Chemicals, Crop Field Trial US EPA OCSPP Guideline No. 860.1500
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in France, Spain and Italy. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of 480 g as/ha after dilution in 300-400 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 24-39 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 12-14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 62-72 days after application.

Details about the design and results of the trials are given in Table 6.3.1- 5.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 22 months (647 days) until analysis. In the French and Spanish trials (13-2028-01 and 13-2028-02, respectively) the temperature rose above -18°C during the shipment of the green material field samples from the respective test site to the test facility. The average temperature during shipment was estimated at -15.6°C and -13.5°C, respectively. However, owing to the relatively short duration of the shipment (less than 21 hours in the French trial, 1 day and 5 hours in the Spanish trial) and since the samples remained frozen, this deviation is unlikely to have significantly impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.5-5.9 mg/kg on day 0 and had decreased to < 0.05-0.26 mg/kg at the growth stage BBCH 75. At harvest, which was 62-72 days after application, the residues of parent ethephon were in the range of 0.021-0.21 mg/kg in grain and 0.23-1.7 mg/kg in straw.

Table 6.3.1- 5: Residue trials performed in the southern part of the EU in 2013 to support the use of ethephon as an anti-lodging agent in barley – overview of trial design and residue results [Study 13-2028]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ha	kg as/hL	Growth stage		ETP	HEPA	
M-529491-01-1 13-2028 13-2028-01	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 39	green material	4.5 0.24 0.15 0.092 < 0.05	0.053 < 0.05 < 0.05 < 0.05 < 0.05	0 7 12 21 39
								grain	0.035	< 0.01	71
								straw	0.23	< 0.05	71
M-529491-01-1 13-2028 13-2028-02	[redacted] 2013	SL	480	1	0.48	0.12	BBCH 39	green material	4.2 0.26	0.058 (0.081)* < 0.05	0 27
								grain	0.21	0.069 (0.023)*	72
								straw	1.7	0.17 (0.17)*	72
M-529491-01-1 13-2028 13-2028-03	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 39	green material	5.9 0.44 0.087 0.078 0.051	0.051 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 24
								grain	0.041	0.012	62
								straw	0.39	0.054	62
M-529491-01-1 13-2028 13-2028-04	[redacted] 2013	SL	480	1	0.48	0.14	BBCH 39	green material	3.5 < 0.05	< 0.05 < 0.05	0 29
								grain	0.021	0.070 (0.060)*	64
								straw	0.24	< 0.05	64

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in barley. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 62-72 days after application, the residues of parent ethephon were in the range of 0.021-0.21 mg/kg in grain and 0.23-1.7 mg/kg in straw.

Report:	KCA 6.3.1/09; [redacted]; [redacted]; 2015; M-533463-01-1
Title:	Determination of the residues of ethephon in/on winter barley after spray application of ethephon SL 480 in southern France, Spain, Italy and Greece
Report No.:	14-2020
Document No.:	M-533463-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market; OECD Guideline for the Testing of Chemicals on Crop Field Trial (TG 509 published in September 2009); US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial
Guideline deviation(s):	none
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. The trial sites were located in France, Spain, Italy and Greece. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray, usually when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of about 480 g as/ha after dilution in 300-400 L/ha of water. In one trial, however, the application was delayed until the growth stage BBCH 43 and conducted at the under-dosed rate of 411 g as/ha. Samples of green material were taken on day 0 (shortly after application) and 29-48 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 6-7, 14 and 20-21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 63-72 days after application.

Details about the design and results of the trials are given in Table 6.3.1- 6.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 15 months (427 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.3-8.2 mg/kg on day 0 and had decreased to < 0.05-0.36 mg/kg at the growth stage BBCH 75. At harvest, which was 63-72 days after application, the residues of parent ethephon were in the range of 0.034-0.14 mg/kg in grain and 0.35-1.1 mg/kg in straw.

Table 6.3.1- 6: Residue trials performed in the southern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in barley – overview of trial design and residue results [Study 14-2020]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage		ETP	HEPA	
M-533463-01-1 14-2020 14-2020-01	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 39	green material	5.6 3.0 3.0 0.38 0.095	0.069 0.055 0.055 < 0.05 < 0.05	0 7 14 21 42
								grain	0.14	0.026	72
								straw	1.1	< 0.05	72
M-533463-01-1 14-2020 14-2020-02	[redacted] 2014	SL	480	1	0.41	0.12	BBCH 43	green material	6.6 0.36	0.14 < 0.05	0 29
								grain	0.039	0.013	64
								straw	0.97	0.080	64
M-533463-01-1 14-2020 14-2020-03	[redacted] 2014	SL	480	1	0.48	0.12	BBCH 39	green material	3.3 1.2 0.34 0.10 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	0 6 14 20 29
								grain	0.047	< 0.01	64
								straw	0.39	< 0.05	64
M-533463-01-1 14-2020 14-2020-04	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 39	green material	8.2 < 0.05	0.14 < 0.05	0 48
								grain	0.034	0.014	63
								straw	0.35	< 0.05	63

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in barley. In three trials there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. In the fourth trial the application was delayed until the growth stage BBCH 43 and conducted at the rate of 411 g as/ha. At harvest, which was 63-72 days after application, the residues of parent ethephon were in the range of 0.034-0.14 mg/kg in grain and 0.35-1.1 mg/kg in straw.

CA 6.3.2 Wheat

Report:	KCA 6.3.2/06; [redacted]; [redacted] 2015; M-529493-01-1
Title:	Determination of the residues of ethephon in/on soft wheat after spray application of ethephon SL 480 in Germany, Belgium and the United Kingdom
Report No.:	13-2029
Document No.:	M-529493-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1997-07-22) OECD 509 Adopted 2009-09-07, OECD Guideline for the testing of Chemicals, Crop Field Trial US EPA OCSPP Guideline No. 860.1500
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Three residue trials were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. The trial sites were located in Germany, Belgium and the United Kingdom. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of 480 g as/ha after dilution in 200-300 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 23-38 days later, at the growth stage BBCH 75-77. In two trials, additional samples of green material were taken 7-8, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 61-75 days after application.

Details about the design and results of the trials are given in Table 6.3.2- 1.

The samples were frozen within 24 hours of sampling and stored deep frozen for a maximum of 20 months (601 days) until analysis. In the Belgian trial (13-2029-02) the temperature rose above -18°C during the shipment of the day 0, day 8 and day 14 green material field samples from the test site to the test facility. The average temperature during shipment was estimated at ca. -11°C. However, owing to the very short duration of the shipment (3 hours and 5 minutes) and since the samples remained frozen, this deviation is unlikely to have impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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

digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 3.1-7.5 mg/kg on day 0 and had decreased to 0.11-0.32 mg/kg at the growth stage BBCH 75. At harvest, which was 61-75 days after application, the residues of parent ethephon were in the range of 0.059-0.11 mg/kg in grain and 0.36-1.3 mg/kg in straw.

Table 6.3.2- 1: Residue trials performed in the northern part of the EU in 2013 to support the use of ethephon as an anti-lodging agent in wheat – overview of trial design and residue results [Study 13-2029]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ha	kg as/hL	Growth stage		ETP	HEPA	
M-529493-01-1 13-2029 13-2029-01	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 51	green material	3.3 0.46 0.21 0.17 0.17	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 23
								grain	0.059	0.027	75
								straw	0.36	0.050	75
M-529493-01-1 13-2029 13-2029-02	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 51	green material	3.1 0.16 0.11 0.11 0.11	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	0 8 14 21 29
								grain	0.059	0.029	61
								straw	0.66	< 0.05	61
M-529493-01-1 13-2029 13-2029-03	[redacted] 2013	SL	480	1	0.48	0.24	BBCH 51	green material	7.5 0.32	0.076 0.050	0 38
								grain	0.11	0.080	74
								straw	1.3	0.083	74

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Three residue trials were conducted in the northern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 61-75 days after application, the residues of parent ethephon were in the range of 0.059-0.11 mg/kg in grain and 0.36-1.3 mg/kg in straw.

Report:	KCA 6.3.2/07; [redacted]; [redacted]; 2015; M-532267-01-1
Title:	Determination of the residues of ethephon in/on winter wheat after spray application of ethephon SL 480 in Germany, the United Kingdom, northern France and the Netherlands
Report No.:	14-2018
Document No.:	M-532267-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market OECD Guideline for the Testing of Chemicals on Crop Field Trial (TG 509 published in September 2009) US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Five residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. The trial sites were located in Germany, the United Kingdom , France and the Netherlands. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the target rate of 480 g as/ha after dilution in 200-400 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 26-36 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7-8, 14-15 and 21-22 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 54-77 days after application.

Details about the design and results of the trials are given in Table 6.3.2- 2.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 10 months (296 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 4.9-7.2 mg/kg on day 0 and had decreased to 0.071-0.23 mg/kg at the growth stage BBCH 75. At harvest, which was 54-77 days after application, the residues of parent ethephon were in the range of 0.052-0.31 mg/kg in grain and 0.44-1.5 mg/kg in straw.

Table 6.3.2- 2: Residue trials performed in the northern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in wheat – overview of trial design and residue results [Study 14-2018]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage		ETP	HEPA	
M-532267-01-1 14-2018 14-2018-01	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 51	green material	7.9 0.28 0.29 0.23 0.22	0.085 < 0.05 < 0.05 < 0.05 < 0.05	0 8 14 21 29
								grain	0.083	0.031 (0.013)*	71
								straw	0.44	< 0.05	71
M-532267-01-1 14-2018 14-2018-02	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 51	green material	7.0 0.23	0.078 < 0.05	0 26
								grain	0.14	0.040	68
								straw	1.2	0.15 (0.23)*	68
M-532267-01-1 14-2018 14-2018-03	[redacted] 2014	SL	480	1	0.48	0.24	BBCH 51	green material	7.0 0.39 0.27 0.17 0.12	0.073 < 0.05 < 0.05 < 0.05 < 0.05	0 7 15 22 36
								grain	0.23	0.089 (0.043)*	64
								straw	1.2	0.055	64
M-532267-01-1 14-2018 14-2018-04	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 51	green material	7.2 0.071	0.087 < 0.05	0 35
								grain	0.052	0.019	77
								straw	0.57	< 0.05	77
M-532267-01-1 14-2018 14-2018-05	[redacted] 2014	SL	480	1	0.48	0.12	BBCH 51	green material	5.9 0.23	0.062 < 0.05	0 32
								grain	0.31	0.046	54
								straw	1.5	< 0.05	54

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Five residue trials were conducted in the northern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar

application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 51. At harvest, which was 54-77 days after application, the residues of parent ethephon were in the range of 0.052-0.31 mg/kg in grain and 0.44-1.5 mg/kg in straw.

Report:	KCA 6.3.2/08; [redacted]; [redacted]; 2015; M-529488-01-1
Title:	Determination of the residues of ethephon in/on soft wheat after spray application of ethephon SL 480 in southern France, Spain and Italy
Report No.:	13-2030
Document No.:	M-529488-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1997-07-22) OECD 509 Adopted 2009-09-07 OECD Guideline for the testing of Chemicals, Crop Field Trial US EPA OCSPP Guideline No. 860.1500
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. The trial sites were located in France, Spain and Italy. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of about 480 g as/ha after dilution in 300-350 L/ha of water. In one trial, however, the application was conducted at the slightly overdosed rate of 515 g as/ha. Samples of green material were taken on day 0 (shortly after application) and 24-45 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 62-80 days after application.

Details about the design and results of the trials are given in Table 6.3.2- 3.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 24 months (713 days) until analysis.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 2 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2013. The average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 5.6-17 mg/kg on day 0 and had decreased to 0.05-0.21 mg/kg at the growth stage BBCH 75. At harvest, which was 62-80 days after application, the residues of parent ethephon were in the range of 0.10-0.13 mg/kg in grain and 0.30-1.7 mg/kg in straw.

Table 6.3.2- 3: Residue trials performed in the southern part of the EU in 2013 to support the use of ethephon as an anti-lodging agent in wheat - overview of trial design and residue results [Study 13-2030]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage		ETP	HEPA	
M-529488-01-1 13-2030 132030-01	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 39	green material	5.7 0.50 0.31 0.24 0.16	0.27 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 45
								grain	0.049	0.037 (0.017)*	80
								straw	0.86	0.051	80
M-529488-01-1 13-2030 132030-02	[redacted] 2013	SL	480	1	0.52	0.16	BBCH 39	green material	17 0.21	0.24 < 0.05	0 43
								grain	0.057	0.029	64
								straw	0.84	< 0.05	64
M-529488-01-1 13-2030 132030-03	[redacted] 2013	SL	480	1	0.48	0.16	BBCH 39	green material	6.9 0.48 0.17 0.19 0.16	< 0.05 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 24
								grain	0.13	0.044	63
								straw	1.7	0.12	63
M-529488-01-1 13-2030 132030-04	[redacted] 2013	SL	480	1	0.48	0.14	BBCH 39	green material	5.6 0.050	0.11 < 0.05	0 25
								grain	0.010	0.014	62
								straw	0.30	0.058	62

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2013 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar

application at the rate of 480-515 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 62-80 days after application, the residues of parent ethephon were in the range of 0.10-0.13 mg/kg in grain and 0.30-1.7 mg/kg in straw.

Report:	KCA 6.3.2/09; [redacted]; [redacted]; 2015; M-532272-01-1
Title:	Determination of the residues of ethephon in/on winter wheat after spray application of ethephon SL 480 in southern France, Spain, Italy and Portugal
Report No.:	14-2019
Document No.:	M-532272-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market OECD Guideline for the Testing of Chemicals on Crop Field Trial (TG 509 published in September 2009) US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

Materials and methods

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. The trial sites were located in France, Spain, Italy and Portugal. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 39. The treatment was conducted at the target rate of 480 g as/ha after dilution in 300-400 L/ha of water. Samples of green material were taken on day 0 (shortly after application) and 30-60 days later, at the growth stage BBCH 75. In two trials, additional samples of green material were taken 7, 14 and 21 days after application. In all trials, samples of grain and straw were taken at maturity (BBCH 89), 58-110 days after application.

Details about the design and results of the trials are given in Table 6.3.2- 4.

The samples were frozen within 24 hours of sampling and stored deep frozen for less than 13 months (384 days) until analysis. In the French trial (14-2019-01) the temperature rose above -18°C during the shipment of the day 0, day 7, day 14 and day 21 green material field samples from the test site to the test facility. The average temperature during shipment was estimated at ca. -16.7°C. However, owing to the relatively short duration of the shipment (1 day and 6 hours) and since the samples remained frozen, this deviation is unlikely to have significantly impacted the study results.

All the samples were analysed for the residues of parent ethephon according to the method 01429. 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 digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.05 mg/kg in/on cereal green material and straw and 0.01 mg/kg in/on cereal grain.

Findings

Table 6.3.1- 4 provides an overview of the procedural recoveries determined during the analysis of the barley and wheat samples from all the ethephon residue studies conducted in Europe in 2014. The

average recoveries and relative standard deviations per matrix (and fortification level) were within guideline requirements and this demonstrates the accuracy of the residue determination.

The residues of parent ethephon in green material were in the range of 6.4-16 mg/kg on day 0 and had decreased to < 0.05-0.26 mg/kg at the growth stage BBCH 75. At harvest, which was 58-110 days after application, the residues of parent ethephon were in the range of 0.011-0.10 mg/kg in grain and 0.21-1.2 mg/kg in straw.

Table 6.3.2- 4: Residue trials performed in the southern part of the EU in 2014 to support the use of ethephon as an anti-lodging agent in wheat – overview of trial design and residue results [Study 14-2019]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues (mg/kg)		DALT (days)
		Type	Content g/L	No	kg as/ha	kg as/hL	Growth stage		ETP	HEPA	
M-532272-01-1 14-2019 14-2019-01	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 39	green material	7.1 0.27 0.16 0.12 < 0.05	0.13 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 41
								grain	0.025	0.019 (0.015)*	77
								straw	0.29	0.079	77
M-532272-01-1 14-2019 14-2019-02	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 39	green material	6.4 < 0.05	0.087 < 0.05	0 39
								grain	0.011	0.019 (0.023)*	72
								straw	0.21	0.092 (0.12)*	72
M-532272-01-1 14-2019 14-2019-03	[redacted] 2014	SL	480	1	0.48	0.12	BBCH 39	green material	10 0.82 0.30 0.30 0.26	0.12 < 0.05 < 0.05 < 0.05 < 0.05	0 7 14 21 30
								grain	0.10	0.042	58
								straw	1.2	< 0.05	58
M-532272-01-1 14-2019 14-2019-04	[redacted] 2014	SL	480	1	0.48	0.16	BBCH 39	green material	16 0.075	0.21 < 0.05	0 60
								grain	0.043	0.031 (0.029)*	110
								straw	0.44	0.084 (0.061)*	110

DALT : days after last treatment
ETP : ethephon; HEPA : 2-hydroxy-ethyl-phosphonic acid.
* If ≥ LOQ, the residues found in the corresponding control sample are shown in brackets.
The residues of parent ethephon are expressed as ethephon and the residues of HEPA as HEPA. HEPA is not part of the proposed residue definitions for dietary risk assessment or MRL setting.

Conclusion

Four residue trials were conducted in the southern part of Europe during the 2014 growing season to support the use of ethephon as an anti-lodging agent in wheat. In each trial there was one foliar application at the rate of 480 g as/ha when the crop had reached the growth stage BBCH 39. At harvest, which was 58-110 days after application, the residues of parent ethephon were in the range of 0.011-0.10 mg/kg in grain and 0.21-1.2 mg/kg in straw.

CA 6.4 Feeding studies

The maximum and mean dietary exposures of livestock to ethephon residues were estimated according to the feed consumption data and principles outlined in the OECD Guidance Document on Residues in Livestock [ENV/JM/MONO(2013)8]. The feed commodities and residue levels taken into account are listed in Table 6.4- 1. The estimated maximum and mean dietary exposures are shown in Table 6.4- 2 and Table 6.4- 3, respectively. Since the exposure estimates for both cattle and poultry exceed the trigger of 0.004 mg/kg bw/day, livestock metabolism and livestock feeding studies to investigate the nature and magnitude of ethephon-derived residues in food of animal origin are needed.

Table 6.4- 1: Feed commodities and residue levels considered to estimate the dietary exposure of livestock

Crop and commodity	Residue level used for maximum / mean dietary burden calculation (mg/kg)	Comment
Barley straw	3.6 / 0.71	HR and STMR based on the dataset for the northern part of the EU. Refer to CA 6.7.2.
Wheat straw	1.7 / 0.93	HR and STMR based on the dataset for the southern and northern part of the EU, respectively. Refer to CA 6.7.2.
Barley grain	0.15	STMR based on the dataset for the northern part of the EU. Refer to CA 6.7.2.
Wheat grain	0.10	STMR based on the dataset for the northern part of the EU. Refer to CA 6.7.2.
Brewer's grain (dried)	0.009	STMR from the northern part of the EU (0.15 mg/kg) x median processing factor for brewers grain (0.06).
Distiller's grain (dried)	-	No processing data for distiller's grain are available but this does not impact the outcome of the calculation since in the group of by-product commodities only one commodity is selected for calculation and "wheat milled by-products" is expected to provide the worst case both in terms of residue levels and in terms of the amounts fed to livestock.
Wheat gluten meal	0.01	STMR from the northern part of the EU (0.10 mg/kg) x median processing factor for wheat gluten meal (0.1).
Wheat milled by-products	0.32	STMR from the northern part of the EU (0.10 mg/kg) x mean processing factor for shorts (3.2). Shorts were chosen to represent "wheat milled by-products" since they represent the worst case in terms of processing

		factor compared to bran, germs or middlings.

Table 6.4- 2: Maximum dietary exposure of livestock to parent ethephon residues in Europe

Livestock category	Maximum dietary exposure		Maximum contributing commodity	Trigger exceeded (Y/N)
	(mg/kg bw/day)	(mg/kg DM)		
Cattle - Beef	0.033	1.39	Barley straw	Y
Cattle - Dairy	0.053	1.39	Barley straw	Y
Sheep - ram/ewe	0.086	2.57	Barley straw	Y
Sheep - lamb	0.109	2.57	Barley straw	Y
Swine - breeding	0.006	0.267	Wheat milled by-products	Y
Swine - finishing	0.008	0.267	Wheat milled by-products	Y
Poultry - broiler	0.014	0.192	Wheat milled by-products	Y
Poultry - layer	0.028	0.403	Barley straw	Y
Poultry - turkey	0.011	0.158	Wheat milled by-products	Y

Table 6.4- 3: Median dietary exposure of livestock to parent ethephon residues in Europe

Livestock category	Median dietary exposure		Maximum contributing commodity	Trigger exceeded (Y/N)
	(mg/kg bw/day)	(mg/kg DM)		
Cattle - Beef	0.010	0.417	Barley straw	Y
Cattle - Dairy	0.016	0.417	Barley straw	Y
Sheep - ram/ewe	0.021	0.624	Barley straw	Y
Sheep - lamb	0.027	0.624	Barley straw	Y
Swine - breeding	0.006	0.267	Wheat milled by-products	Y
Swine - finishing	0.008	0.267	Wheat milled by-products	Y
Poultry - broiler	0.014	0.192	Wheat milled by-products	Y
Poultry - layer	0.020	0.298	Wheat straw	Y
Poultry - turkey	0.011	0.158	Wheat milled by-products	Y

CA 6.4.1 Poultry

A poultry feeding study with parent ethephon was submitted in the Annex II dossier of 2002. The study included three dose groups (1X, 3X and 10X) with a 1X level of 2.3 mg/kg DM, which corresponds to 5.7 and 12 times the maximum estimated exposure in the diet of layer and broiler poultry, respectively. The animals (10 per dose group, distributed in 3 subgroups of 3-4 individuals) were dosed for 28 consecutive days. An overview of the study results is given in Table 6.4.1- 1. The active substance was found to be only minimally transferred to tissues and eggs. The residues in eggs were especially low with a maximum of 0.0036 mg/kg in the eggs of the 10X dose group. At the 1X dose rate the highest residues of ethephon were < 0.010 mg/kg in muscle, 0.014 mg/kg in fat and skin and 0.033 mg/kg in liver.

The potential residues of parent ethephon in poultry tissues and eggs may be estimated taking into account the potential residues in the feed of poultry and the transfer factors of the poultry feeding study. As shown in Table 6.4.1- 1 the anticipated maximum residues of parent ethephon in poultry

tissues and eggs are extremely low (< 0.01 mg/kg). Therefore, based on the representative uses it would be justified to set the MRL of ethephon at 0.01 mg/kg (LOQ) in poultry muscle, fat, liver and eggs.

Table 6.4.1- 1: Overview of hen feeding study results and estimated residues in poultry tissues and eggs

Commodity	Results of hen feeding study				Estimates based on dietary exposure of poultry for representative uses *		
	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest residue (mg/kg)	MRL proposal (mg/kg)
Muscle	2.3	2	< 0.010	< 0.010	0.0013	0.0018	0.01
	6.9	3	0.012	0.015			
	23.0	3	0.037	0.060			
Skin with fat	2.3	2	0.013	0.014	0.0017	0.0025	0.01
	6.9	3	0.024	0.032			
	23.0	3	0.093	0.117			
Liver	2.3	2	0.031	0.033	0.0040	0.0058	0.01
	6.9	3	0.062	0.068			
	23.0	3	0.227	0.289			
Eggs	2.3	3	0.002	0.002	0.0003	0.0004	0.01
	6.9	3	< 0.002	< 0.002			
	23.0	3	0.003	0.004			

* The median and highest residues in poultry tissues and eggs were estimated based on the maximum transfer factors of the hen feeding study for the mean and maximum residues, respectively. The maximum transfer factors were always found at the 1X dose level (2.3 mg/kg DM).
The maximum and median dietary exposures used for the calculation were 0.403 mg/kg DM and 0.298 mg/kg DM, respectively.

CA 6.4.2 Ruminants

A cow feeding study with parent ethephon was submitted in the Annex II dossier of 2002. The study included three dose groups (1X, 3X and 10X) with a 1X level of 43 mg/kg DM, which corresponds to 31 times the maximum estimated exposure in the diet of dairy cattle. The animals (3 per dose group) were dosed for 28 consecutive days. An overview of the study results is given in Table 6.4.2- 1.
Ethephon was only slightly transferred to milk and edible tissues. At the 1X dose level, the highest residues of ethephon were 0.007 mg/kg in milk, < 0.01 mg/kg in fat, 0.016 mg/kg in muscle, 0.095 mg/kg in liver and 0.64 mg/kg in kidney.
The potential residues of parent ethephon in cattle tissues and milk may be estimated taking into account the potential residues in the feed of beef and dairy cattle and the transfer factors of the cow feeding study. As shown in Table 6.4.2- 1, the residues of parent ethephon may reach 0.038 mg/kg in cattle kidney and are anticipated to remain < 0.01 mg/kg in cattle muscle, fat, liver and milk.
Therefore, based on the representative uses it would be justified to set the MRL of ethephon at 0.04 mg/kg in cattle kidney and 0.01 mg/kg (LOQ) in cattle muscle, fat, liver and milk.
The results of cow feeding study may also be used to estimate the potential residues of ethephon in sheep tissues and milk. The calculation details are shown in Table 6.4.2- 2. Using this approach and based on the representative uses, it would be justified to set the MRL of ethephon at 0.02 mg/kg in sheep liver, 0.07 mg/kg in sheep kidney and 0.01 mg/kg (LOQ) in sheep muscle, fat and milk.

Table 6.4.2- 1: Overview of cow feeding study results and estimated residues in cattle tissues and milk

Commodity	Results of cow feeding study				Estimates based on dietary exposure of cows for representative uses*		
	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest residue (mg/kg)	MRL proposal (mg/kg)
Muscle	43	3	0.013	0.016	0.0002	0.0007	0.01
	129	3	0.051	0.061			
	430	3	0.117	0.170			
Fat	43	3	< 0.010	< 0.010	0.0001	0.0007	0.01
	129	3	0.041	0.069			
	430	3	0.065	0.127			
Liver	43	3	0.082	0.095	0.0017	0.0070	0.01
	129	3	0.511	0.646			
	430	3	0.994	1.503			
Kidney	43	3	0.486	0.638	0.0103	0.0378	0.04
	129	3	3.177	3.509			
	430	3	7.846	10.918			
Milk	43	3	0.007	0.007	0.0005	0.0002	0.01
	129	3	0.16	0.019			
	430	3	0.032	0.033			

* The median and highest residues in cattle tissues and milk were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found at the 3X dose level (129 mg/kg DM), except for the highest residues in milk, for which the maximum transfer factor was obtained at the 1X dose level (43 mg/kg DM). Especially for liver and kidney, the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered suitable to estimate the residues at dose levels far below the 1X level of the study.
The maximum and median dietary exposures used for the calculation were 1.391 mg/kg DM and 0.417 mg/kg DM, respectively.

Table 6.4.2- 2: Overview of cow feeding study results and estimated residues in sheep tissues and milk

Commodity	Results of cow feeding study				Estimates based on dietary exposure of sheep for representative uses*		
	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest residue (mg/kg)	MRL proposal (mg/kg)
Muscle	43	3	0.013	0.016	0.0002	0.0012	0.01
	129	3	0.051	0.061			
	430	3	0.117	0.170			
Fat	43	3	< 0.010	< 0.010	0.0002	0.0014	0.01
	129	3	0.041	0.069			
	430	3	0.065	0.127			
Liver	43	3	0.082	0.095	0.0025	0.0129	0.02
	129	3	0.511	0.646			
	430	3	0.994	1.503			
Kidney	43	3	0.486	0.638	0.0154	0.0700	0.07
	129	3	3.177	3.509			
	430	3	7.846	10.918			
Milk	43	3	0.007	0.007	0.0008	0.0004	0.01
	129	3	0.16	0.019			
	430	3	0.032	0.033			

* The median and highest residues in sheep tissues and milk were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found at the 3X dose level (129 mg/kg DM), except for the highest residues in milk, for which the maximum transfer factor was obtained at the 1X dose level (43 mg/kg DM). Especially for liver and kidney, the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered suitable to estimate the residues at dose levels far below the 1X level of the study.
The maximum and median dietary exposures used for the calculation were 2.572 mg/kg DM and 0.624 mg/kg DM, respectively.

CA 6.4.3 Pigs

The potential residues of parent ethephon in pig tissues may be estimated taking into account the potential residues in the feed of breeding and finishing swine and the transfer factors of the cow feeding study.
Based on the outcome of the calculation (Table 6.4.3- 1) and considering the herein supported representative uses it would be justified to set the MRL of ethephon at 0.01 mg/kg (LOQ) in pig muscle, fat, liver and kidney.

Table 6.4.3- 1: Overview of cow feeding study results and estimated residues in pig tissues

Commodity	Results of cow feeding study				Estimates based on dietary exposure of cows for representative uses*		
	Dose level (mg/kg DM)	n	Mean residue (mg/kg)	Max residue (mg/kg)	Median residue (mg/kg)	Highest residue (mg/kg)	MRL proposal (mg/kg)
Muscle	43	3	0.013	0.016	0.0001	0.0001	0.01
	129	3	0.051	0.061			
	430	3	0.117	0.170			
Fat	43	3	< 0.010	< 0.010	0.0001	0.0001	0.01
	129	3	0.041	0.069			
	430	3	0.065	0.127			
Liver	43	3	0.082	0.095	0.0011	0.0013	0.01
	129	3	0.511	0.646			
	430	3	0.994	1.503			
Kidney	43	3	0.486	0.638	0.0066	0.0073	0.01
	129	3	3.177	3.509			
	430	3	7.846	10.918			

* The median and highest residues in pig tissues were estimated based on the maximum transfer factors of the cow feeding study for the mean and maximum residues, respectively. The maximum transfer factors were found at the 3X dose level (129 mg/kg DM). Especially for liver and kidney, the linear correlation lines established based on the residues found at the 1X, 3X and 10X levels had a non-negligible ordinate at the origin and, therefore, were not considered suitable to estimate the residues at dose levels far below the 1X level of the study.
The maximum and median dietary exposures used for the calculation were both 0.267 mg/kg DM.

CA 6.4.4 Fish

No suitable test method for fish feeding studies is listed in Commission Communication 2013/C 95/01 about the implementation of Regulation (EU) No 283/2013. Therefore, this point does not need to be addressed.
However, according to the working document SANCO/11187/2013 rev. 3 on the nature of pesticide residues in fish, it seems that in future the nature and magnitude of residues in fish only need to be investigated for active substances that are fat soluble, i. e. substances with log Pow ≥ 3. Since ethephon is hydrophilic (log Pow = -1.89 at pH 7), it is expected that even when a suitable test method has been issued no fish feeding study will be required for ethephon.

CA 6.5 Effects of processing

CA 6.5.1 Nature of the residue

A model hydrolysis study with [U-^{14}C]-ethephon to investigate the nature of the ethephon-derived residues in processed commodities is included in the Annex II dossier of 2002 and was reviewed in the Draft Assessment Report issued by the Rapporteur Member State in 2004. Ethephon was shown to hydrolyze to ethylene as the main degradation product. The degradation rate differed significantly depending on the tested conditions. While under conditions representative of pasteurization (pH 4, 90°C) about 10% of the active substance was degraded to ethylene, more than 75% was degraded to ethylene under conditions representative of brewing, baking, boiling, or sterilization (pH 5, 100°C; or

pH 6, 120°C). The thus formed ethylene was entirely released into the atmosphere. Minor degradation routes resulted in the formation of HEPA and an unknown product, which totalled less than 10% of the initial amount of ethephon.
Based on these results the residue definition in the processed commodities was considered to be parent ethephon, like in the raw agricultural commodities (EFSA Reasoned opinion on the review of the existing MRLs for ethephon, EFSA Journal 2009;7(10):1347).

CA 6.5.2 Distribution of the residue in peel and pulp

Studies to investigate the distribution of residues in peel and pulp are not relevant to cereals. Therefore, no data on the distribution of residues between peel and pulp need to be submitted for the herein supported representative uses.

CA 6.5.3 Magnitude of residues in processed commodities

Information about the residues of ethephon in processed cereal commodities was already provided in the Annex II dossier of 2002. However, in the then submitted studies the samples of grain and grain processed commodities were extracted with methanol, which is not in line with the extraction procedure of the wheat metabolism study. In order to comply with new data requirements [Regulation (EU) No 283/2013) and new guidelines [OECD Guidance document on pesticide residue analytical methods, ENV/JM/MONO(2007)17] it was decided to conduct new processing studies, in which the samples were extracted in the same way as in the wheat metabolism study (i.e. first by blending with methanol and then by digestion with hydrochloric acid).

- Processing of wheat

Report: KCA 6.5.3/13; [redacted]; 2015; M-533330-02-1
Title: Determination of the residues of ethephon in/on wheat, soft and the processed fractions (semolina; bran; middlings; semolina bran; shorts; white flour; whole meal; wholemeal bread; wheat germ; starch A; gluten; starch B and gluten feed meal) after spraying of ethephon SL 480 in the field in Germany
Report No.: 13-3406
Document No: M-533330-02-1
Guideline(s): Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC,
EC Guidance working document 7029/VI/95 rev.5 (1997-07-22),
OECD 509 Adopted 2009-09-07, OECD Guideline for the Testing of Chemicals, Crop Field Trial
OECD 508 Adopted 2008-10-3, OECD Guideline for the Testing of Chemicals, Magnitude of Pesticide Residues in Processed Commodities
US EPA OCSPP Guideline No. 860.1500
Guideline deviation(s): none
GLP/GEP: **yes**

Materials and methods

A field trial was conducted in Germany during the 2013 growing season in order to obtain ethephon-treated wheat grain for a processing study. The product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the rate of 720 g as/ha after dilution in 300 L/ha of water. Wheat grain was harvested at

maturity (BBCH 89), which was 75 days after application. The harvest was divided in three types of field samples :

- A sample of ≥ 1 kg that was deep frozen on the day of harvest and kept at ≤ -18°C until analysis. The purpose of this sample was to determine the residues in the raw agricultural commodity on the day of harvest.
- A field sample of about 50 kg intended for processing, which was kept at ambient temperature until the beginning of processing.
- Two field samples of ≥ 1 kg that were stored under the same conditions as the samples for processing and deep frozen at the beginning of processing. The purpose of these samples was to determine the residues in the raw agricultural commodity at the beginning of processing.

Details about the design and results of the field trial are given in Table 6.5.3- 1.

Table 6.5.3- 1: Field trial conducted to generate wheat grain for processing – overview of trial design and residue results [Study 13-3406]

Report Study Trial	Location Country Year	Formulation		Application					Crop part	Residues of ethephon (mg/kg)	DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage				
M-533330-02-1 13-3406 13-3406-01	[redacted] 2013	SL	480	1	0.72	0.24	BBCH 51		grain	0.077*	75

DALT : days after last treatment
* Residue level measured in the sample frozen on the day of harvest.

The raw agricultural commodity for the processing phase was shipped to the processing site 2 days after harvest and stored at ambient temperature until the beginning of processing, which was 105 days after harvest. The 50 kg field sample was divided in four subsamples for the various processes to be investigated during the study :

- A subsample of ca. 10 kg for the preparation of semolina and white flour.
- A subsample of ca. 10 kg for the preparation of wholemeal flour and wholemeal bread.
- A subsample of ca. 20 kg for the preparation of wheat germs.
- A subsample of ca. 10 kg for the preparation of starch and gluten.

Each subsample was first cleaned to remove foreign matters and impurities. Thereafter the cleaned grain was conditioned by slightly increasing the moisture content from 14.8% to 15.2%.

Milling was performed by using a roller mill. In this type of device, grain is crushed by passing between pairs of rollers. As the grain material progresses through the machine the spacing between the rollers decreases, which yields milled commodities of decreasing particle size. At each step of the milling process, sifters allow separation of different types of milled commodities.

Semolina and semolina bran were produced at the very beginning of the milling process. By further milling and sieving, straight flour was obtained from semolina while coarse bran and fine bran (middlings) were obtained from semolina bran. The bran fractions were combined again and centrifuged to yield low-grade meal and shorts. White flour (type 550) was obtained by mixing straight flour and low-grade flour in appropriate amounts to reach a mineral content of 0.51-0.63%.

For wholemeal flour production, the combined coarse bran and fine bran fractions were ground to produce low-grade meal and fine shorts. The straight flour, low-grade flour and fine shorts were mixed to obtain wholemeal flour. Wholemeal bread (1.6 kg) was prepared with wholemeal flour (1.3 kg), yeast (52 g), salt (26 g) and water (0.91 L) which were mixed, kneaded, let stand for fermentation and baked at 210°C for 50 minutes.

For the preparation of wheat germ the grain was broken by passing successively between pairs of rollers with a decreasing spacing (0.5, 0.3 and 0.2 mm). The fraction with a particle size of 400-1000 µm was collected by sieving. Coarse bran was removed by gravity separation. The remaining fraction consisting of middlings and germs was further milled and sieved to obtain flour, bran and germs.

For the preparation of starch and gluten the straight flour (1 kg) was mixed with water (1.2 L). The thus obtained dough was centrifuged to separate process water, wet starch and gluten. The process was repeated twice with the starch fraction. The thus obtained starch was dried at 60°C to produce "starch A". The gluten fractions of the previous steps (which also contained some starch) were washed repeatedly and centrifuged with the process water in order to separate (purified) gluten, (remaining) starch and fibre. Starch was dried at 60°C to produce "starch B". Fibre was also dried at 60°C while gluten was dried by freeze drying. The dried commodities were milled. Gluten feed meal was obtained by mixing starch B, dried gluten and dried fibre.

Representative samples of the underlined processing fractions were taken for analysis and deep frozen at < -18°C within less than 24 hours of sampling.

Simplified flow charts of the various processes are shown in Figure 6.5.3- 1 (Preparation of semolina and white flour), Figure 6.5.3- 2 (Preparation of wholemeal flour and wholemeal bread), Figure 6.5.3-3 (Preparation of germs) and Figure 6.5.3-4 (Preparation of starch and gluten).

Figure 6.5.3- 1: Flow-chart for the processing of wheat grain in semolina and white flour

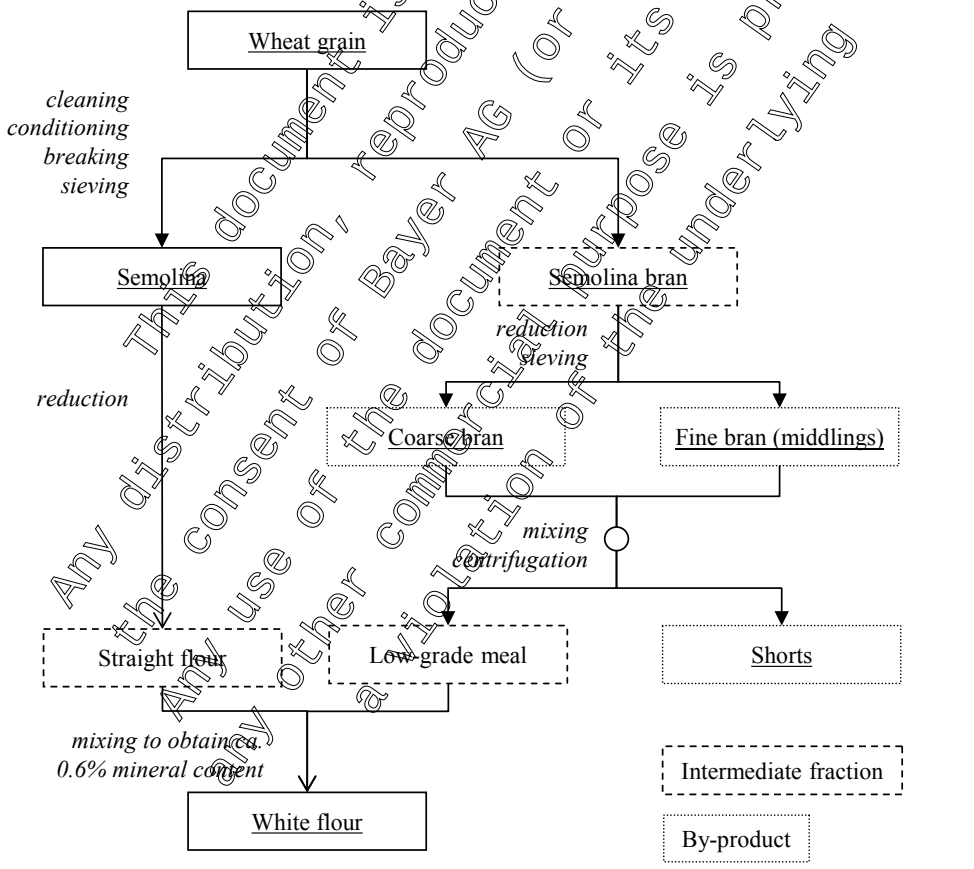


Figure 6.5.3- 2: Flow-chart for the processing of wheat grain in wholemeal flour and wholemeal bread

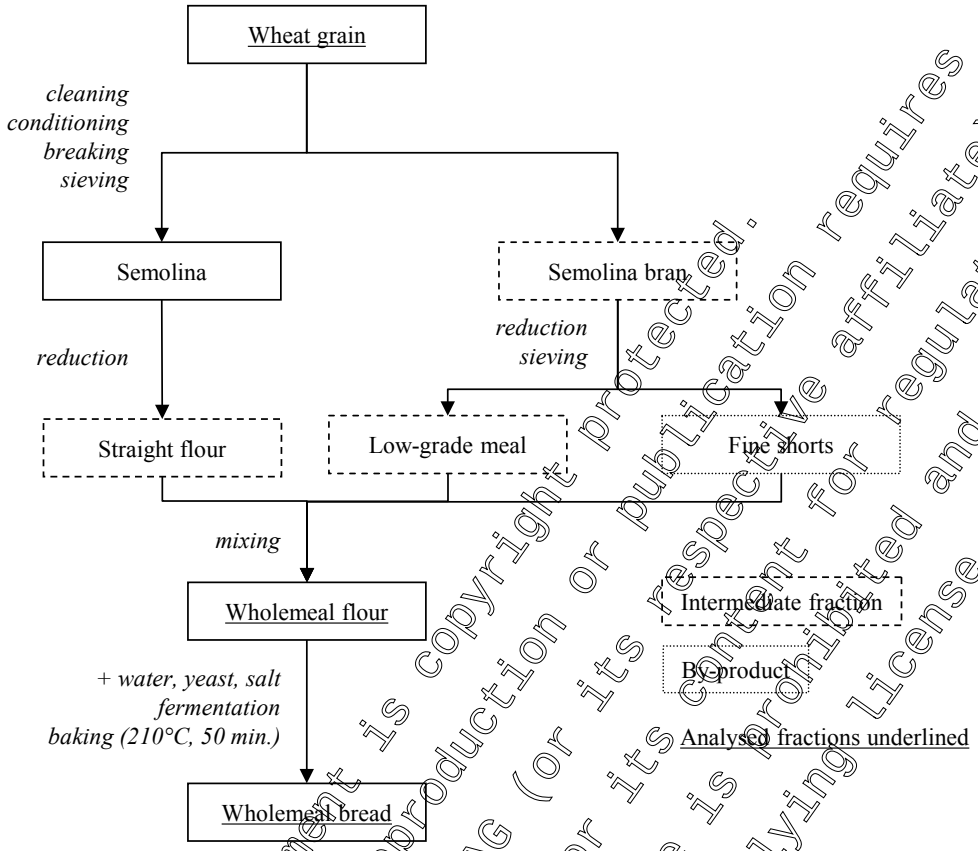


Figure 6.5.3- 3: Flow-chart for the processing of wheat grain in wheat germ

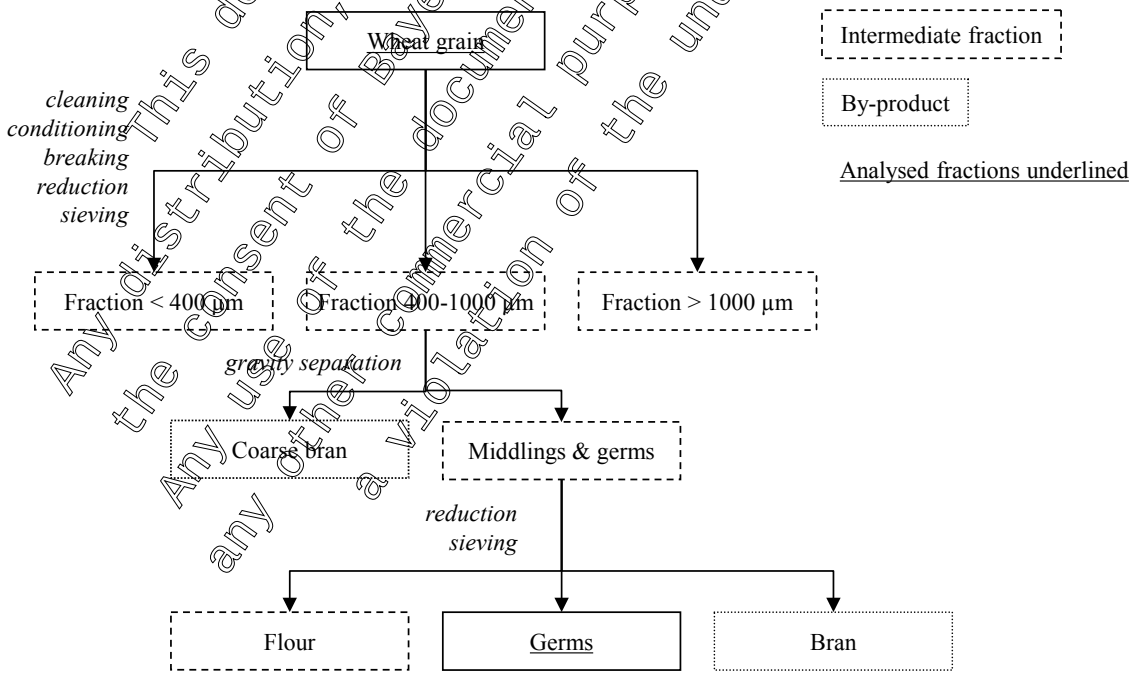
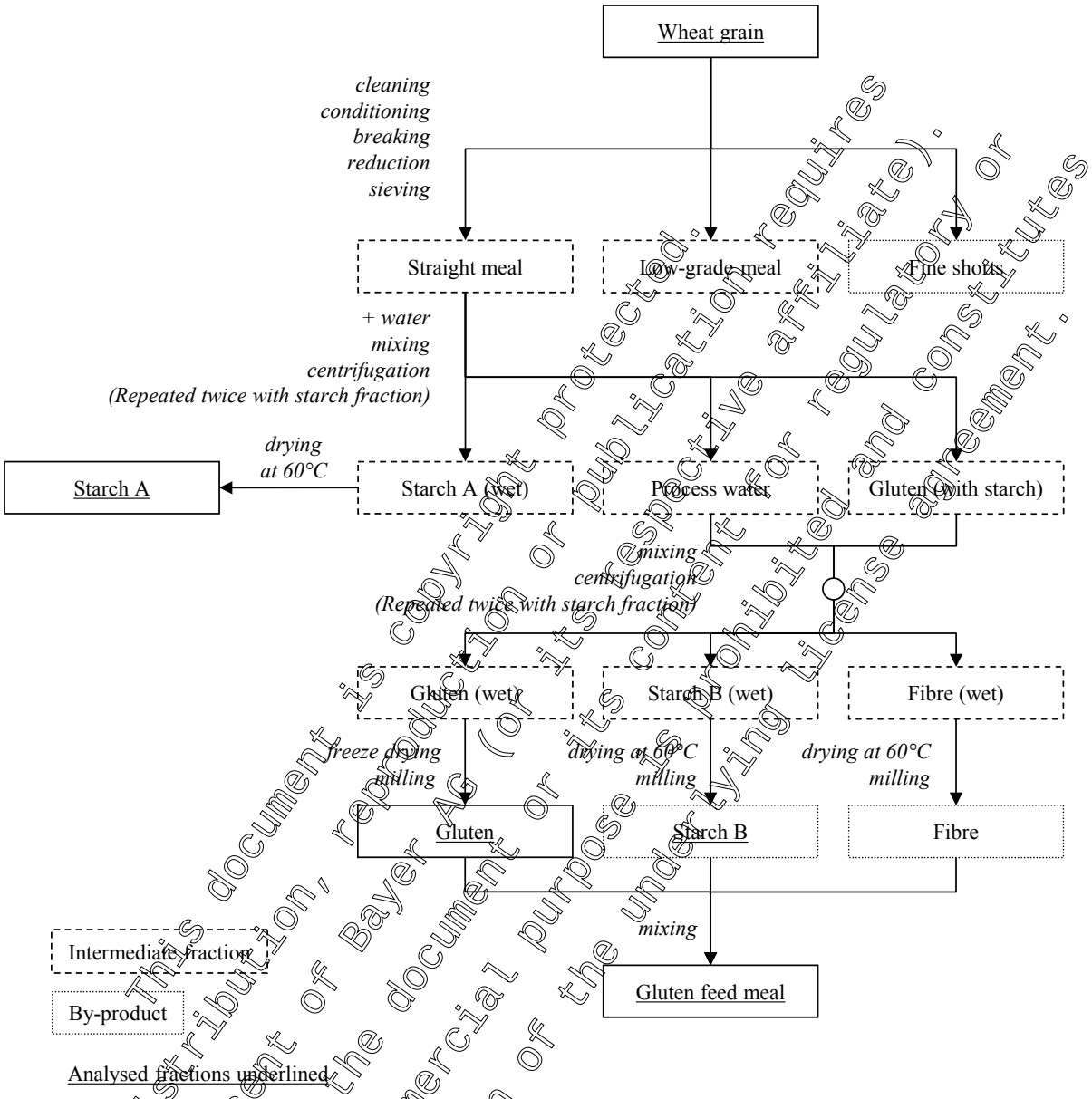


Figure 6.5.3- 4: Flow-chart for the processing of wheat grain in starch and gluten



The unprocessed wheat grain and the various processed wheat commodities were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain. In the context of the study 13-3406 limited validation sets (3 replicates at each 0.01 mg/kg and 0.1 mg/kg) were run to demonstrate the applicability of the method for the determination of ethephon in semolina, middlings, wholemeal bread, gluten and starch. These validation data were considered to also cover the residue determination in comparable processed commodities (bran, germs, shorts, white flour, wholemeal flour, gluten meal feed).

The unprocessed grain samples which were frozen immediately after sampling in the field were stored deep-frozen for a maximum of 667 days (less than 23 months) before analysis. The samples taken during processing (including the wheat grain samples taken just before the beginning of processing) were stored deep-frozen for a maximum of 574 days (less than 20 months) before analysis.

Findings

The method validation data and procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3- 2. Based on these results the limit of quantification of the method 01429 for the determination of parent ethephon residues in wheat processed commodities was established at 0.01 mg/kg.

Table 6.5.3- 2: Validation data and concurrent recoveries for the determination of parent ethephon residues in wheat grain and wheat processed commodities [Study 13-3406]

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-533330-02-1 (01429)	Wheat grain	0.01 1.0 overall	2 2 4	97, 98 89, 95 -	98 92 95	- - 4.3
M-533330-02-1 (01429)	Wheat semolina	0.01 0.10 1.0 overall	3 3 1 7	88, 90, 98 96, 97, 98 93 -	92 97 93 94	5.8 1.0 - 4.3
M-533330-02-1 (01429)	Wheat middlings	0.01 0.10 1.0 overall	3 3 1 7	95, 96, 100 95, 98, 103 95 -	97 99 95 97	2.7 4.1 - 3.2
M-533330-02-1 (01429)	Wholemeal wheat bread	0.01 0.10 overall	3 3 6	79, 83, 89 85, 92, 94 -	84 90 87	6.0 5.2 6.5
M-533330-02-1 (01429)	Wheat germ	0.01 0.10 overall	3 2 5	90, 97, 105 80, 88 -	97 84 92	7.7 - 10.3
M-533330-02-1 (01429)	Wheat gluten	0.01 0.10 overall	3 3 6	104, 107, 112 89, 101, 105 -	108 98 103	3.8 8.5 7.5
M-533330-02-1 (01429)	Wheat starch	0.01 0.10 overall	3 3 6	77, 89, 97 93, 95, 97 -	88 95 91	11.5 2.1 8.4

The fortification levels are expressed as ethephon.

The residues of parent ethephon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.3- 3. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain (semolina bran, bran, middlings, shorts and germs) while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. Comparison between the residue

levels in wholemeal and wholemeal bread indicates that about 66% of the ethephon residues degraded during baking.

Table 6.5.3- 3: Residue levels and transfer factors for parent ethephon in wheat processed commodities [Study 13-3406]

Processing type / Processed commodity	Trial 13-3406-01 (Germany)	
	Residues (mg/kg)	Processing factor
Raw agricultural commodity		
Wheat grain	0.070*	-
Preparation of semolina and white flour		
Semolina	0.036	0.52
Semolina bran	0.22	3.2
Coarse bran	0.26	3.7
Middlings	0.12	1.7
Shorts	0.30	4.3
White flour	0.013	0.19
Preparation of wholemeal and wholemeal bread		
Wholemeal flour	0.069	0.99
Wholemeal bread	0.019	0.27
Preparation of wheat germ		
Germs	0.17	2.4
Preparation of starch and gluten		
Starch A	< 0.01	< 0.14
Gluten	0.01	0.14
Starch B	< 0.01	< 0.14
Gluten feed meal	< 0.01	< 0.14

* Average of the residues measured in the two replicate samples frozen at the beginning of processing (0.064 mg/kg and 0.075 mg/kg)

Conclusion

A trial was performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. The processing factors were 3.7 for bran, 2.4 for germs, 0.52 for semolina, 0.19 for white flour, 0.99 for wholemeal flour and 0.27 for wholemeal bread. The data indicate that ethephon partially degrades during baking. The residues in starch and gluten were ≤ 0.01 mg/kg (LOQ) with processing factors ≤ 0.14.

Report:	KCA 6.5.3/14; [redacted]; [redacted]; 2015; M-535996-01-1
Title:	Determination of the residues of ethephon in/on winter wheat and the processed fractions (bran; gluten; gluten feed meal; grain, stored; middlings; semolina; semolina bran; shorts; starch A; starch B; wheat germ; white flour; whole meal and wholemeal bread) after spray application of ethephon SL 480 in Germany
Report No.:	14-3401
Document No.:	M-535996-01-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC EC Guidance working document 7029/VI/95 rev.5 (1997-07-22) OECD Guideline for the Testing of Chemicals, Crop Field Trial (TG 509 published September 2009) OECD 508, Adopted 2008-10-03, OECD Guideline for the Testing of Chemicals, Magnitude of Pesticide Residues in Processed Commodities US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial US EPA OCSPP Guideline No. 860.1520
Guideline deviation(s):	not specified
GLP/GEP:	**yes**

The wheat processing study 13-3406 (see above) was initially designed to include two trials. However, one of these trials had to be cancelled due to crop failure. Therefore, a second wheat processing study (14-3401) was initiated in 2014 to generate data from a second trial. Since the study 14-3401 was designed in the same way as the study 13-3406, the experimental approach is not described again in full detail and reference is largely made to the study 13-3406.

Materials and methods

A field trial was conducted in Germany during the 2014 growing season in order to obtain ethephon-treated wheat grain for a processing study. The product Ethephon SL 480 g/L was applied once as a broadcast foliar spray at the rate of 720 g as/ha after dilution in 300 L/ha of water. The treatment was intended to be conducted at the growth stage BBCH 51 but had to be conducted at the growth stage BBCH 58 due the late issuance of the study protocol. Wheat grain was harvested at maturity (BBCH 89), which was 66 days after application. The harvest was divided in three types of field samples :

- A sample of ≥ 1 kg that was deep frozen on the day of harvest. The purpose of this sample was to determine the residues in the raw agricultural commodity on the day of harvest.
- A field sample of about 50 kg intended for processing, which was kept at ambient temperature until the beginning of processing.
- Two field samples of ≥ 1 kg that were stored under the same conditions as the samples for processing and deep frozen at the beginning of processing. The purpose of these samples was to determine the residues in the raw agricultural commodity at the beginning of processing.

Details about the design and results of the field trial are given in Table 6.5.3- 4.

Table 6.5.3- 4: Field trial conducted to generate wheat grain for processing – overview of trial design and residue results [Study 14-3401]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues of ethephon (mg/kg)	DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage			
M-535996-01-1 14-3401 14-3401-01	[redacted] 2014	SL	480	1	0.72	0.24	BBCH 58	grain	0.30	66

DALT : days after last treatment
* Residue level measured in the sample frozen on the day of harvest.

The raw agricultural commodity for the processing phase was shipped to the processing site on the day following harvest and stored there at ambient temperature until the beginning of processing which was 30 days after harvest. The 50 kg field sample of wheat grain was divided in four smaller subsamples which were used for the four following processing types : preparation of semolina and white flour, preparation of wholemeal flour and wholemeal bread, preparation of germs, preparation of starch and gluten. Processing was conducted in the same way as in the study 13-3406. However, there was no need to condition the wheat grain after cleaning since its moisture content (15%) was already appropriate for milling. Details about the processing operations including simplified flowcharts may be found in the above summary for the study 13-3406. Representative samples of the main processing fractions were taken for analysis and deep frozen at ≤ -18°C within less than 24 hours of sampling.

The unprocessed wheat grain and the various processed wheat commodities were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain. In the context of the study 13-3406 (see above) the applicability of the method was also demonstrated for the determination of ethephon in semolina, middlings, wholemeal bread, gluten and starch with a limit of quantification of 0.01 mg/kg. These validation data were considered to also cover the residue determination in comparable processed commodities (bran, germs, shorts, white flour, wholemeal flour, gluten meal feed).

The unprocessed grain samples which were frozen immediately after sampling in the field were stored frozen for 374 days (less than 13 months) before analysis. The samples taken during processing (including the wheat grain samples taken just before the beginning of processing) were stored frozen for a maximum of 356 days (less than 12 months) before analysis. Due to a technical failure, the storage temperature of the laboratory samples exceeded -18°C for about 15 hours with a maximum temperature of -12°C. When the samples were transferred in a different freezer they appeared to be still frozen. However, a specific storage stability study (P642151808) was initiated to evaluate the impact of this incident (refer to Point CA 6.1). No significant degradation of ethephon was observed in cereal grain, starch and wholemeal bread after storage at ≥ -1°C for 24 hours. It may be concluded that the temperature deviation that occurred during the study 14-3401 had no negative impact on the study results.

Findings

The procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3- 5.

Table 6.5.3- 5: Validation data and concurrent recoveries for the determination of parent ethephon residues in wheat grain and wheat processed commodities [Study 14-3401]

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-535996-01-1 (01429)	Wheat grain	0.01	2	93, 94	94	-
		0.10	1	102	102	-
		5.0	2	92, 93	93	-
		overall	5	-	95	4.3
M-535996-01-1 (01429)	Wheat semolina	0.01	2	95, 100	98	-
		5.0	1	79	79	-
		overall	3	-	91	12.0
M-535996-01-1 (01429)	Wheat bran	0.01	1	99	99	-
		0.10	1	98	98	-
		overall	2	-	99	-
M-535996-01-1 (01429)	Wheat middlings	0.01	1	101	101	-
		1.0	1	96	96	-
		overall	2	-	99	-
M-535996-01-1 (01429)	Wholemeal wheat bread	0.01	1	92	92	-
		1.0	1	98	98	-
		overall	2	-	95	-
M-535996-01-1 (01429)	Wheat gluten	0.01	1	102	102	-
		1.0	1	86	86	-
		overall	2	-	94	-
M-535996-01-1 (01429)	Wheat starch	0.01	1	105	105	-
		1.0	1	94	94	-
		overall	2	-	100	-
M-535996-01-1 (01429)	Wheat gluten feed meal	0.01	1	108	108	-
		1.0	1	91	91	-
		overall	2	-	100	-

The fortification levels are expressed as ethephon.

The residues of parent ethephon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.3-6. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain (semolina bran, bran, middlings, shorts and germs) while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. Comparison between the residue levels in wholemeal and wholemeal bread indicates that about 59% of the ethephon residues degraded during baking.

Table 6.5.3- 6: Residue levels and transfer factors for parent ethephon in wheat processed commodities [Study 14-3401]

Processing type Processed commodity	Trial 14-3401-01 (Germany)	
	Residues (mg/kg)	Processing factor
Raw agricultural commodity		
Wheat grain	0.27*	
Preparation of semolina and white flour		
Semolina	0.18	0.68
Semolina bran	0.65	2.5
Coarse bran	0.67	2.5
Middlings	0.55	2.1
Shorts	0.53	2.0
White flour	0.066	0.25
Preparation of wholemeal and wholemeal bread		
Wholemeal flour	0.20	0.74
Wholemeal bread	0.064	0.24
Preparation of wheat germ		
Germs	0.41	1.6
Preparation of starch and gluten		
Starch A	< 0.01	< 0.04
Gluten	0.029	0.11
Starch B	0.012	0.05
Gluten feed meal	0.014	0.05

* Average of the residues measured in the two replicate samples frozen at the beginning of processing (0.26 mg/kg and 0.27 mg/kg)

Conclusion

A trial was performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A concentration of residues was observed in the processed commodities which correspond to the outer parts of the grain while in the commodities that correspond to the inner parts of the grain (semolina, white flour, gluten and starch) the residues were less than in whole grain. The processing factors were 2.5 for bran, 1.6 for germs, 0.68 for semolina, 0.25 for white flour, 0.74 for wholemeal flour and 0.24 for wholemeal bread. The data indicate that ethephon partially degrades during baking. The residues in starch and gluten were low with processing factors ≤ 0.05 for starch and a processing factor of 0.11 for gluten.

General conclusion on the processing of wheat

Two trials were performed to investigate the fate of parent ethephon residues during wheat grain milling, baking of bread and processing into starch and gluten. A comparison of the processing factors obtained during these trials is provided in Table 6.5.3- 7. The processing factors from the two trials were found to be comparable according to the criterion of the OECD guideline 508 on the magnitude

of the pesticide residues in processed commodities (difference of less than 50%), except for shorts (difference of 53%). Since shorts are not a major wheat processed commodity and since the difference between the two processing factors is only marginally above 50%, it is not considered necessary to conduct a further wheat processing trial. The residues were found to concentrate in the processed commodities which correspond to the outer parts of the grain (median processing factors of 3.1 for bran, 3.2 for shorts and 2.0 for germs) while in the commodities that correspond to the inner parts of the grain the residues were less than in whole grain (median processing factors of 0.60 for semolina, 0.22 for white flour, 0.87 for wholemeal flour and about 0.1 for gluten and starch).

Table 6.5.3- 7: Compilation of processing factors for ethephon in wheat processed commodities

Processing type Processed commodity	Processing factors			
	Trial 13-3406-01 (Germany)	Trial 14-3401-01 (Germany)	Difference *	Median
Preparation of semolina and white flour				
Semolina	0.52	0.68	24%	0.60
Semolina bran	3.2	2.5	22%	2.9
Coarse bran	3.7	2.5	32%	3.1
Middlings	1.7	2.1	19%	1.9
Shorts	4.3	2.0	53%	3.2
White flour	0.19	0.25	24%	0.22
Preparation of wholemeal and wholemeal bread				
Wholemeal flour	0.99	0.74	25%	0.87
Wholemeal bread	0.27	0.24	11%	0.26
Preparation of wheat germ				
Germs	2.4	1.6	33%	2.0
Preparation of starch and gluten				
Starch A	< 0.14	< 0.04	n. a.	< 0.09
Gluten	0.14	0.11	21%	0.13
Starch B	< 0.14	0.05	n. a.	< 0.10
Gluten feed meal	< 0.14	0.05	n. a.	< 0.10

* Calculated according to the formula provided in the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities : *[Pf (high value) - Pf (low value)]/Pf (high value)*.

n. a. : Not applicable; the difference between the two processing factors cannot be calculated since at least one of them is not known precisely.

- Processing of barley

Report:	KCA 6.5.3/15; [redacted]; 2016; M-535989-02-1
Title:	Amendment no. 1 to final report no.: 14-3400 - Determination of the residues of ethephon in/on spring barley and the processed fractions (beer; grain, stored; hops draff; malt sprouts; brewers yeast; brewers malt; brewers grain; pearl barley and pearl barley rub off) after spray application of ethephon SL 480 in Germany and the Netherlands
Report No.:	14-3400
Document No.:	M-535989-02-1
Guideline(s):	Regulation (EC) No 1107/2009 of the European Parliament and of the Council of 21 October 2009 concerning the placing of plant protection products on the market and repealing Council Directives 79/117/EEC and 91/414/EEC, EC Guidance working document 7029/VI/95 rev.5 (1997-07-22), OECD Guideline for the Testing of Chemicals, Crop Field Trial (TG 509 published September 2009) OECD 508, Adopted 2008-10-03, OECD Guideline for the Testing of Chemicals, Magnitude of Pesticide Residues in Processed Commodities US EPA OCSPP Guideline No. 860.1500 on Crop Field Trial US EPA OCSPP Guideline No. 860.1520
Guideline deviation(s):	see Appendix 8
GLP/GEP:	**yes**

Materials and methods

Two field trials were conducted in Germany and the Netherlands during the 2014 growing season in order to obtain ethephon-treated barley grain for a processing study. In each trial the product Ethephon SL 480 g/L was applied once as a broadcast foliar spray when the crop had reached the growth stage BBCH 51. The treatment was conducted at the rate of 720 g as/ha after dilution in 300 L/ha of water. Barley grain was harvested at maturity, which was 49 and 38 days after application in the two trials, respectively. In each trial, the harvest was divided in three types of field samples :

- A sample of ≥ 1 kg that was deep frozen on the day of harvest. The purpose of this sample was to determine the residues in the raw agricultural commodity on the day of harvest.
- Two field sample of about 25 kg for processing into beer and 5 kg for processing into pearl barley, which were kept at ambient temperature until the beginning of processing.
- Four field samples of ≥ 1 kg that were stored under the same conditions as the samples for processing and deep frozen at the beginning of processing (two samples per processing type). The purpose of these samples was to determine the residues in the raw agricultural commodity at the beginning of processing.

Details about the design and results of the field trial are given in Table 6.5.3- 8.

Table 6.5.3- 8: Field trials conducted to generate barley grain for processing – overview of trial design and residue results [Study 14-3400]

Report Study Trial	Location Country Year	Formulation		Application				Crop part	Residues of ethephon (mg/kg)	DALT (days)
		Type	Content g/L	No	kg as/ ha	kg as/ hL	Growth stage			
M-535989-02-1 14-3400 14-3400-01	[redacted] 2014	SL	480	1	0.72	0.24	BBCH 51	grain	0.19*	49
M-535989-02-1 14-3400 14-3400-02	[redacted] 2014	SL	480	1	0.72	0.24	BBCH 51	grain	2.3*	38

DALT : days after last treatment
* Residue level measured in the sample frozen on the day of harvest.

Note : In the trial 14-3400-02 the barley was sown at an unusually late date (25 April 2014). Because of that, the crop developed extremely quickly (38 days between application at BBCH 51 and mature harvest). This probably accounts for the higher residue levels found in this trial (up to 2.4 mg/kg of parent ethephon in grain). Therefore, the trial is not considered valid for MRL-setting. Under normal conditions the minimum time between application at BBCH 51 and mature harvest is expected to be about 50 days. The trial, however, is considered valid for the determination of the transfer of ethephon residues in processed barley commodities. According to the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities it is acceptable to shorten the PHI in order to ensure the presence of measurable residues in the raw agricultural commodity.

The raw agricultural commodity for the processing phase was shipped to the processing site 3-6 days after harvest and stored at ambient temperature until the beginning of processing, which was 19-35 days after harvest. The field samples of about 25 kg and 5 kg were used for processing into beer and pearl barley, respectively.

The field samples of barley grain were first cleaned in a winnowing machine to remove soil particles and other impurities.

For the preparation of beer, the cleaned barley grain was first steeped in water at 12-15°C in order to increase the moisture content of the grain to 40-45%. The steeping process consisted of wet steeping phases, during which the grain was soaked in water, and dry steeping phases, during which the soaked grain was ventilated. In total there were three wet steeping phases, which were separated by two dry steeping phases. Thereafter, in order to induce germination the steeped grain was kept for nearly 6 days at about 14°C under continuous stirring. The germination phase was stopped by heating the germinated grain stepwise, first at 45-55°C for 15-16 h, then at 60-70°C for 2 h and finally at 80-90°C for 5 h. By this process (known as kiln-drying) malt with a moisture content of 4.9-5.0% was obtained. In the next step, the germs were separated mechanically from the malt with a trimmer to produce malt sprouts and brewer's malt.

For brewing the brewer's malt was milled and mixed with water. The resulting mash was heated successively at 55°C, 62°C, 72°C and finally at 76°C. The whole mashing step lasted for about 2 h. The aqueous malt extract (wort) was then separated from the insoluble malt components (brewer's grain). The malt extract remaining on brewer's grain was washed with hot water and combined with the wort. After addition of hop pellets, the wort was boiled for 90 min. at normal pressure and cooled down to 18.5-18.8°C. The flocs (hop draff) where separated by producing a whirlpool which caused the sludge to deposit on the bottom of the vat. The fermentation process was induced by adding yeast and lasted for about 9 days. During this time the wort temperature was maintained at about 9°C. At

the end of the fermentation process the yeast deposit at the bottom of the tank was sampled as brewer's yeast. For maturation the young beer was first kept at room temperature (20°C) for two days before being stored under pressure at 2°C for 4 weeks. After maturation the final product (beer ready for consumption) was obtained by filtration.

For the preparation of pearl barley, the cleaned barley grain was hulled using a decorticator until an abrasion level of 33% was reached. This resulted in pearl barley and barley rub off.

Representative samples of the underlined processing fractions were taken for analysis and deep frozen at < -18°C within less than 24 hours of sampling.

Simplified flow charts of the two processes are shown in Figure 6.5.3- 5 (Preparation of beer) and Figure 6.5.3- 6 (Preparation of pearl barley).

Figure 6.5.3- 5: Flow-chart for the processing of barley grain in beer

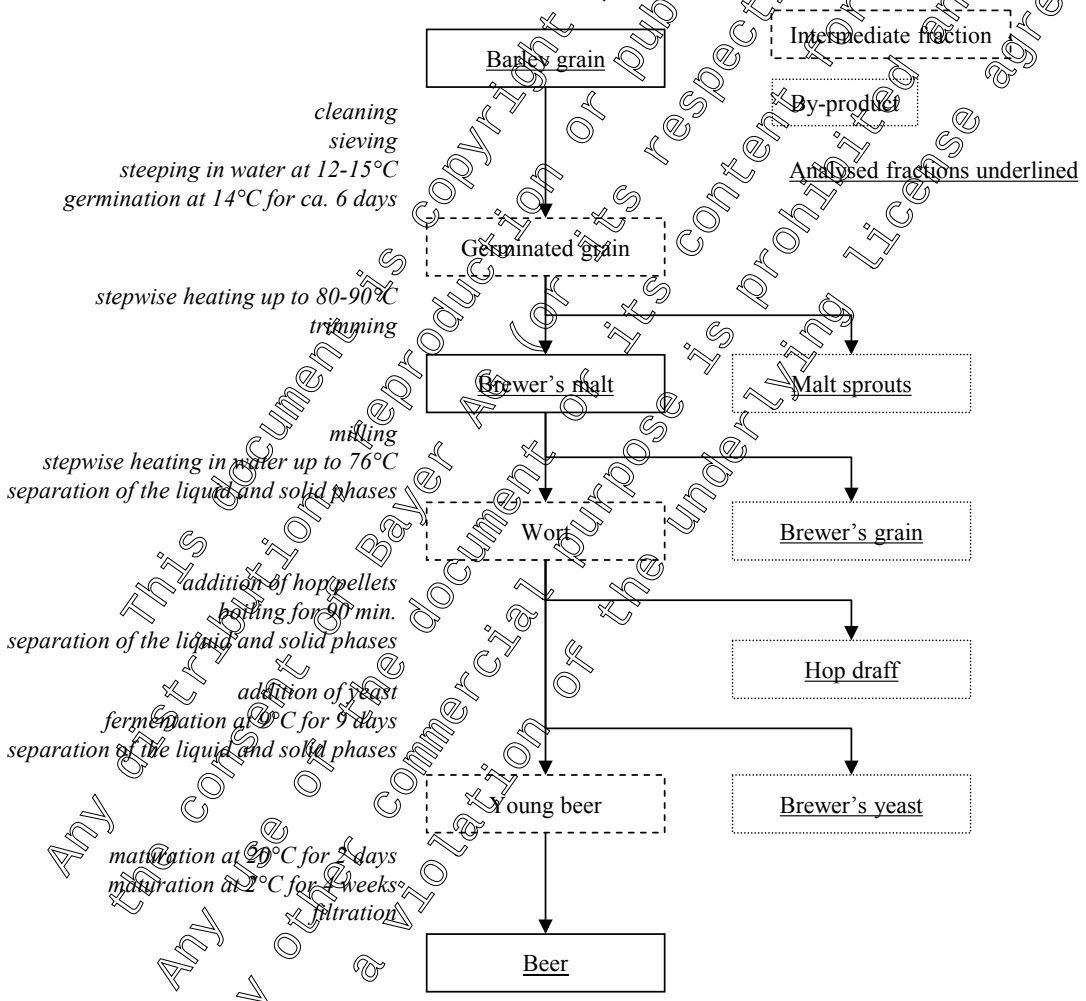
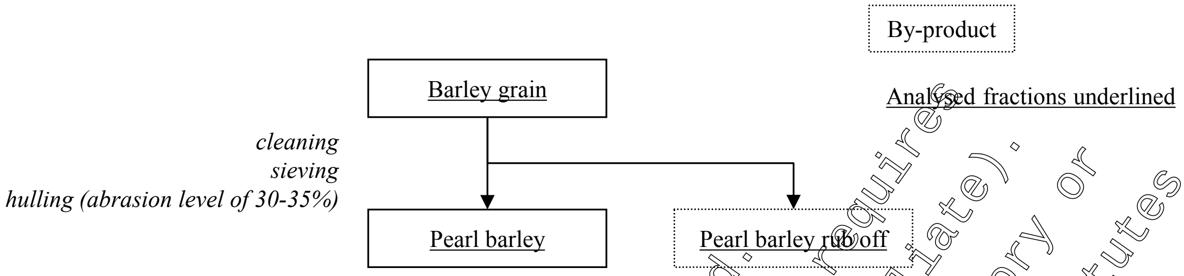


Figure 6.5.3- 6: Flow-chart for the processing of barley grain in pearl barley



The unprocessed barley grain and the various processed barley commodities were analysed for the residues of parent ethephon according to the method 01429. The residues were extracted from solid samples by blending three times with methanol followed by digestion with a mixture of hydrochloric acid (32%) / water (1/7, v/v) at 50°C overnight. For the analysis of beer the residues were extracted by blending once with methanol. After addition of an isotopically labelled internal standard the extracts were analysed by LC-MS/MS using a cation exchange column (e.g. Luna SCX 5 µm, 150 x 2 mm) in the HILIC (Hydrophilic Interaction Liquid Chromatography) mode. During method validation the limit of quantification (LOQ) for ethephon was established at 0.01 mg/kg in/on cereal grain. In the context of the study 14-3400 limited validation sets (3 replicates at each 0.01 mg/kg and 0.1 mg/kg) were run to demonstrate the applicability of the method for the determination of ethephon in malt sprouts, hop draff and pearl barley. These validation data were considered to also cover the residue determination in comparable processed commodities (brewer's grain, brewer's malt, brewer's yeast and pearl barley rub off). Furthermore a complete validation set (5 replicates at each 0.01 mg/kg and 0.1 mg/kg) was run to demonstrate the applicability of the method for the determination of ethephon in beer.

The unprocessed grain samples which were frozen immediately after sampling in the field were stored deep-frozen for a maximum of 356 days (less than 12 months) before analysis. The samples taken during processing (including the barley grain samples taken just before the beginning of processing) were stored deep-frozen for a maximum of 332 days (about 11 months) before analysis. Due to a technical failure, the storage temperature of the laboratory samples exceeded -18°C for about 15 hours with a maximum temperature of -1.2°C. When the samples were transferred in a different freezer they appeared to be still frozen. However, a specific storage stability study (P642151808) was initiated to evaluate the impact of this incident (refer to Point CA 6.1). No significant degradation of ethephon was observed in cereal grain, malt sprouts and beer after storage at ≥ -1°C for 24 hours. It may be concluded that the temperature deviation that occurred during the study 14-3400 had no negative impact on the study results.

Findings

The method validation data and procedural recoveries determined during sample analysis were satisfactory as shown in Table 6.5.3- 8. Based on these results the limit of quantification of the method 01429 for the determination of parent ethephon residues in barley processed commodities was established at 0.01 mg/kg.

Table 6.5.3- 9: Validation data and concurrent recoveries for the determination of parent ethephon residues in barley grain and barley processed commodities [Study 14-3400]

Report (Method)	Matrix	Fortification level [mg/kg]	Number of replicates [n]	Individual recoveries [%]	Mean recovery [%]	RSD [%]
M-535989-02-1 (01429)	Barley grain	0.01	2	100, 74	87	-
		0.10	2	106, 92	99	-
		1.0	2	98, 84	91	-
		5.0	1	89	89	-
		overall	7	-	92	11.7
M-535989-02-1 (01429)	Brewer's malt	0.01	1	99	99	-
		0.10	1	99	99	-
		5.0	1	92	92	-
		overall	3	-	97	4.2
M-535989-02-1 (01429)	Malt sprouts	0.01	3	95, 102, 105	101	5.1
		0.10	3	93, 101, 117	104	11.8
		5.0	1	96	96	-
		overall	7	-	101	8.0
M-535989-02-1 (01429)	Brewer's grain	0.01	1	89	89	-
		0.10	1	92	92	-
		5.0	1	109	109	-
		overall	3	-	97	11.2
M-535989-02-1 (01429)	Hop draff	0.01	3	87, 95, 96	93	5.3
		0.10	3	94, 94, 98	95	2.4
		overall	6	-	94	4.0
M-535989-02-1 (01429)	Brewer's yeast	0.01	1	106	106	-
		0.10	1	99	99	-
		5.0	1	87	87	-
		overall	3	-	97	9.9
M-535989-02-1 (01429)	Beer	0.01	5	91, 92, 96, 97, 103	96	5.0
		0.10	5	98, 100, 101, 105, 107	102	3.6
		1.0	1	102	102	-
		overall	11	-	99	5.1
M-535989-02-1 (01429)	Pearl barley	0.01	3	103, 103, 107	104	2.2
		0.10	3	95, 96, 97	96	1.0
		5.0	1	92	92	-
		overall	7	-	99	5.4
M-535989-02-1 (01429)	Pearl barley rub off	0.01	1	97	97	-
		0.10	1	97	97	-
		5.0	1	92	92	-
		overall	3	-	95	3.0

The fortification levels are expressed as ethephon.

The residues of parent ethephon in the various processing fractions and the corresponding processing factors are shown in Table 6.5.3- 10. A comparison of the processing factors obtained during these trials is provided in Table 6.5.3- 11.
During the malt and beer processing a concentration of the residues was only observed in malt sprouts while in brewer's malt and all the other by-products the residues were less than in the raw agricultural

commodity. Due to dilution with water, the residues were < 0.01 mg/kg (LOQ) in beer. For brewer's malt and malt sprout, the processing factors from the two trials were found to be comparable according to the criterion of the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities (difference of less than 50%). The median processing factors for these commodities were estimated at 0.44 and 1.2, respectively. An accurate comparison of the processing factors for the other commodities of beer processing was not possible since in at least one trial the processing factor could not be calculated.

During the hulling of barley grain a concentration of residues was observed in the processed commodity which corresponds to the outer part of the grain (pearl barley rub off) while in the commodity that correspond to the inner parts of the grain (pearl barley) the residues were less than in whole grain. The processing factors from the two trials did not appear to be very consistent according to the criterion of the OECD guideline 508 (differences of 53-54%). However, on closer examination, the processing factors for the trial 14-3400-01 seem to be overestimated. Based on an abrasion level of 33%, it is expected that pearl barley and pearl barley rub off represent 67% and 33% of the raw agricultural commodity, respectively. If no loss of residues occurred during hulling and considering the residues of 0.93 mg/kg and 2.9 mg/kg in pearl barley and pearl barley rub off, respectively, the residues in the raw agricultural commodity should be at least 0.098 mg/kg (= 67% x 0.93 + 33% x 2.9), which happens to be the same as the average residue level in the raw agricultural commodity before the beer processing. Based on this level, the processing factors for pearl barley and pearl barley rub off are estimated at 0.59 and 1.8, respectively. Using the same approach for the other trial, the processing factors for pearl barley and pearl barley rub off are estimated at 0.60 and 1.8, respectively, which suggests that the two trials are extremely consistent (difference of about 1%). This is because in both cases there is a 3-fold factor between the residues in pearl barley rub off and the residues in pearl barley. Therefore, it is proposed to use processing factors of 0.60 and 1.8 for pearl barley and pearl barley rub off, respectively. These values are conservative since it is assumed that there was no loss of residues during hulling.

Table 6.5.3- 10: Residue levels and transfer factors for parent ethephon in barley processed commodities [Study 14-3400]

Processing type / Processed commodity	Trial 14-3400-01 (Germany)		Trial 14-3400-02 (Netherlands)	
	Residues (mg/kg)	Processing factor	Residues (mg/kg)	Processing factor
Preparation of beer				
Barley grain (RAC)	0.098* (0.14, 0.055)		2.0* (1.5, 2.4)	-
Brewer's malt	0.046	0.47	0.78	0.40
Malt sprouts	0.10	1.0	2.7	1.4
Brewer's grain	< 0.01	< 0.1	0.041	0.021
Hop draff	< 0.01	< 0.1	0.073	0.037
Brewer's yeast	< 0.01	< 0.1	0.070	0.036
Beer	< 0.01	< 0.1	< 0.01	< 0.005
Preparation of pearl barley				
Calculation 1				
Barley grain (RAC)	0.062* (0.057, 0.067)	-	2.3* (2.4, 2.1)	-
Pearl barley	0.058	0.94	0.99	0.44
Pearl barley rub off	0.18	2.9	3.0	1.3
Calculation 2				
Barley grain (RAC)	0.098	-	1.65	-
Pearl barley	0.058	0.59	0.99	0.60
Pearl barley rub off	0.18	1.8	3.0	1.8

* Average of the residues measured in the two replicate samples frozen at the beginning of processing. The individual values are shown in brackets.

Calculation 1 : calculation of processing factors based on the mean residue levels measured in barley grain.
Calculation 2 : calculation of processing factors based on the residue levels in barley grain estimated based on the residues in pearl barley and pearl barley rub off assuming an abrasion factor of 33% and no loss of residues during hulling.

Table 6.5.3- 11: Compilation of processing factors for ethephon in barley processed commodities

Processing type Processed commodity	Processing factors			
	Trial 14-3400-01 (Germany)	Trial 14-3400-02 (Netherlands)	Difference*	Median
Preparation of beer				
Brewer's malt	0.47	0.40	15%	0.44
Malt sprouts	1.0	1.4	26%	1.2
Brewer's grain	< 0.1	0.021	n. a.	< 0.06
Hop draff	< 0.1	0.037	n. a.	< 0.07
Brewer's yeast	< 0.1	0.036	n. a.	< 0.07
Beer	< 0.1	< 0.005	n. a.	< 0.05
Preparation of pearl barley				
Calculation 1				
Pearl barley	0.94	0.44	53%	0.69
Pearl barley rub off	2.9	1.3	54%	2.1
Calculation 2				
Pearl barley	0.59	0.60	1%	0.60
Pearl barley rub off	1.8	1.8	1%	1.8

* Calculated according to the formula provided in the OECD guideline 508 on the magnitude of the pesticide residues in processed commodities : *[Pf (high value) - Pf(low value)]/Pf (high value)*.

n. a. : Not applicable; the difference between the two processing factors cannot be calculated since at least one of them is not known precisely.

Calculation 1 : calculation of processing factors based on the mean residue levels measured in barley grain.
Calculation 2 : calculation of processing factors based on the residue levels in barley grain estimated based on the residues in pearl barley and pearl barley rub off assuming an abrasion factor of 33% and no loss of residues during hulling.

Conclusion

Two trials were performed to investigate the fate of parent ethephon residues during barley grain processing into beer and pearl barley. During the processing in beer a concentration of residues was only observed in malt sprout while in all the other processed commodities the residues were less than in barley grain. During the processing in pearl grain a concentration of residues was observed in pearl barley rub off while the residues in pearl barley were less than in barley grain. The median processing factors were 1.2 for malt sprouts, 0.44 for brewer's malt, 0.60 for pearl barley, 1.8 for pearl barley rub off , < 0.1 in brewer's grain, hop draff and brewer's yeast, and < 0.05 in beer.

CA 6.6 Residues in rotational crops

CA 6.6.1 Metabolism in rotational crops

The confined rotational crop study submitted in the baseline dossier of 2002 was summarised as follows in the EFSA Conclusions [EFSA Scientific Report (2008) 174, 1-65] :

A rotational crop study was submitted with ethephon on radishes, collards and wheat. ^{14}C-ethephon steadily declined 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 2-hydroxyethyl phosphonic acid were detected in certain samples of the crops examined (radishes, collards and wheat). The radioactivity found in plant matrices was attributable to incorporation into all categories of biomolecules. Following application of ethephon according to GAP on cereals no residues are expected in follow up crops.

Since the representative use for the renewal of the active substance approval is the same as the representative use considered during the previous review, the above conclusion still applies. In this context it is important to note that the confined rotational crop study was conducted using a sandy loam soil of pH 4.6, which – due to the susceptibility of ethephon to basic hydrolysis – constitutes a worst case situation with regard to residues. It is also important to note that the study was conducted at the highly exaggerated rate of 2360 g as/ha, which represents about 4.9 times the representative use rate of 480 g as/ha. Since ethephon does not accumulate in soil, there is no need to consider the possible plateau concentration in soil.

CA 6.6.2 Magnitude of residues in rotational crops

Based on the results of the confined rotational crop study, no residues of ethephon or ethephon-derived metabolites are expected to occur in rotational crops at levels ≥ 0.01 mg/kg after the use of ethephon in cereals according to the herein considered representative GAPs. Therefore no field study to determine the magnitude of residues in rotational crops is needed.

CA 6.7 Proposed residue definitions and maximum residue levels

CA 6.7.1 Proposed residue definitions

The residue definition of ethephon in food commodities of plant and animal origin was up-dated in the EFSA Reasoned opinion on the review of the existing MRLs for ethephon (EFSA Journal 2009;7(10):1347).

<u>Residue definition in commodities of plant origin :</u>

Metabolism of ethephon was investigated in cereals (wheat) and in fruits and fruiting vegetables (tomato and pineapples) (EFSA, 2008a). Additional information on the fate of ethephon was also available after application to squash, cucumber, apple and cherry trees. These studies indicate that metabolism of ethephon in plants mainly proceeds via conversion to 2-hydroxyethyl phosphonic acid (HEPA) and via decomposition via ethylene, which is released in the atmosphere, and phosphate, which is incorporated in the natural phosphate cycle of the plant. The wheat metabolism study shows that in the edible part (grain) of cereals treated at normal field rates, the metabolite HEPA and ethephon are present at similar levels. In tomatoes, HEPA was found to increase over time but 12 days after treatment, which corresponds to the supported PHI for most fruiting crops, the metabolite was still present at levels four times lower than ethephon (The Netherlands, 2004). Moreover, residues trials on grapes where levels of both ethephon and HEPA were measured were reported by the

Netherlands (2009). After a PHI of 28 days, all trials demonstrated that HEPA was present at levels lower or similar to the parent compound. Considering that HEPA was shown to be of different toxicity than the parent compound (see also section 2), there is no need to include HEPA in the residue definition for risk assessment together with the parent compound but the question could be raised whether a separate risk assessment for HEPA would be necessary. EFSA concludes that a separate risk assessment for HEPA will not be more critical than the risk assessment for ethephon because HEPA is not expected to be present in higher amounts than the parent compound and adverse effects for HEPA are expected to occur at exposure levels 5-10 times higher than for ethephon (see also section 2). A separate residue definition for risk assessment of HEPA is therefore not required.

Consequently, the residue definition for enforcement and risk assessment in cereals, fruits and fruiting vegetables is defined as ethephon only. Validated analytical methods for enforcement of the proposed residue definition are available (see also section 1.1). These conclusions reflect the views of the RMS (The Netherlands, 2008) and are also in line with the findings of the 1994 JMPR (WHO/FAO, 1995). During the peer review of ethephon (EFSA, 2008a), it was decided to include HEPA in the residue definition for risk assessment but this conclusion is no longer relevant as additional information on the toxicity of HEPA has been considered in the meantime.

It is noted that ethephon is also authorised for use on cotton seed, for which no representative metabolism study is available. In order to extend the proposed residue definition to oilseeds, a representative metabolism study for this crop group should be submitted. Awaiting such information to be submitted and evaluated, it is proposed on a provisional basis to define the residue for enforcement and risk assessment in cotton seeds as ethephon.

Residue definition in commodities of animal origin :

Considering that the dietary burden of ruminants and pigs is triggered, investigation on the fate of residues in these animals is necessary. During the peer review of ethephon, a metabolism study was assessed where lactating goats were dosed with 0.37 and 0.46 mg/kg bw/d of ^{14}C-ethephon, corresponding to the 7N and 8N exposure of meat ruminants (The Netherlands, 2004). This study demonstrates that the parent compound is hydrolysed to lose its chlorine and phosphate groups and that the carbon units are taken up into the tricarboxylic acid cycle to yield natural products like fat, protein, carbohydrate and CO_2. Ethephon and HEPA are expected to be the only toxicologically relevant compounds and the highest radioactive residue level was found in liver (1 mg/kg) of which 0.15% was considered ethephon and/or HEPA (max. 0.0015 mg/kg). Since metabolism in rats and ruminants was demonstrated to be similar, the findings in ruminants can also be extrapolated to pigs. Based on these data and the fact that residues in all ruminant commodities were expected to be very low, no residue definition was proposed in the framework of the peer review (EFSA, 2008a). In the framework of this review, however, additional crops contribute to the dietary burden of livestock resulting in a higher exposure of livestock to ethephon residues and the necessity to establish a residue definition in pigs and ruminants. Also in contrast to the peer review, data are now available indicating that HEPA is expected to result in adverse effects at much higher exposure levels than ethephon (see also section 2). Therefore, the relevant residue in pigs and ruminants is now defined as ethephon, both for enforcement and risk assessment purposes.

For poultry there is in principle no necessity to establish a residue definition because the calculated dietary burden of poultry to ethephon residues amounted to less than 0.1 mg/kg DM. Nevertheless, a metabolism study with laying hens is reported in the DAR on ethephon. This study demonstrates that metabolic pathways of ethephon in ruminants and poultry are very similar (The Netherlands, 2004). It is therefore concluded that the relevant residue in poultry could also be defined as ethephon, provided that the use of ethephon is supported on additional crops resulting in a higher exposure of poultry to ethephon residues. In the meantime, a residue definition for poultry products is not required.

The above considerations and conclusions are still considered valid except that a cotton metabolism study is now available and its results are in line with those of the wheat and tomato metabolism studies (refer to CA 6.2.1). Therefore, the provisional residue definition in food commodities of plant origin is confirmed and can be considered "final". Furthermore, the exposure level that makes it necessary to investigate the nature and level of residues in food of poultry origin is now exceeded (refer to CA 6.4). Therefore, it is appropriate to set a residue definition for ethephon in food of poultry origin.

In summary the proposed residue definition of ethephon in food and feed of plant and animal origin is parent ethephon. This residue definition applies to MRL setting / enforcement and to risk assessment as well.

Table 6.7.1- 1 Proposed residue definition of ethephon

Commodities	MRL setting / Enforcement	Risk assessment
Food / feed of plant origin	Ethephon	Ethephon
Food of animal origin	Ethephon	Ethephon

CA 6.7.2 Proposed MRLs and justification of the acceptability of the levels proposed

The existing EU MRLs for ethephon in barley grain, wheat grain and food commodities of animal origin are shown in Table 6.7.2- 1.

Table 6.7.2- 1: Current EU MRLs of ethephon relevant to the representative uses of the active substance as an anti-lodging agent in barley and wheat

Code	Commodity	MRL (mg/kg)
0500010	Barley (grain)	1
0500090	Wheat (grain)	1
1000000	Products of animal origin - terrestrial animals	0.05*

An overview of the available residue data that support the representative uses of ethephon as an anti-lodging agent in barley and wheat is given in Table 6.7.2- 2. For both barley grain and wheat grain 8 trials are available from each zone to derive an MRL. Currently no MRLs are set for straw but theoretically the same number of data would be available to derive MRLs for ethephon in straw.

Overall, higher levels of ethephon residues were found in barley and wheat grain samples from the northern zone than in barley and wheat grain samples from the southern zone. This is an expected result since the supported GAPs are different for the two zones. In the northern zone the compound may be applied up the growth stage BBCH 51 while in the southern zone the latest growth stage for application is BBCH 39. Consequently, it is appropriate to derive the MRLs for ethephon in barley grain and wheat grain from the data generated in the northern zone. Using the OECD MRL calculator an MRL of 1.5 mg/kg is derived for barley grain based on the residue data generated for barley grain in the northern residue zone. Similarly an MRL of 0.5 mg/kg is derived for wheat grain based on the residue data generated for wheat grain in the northern residue zone.

However, since application is performed before the development of grain and according to the guideline SANCO 7525/VI/95 - rev.9, it is possible to extrapolate between barley and wheat. Furthermore, according to both the Mann-Whitney U-test and the Kruskal-Wallis H-test, the residue

data for the two crops are likely to belong to similar distributions and it may, therefore, be justified to combine the two residue datasets to calculate a common MRL for ethephon in barley and wheat grain. Using this approach, an MRL of 0.9 mg/kg is derived.

Both approaches (derivation of different MRLs for each crop based on the respective datasets or derivation of a common MRL based on the combined datasets) are scientifically justifiable. The first option would make it necessary to increase the current EU MRL for ethephon in barley (grain) from 1 mg/kg to 1.5 mg/kg while the second option would not make it necessary to modify the existing MRLs for ethephon in barley (grain) and wheat (grain). In the following it is assumed that based on the representative uses in barley and wheat **it is suitable to set a common MRL of 0.9 mg/kg for ethephon in barley and wheat grain**. However, the other approach would also be possible and would not change the conclusions of the consumer risk assessment. Noticeably, in the context of the periodic review of the Codex MRLs of ethephon, the JMPR 2015 favoured the approach which consists in setting different MRLs for barley and wheat grain.

Table 6.7.2- 2: Overview of the available residue trial data to support the representative uses of ethephon as an anti-lodging agent in barley and wheat

Commodity	Residue region	Individual trial results - ethephon (mg/kg)	STMR (mg/kg)	HR (mg/kg)	Calculated MRL* (mg/kg)
Barley grain	NEU	0.031, 0.067, 0.090, 0.13, 0.16, 0.23, 0.41, 0.73	0.15	0.73	1.5 (1.167)
Wheat grain	NEU	0.052, 0.059, 0.059, 0.083, 0.11, 0.14, 0.23, 0.31	0.097	0.31	0.5 (0.505)
Cereal grain	NEU	0.031, 0.052, 0.059, 0.059, 0.067, 0.083, 0.090, 0.14, 0.13, 0.14, 0.16, 0.23, 0.23, 0.31, 0.41, 0.73	0.12	0.73	0.9 (0.900)
Barley grain	SEU	0.021, 0.034, 0.035, 0.039, 0.041, 0.047, 0.14, 0.21	0.040	0.21	0.4 (0.340)
Wheat grain	SEU	0.010, 0.011, 0.025, 0.043, 0.049, 0.057, 0.10, 0.13	0.046	0.13	0.3 (0.223)
Cereal grain	SEU	0.010, 0.011, 0.021, 0.025, 0.034, 0.035, 0.039, 0.041, 0.043, 0.047, 0.049, 0.057, 0.10, 0.13, 0.14, 0.21	0.042	0.21	0.3 (0.283)
Barley straw	NEU	0.35, 0.43, 0.51, 0.64, 0.78, 1.2, 1.5, 3.6	0.71	3.6	6 (5.426)
Wheat straw	NEU	0.36, 0.44, 0.57, 0.66, 1.2, 1.2, 1.3, 1.5	0.93	1.5	3 (2.795)
Cereal straw	NEU	0.35, 0.36, 0.43, 0.44, 0.51, 0.57, 0.64, 0.66, 0.78, 1.2, 1.2, 1.2, 1.3, 1.5, 1.5, 3.6	0.72	3.6	5 (4.224)
Barley straw	SEU	0.23, 0.24, 0.35, 0.39, 0.39, 0.97, 1.1, 1.7	0.39	1.7	3 (2.795)
Wheat straw	SEU	0.21, 0.29, 0.30, 0.44, 0.84, 0.86, 1.2, 1.7	0.64	1.7	3 (2.827)
Cereal straw	SEU	0.21, 0.23, 0.24, 0.29, 0.30, 0.35, 0.39, 0.39, 0.44, 0.84, 0.86, 0.97, 1.1, 1.2, 1.7, 1.7	0.42	1.7	3 (2.743)

* The MRLs were estimated based on the OECD MRL calculator. The values in brackets correspond to the calculated values before rounding to the appropriate MRL classes.

The highest residues of ethephon in food commodities of animal origin that might result from the herein supported representative uses were estimated and the appropriate MRLs were derived under Point CA 6.4. A comparison of these MRLs with the current EU MRLs for ethephon in food commodities of animal origin is provided in Table 6.7.2- 3. Except for kidney of sheep all the MRLs derived based on the representative uses are below the current EU MRL of 0.05 mg/kg.

Table 6.7.2- 3: EU MRLs for ethephon in food of animal origin : current values and values derived based on the representative uses

Food commodity	Current EU MRL (mg/kg)	MRL derived based on the representative uses (mg/kg)	Comment
Swine - muscle	0.05*	0.01	See CA 6.4.3
Swine - fat tissue	0.05*	0.01	See CA 6.4.3
Swine - liver	0.05*	0.01	See CA 6.4.3
Swine - kidney	0.05*	0.01	See CA 6.4.3
Bovine - muscle	0.05*	0.01	See CA 6.4.2
Bovine - fat tissue	0.05*	0.01	See CA 6.4.2
Bovine - liver	0.05*	0.01	See CA 6.4.2
Bovine - kidney	0.05*	0.04	See CA 6.4.2
Sheep - muscle	0.05*	0.01	See CA 6.4.2
Sheep - fat tissue	0.05*	0.01	See CA 6.4.2
Sheep - liver	0.05*	0.02	See CA 6.4.2
Sheep - kidney	0.05*	0.07	See CA 6.4.2
Poultry - muscle	0.05*	0.01	See CA 6.4.1
Poultry - fat tissue	0.05*	0.01	See CA 6.4.1
Poultry - liver	0.05*	0.01	See CA 6.4.1
Poultry - kidney	0.05*	0.01	LOQ - not investigated in feeding studies
Milk - cattle	0.05*	0.01	See CA 6.4.2
Milk - sheep	0.05*	0.01	See CA 6.4.2
Bird eggs - chicken	0.05*	0.01	See CA 6.4.1

CA 6.7.3 Proposed MRLs and justification of the acceptability of the levels proposed for imported products (import tolerance)

No import tolerances are applied for in the context of this re-approval dossier. However, according to Article 14 of Regulation EC No 396/2005, the existing Codex MRLs have to be taken into account when setting EU MRLs.

CA 6.8 Proposed safety intervals

The application time for the use of ethephon in cereals to prevent lodging is expressed in terms of growth stage. Treatment may be conducted up to the growth stage BBCH 51 in the northern part of Europe and up to the growth stage BBCH 39 in the southern part of Europe.

In the 16 trials conducted in the northern part of Europe, the interval between application and harvest ranged between 54 days and 78 days. The highest residue of 0.73 mg/kg in grain was observed in a trial in which harvest was conducted 56 days after application but two other trials with a comparable interval between application and harvest (55 and 56 days, respectively) showed rather low residues (0.067 mg/kg and 0.09 mg/kg). Therefore, intervals of less than 60 days between application and harvest do not necessarily imply high residue levels.

In the 16 trials conducted in the southern part of Europe, the interval between application and harvest ranged between 58 days and 110 days. The residues in mature grain (Highest residue of 0.21 mg/kg) were far below the MRLs proposed based on the representative use for the northern part of Europe.

Based on these considerations it is not deemed necessary to set a minimum interval between treatment of cereals with ethephon and harvest of grain and straw. Adherence to the GAP growth stages should ensure that the residues in treated grain do not exceed the proposed MRLs.

In Europe, immature cereals are normally not fed to livestock. Therefore, no waiting period before feeding treated cereals to livestock is proposed.

CA 6.9 Estimation of the potential and actual exposure through diet and other sources

The toxicity endpoints considered for the dietary risk assessment are shown in Table 6.9- 1. Detailed justification for these proposals is provided in Section 5 of this dossier.

Table 6.9- 1: Toxicity endpoints considered for the dietary risk assessment

Endpoint	Value (mg/kg bw/day)	Source	Safety factor
ADI	0.02	90 day dog study	100
ARfD	0.05	28 days oral dog study (AChE inhibition), lowered to get a 10 fold MoS to the NOAEL from human data	100

In the context of this dossier for the renewal of the approval of ethephon, the dietary risk assessment was limited to the residues likely to result from the representative uses. As shown in Table 6.9- 2 the chronic exposure was estimated based on the median residue levels in food of plant and animal origin while for the acute exposure the highest residues were taken into account. For barley and wheat grain the median and highest residue values were derived from the combined residue dataset for the two crops in the northern residue zone, which is consistent with the proposed approach for MRL setting.

All calculations were performed using the revision 2 of the EFSA Pesticide Residues Intake Model (PRIMo 2). The outcome of the chronic and acute dietary risk assessments is shown in Table 6.9- 3 and Table 6.9- 4, respectively. The highest IEDI was estimated to be 5.6% of the ADI (for the WHO cluster diet B) while the highest IESTI was 21.1% of the ARfD (due to consumption of wheat by children). It may be concluded that the representative uses supported for the renewal of the approval

of ethephon do not result in chronic or acute consumer exposures exceeding the respective toxicological endpoints. Therefore, these uses do not cause chronic or acute health concerns for consumers.

Table 6.9- 2: Residue values considered for the dietary risk assessment (Residue definition for dietary risk assessment : parent ethephon)

Commodity	Chronic risk assessment		Acute risk assessment	
	Residue level (mg/kg)	Comment	Residue level (mg/kg)	Comment
Barley grain	0.12	STMR for cereals in the northern zone	0.73	HR for cereals in the northern zone
Wheat grain	0.12	STMR for cereals in the northern zone	0.73	HR for cereals in the northern zone
Swine - muscle	0.01	Median residue*	0.01	Maximum residue*
Swine - fat tissue	0.01	Median residue*	0.01	Maximum residue*
Swine - liver	0.01	Median residue*	0.01	Maximum residue*
Swine - kidney	0.01	Median residue*	0.01	Maximum residue*
Bovine - muscle	0.01	Median residue*	0.01	Maximum residue*
Bovine - fat tissue	0.01	Median residue*	0.01	Maximum residue*
Bovine - liver	0.01	Median residue*	0.01	Maximum residue*
Bovine - kidney	0.01	Median residue	0.04	Maximum residue
Sheep - muscle	0.01	Median residue*	0.01	Maximum residue*
Sheep - fat tissue	0.01	Median residue*	0.01	Maximum residue*
Sheep - liver	0.01	Median residue*	0.01	Maximum residue
Sheep - kidney	0.02	Median residue	0.07	Maximum residue
Poultry - muscle	0.01	Median residue*	0.01	Maximum residue*
Poultry - fat tissue	0.01	Median residue*	0.01	Maximum residue*
Poultry - liver	0.01	Median residue*	0.01	Maximum residue*
Poultry - kidney	0.01	Median residue*	0.01	Maximum residue*
Milk - cattle	0.01	Median residue*	0.01	Maximum residue*
Milk - sheep	0.01	Median residue*	0.01	Maximum residue*
Bird eggs - chicken	0.01	Median residue*	0.01	Maximum residue*

* Rounded to the LOQ of enforcement method.

Table 6.9- 3: Chronic risk assessment according to PRIMo 2 for the representative uses of ethephon

IEDI (% ADI)	MS Diet	Highest contributor to IEDI	
		(% ADI)	Commodity
5.6	WHO Cluster diet B	5.1	Wheat
4.5	NL child	2.8	Wheat
4.4	WHO cluster diet D	3.9	Wheat
4.0	IT kids/toddler	4.0	Wheat
3.5	ES child	2.7	Wheat
3.4	DK child	3.3	Wheat
3.3	DE child	2.5	Wheat
3.2	WHO cluster diet E	2.4	Wheat
2.9	WHO Cluster diet F	2.2	Wheat
2.6	SE general population 90th percentile	1.9	Wheat
2.5	IT adult	2.5	Wheat
2.4	WHO regional European diet	1.8	Wheat
2.4	UK Toddler	2.4	Wheat
2.4	PT General population	2.4	Wheat
2.4	IE adult	1.4	Wheat
2.2	FR all population	2.0	Wheat
2.1	ES adult	1.4	Wheat
1.9	NL general	1.2	Wheat
1.9	FR infant	1.3	Cattle Milk
1.8	FR toddler	1.6	Wheat
1.6	UK Infant	1.6	Wheat
1.3	UK vegetarian	1.2	Wheat
1.3	DK adult	1.2	Wheat
1.0	UK Adult	1.0	Wheat
1.0	LT adult	0.6	Wheat
0.6	FI adult	0.6	Wheat

Table 6.9- 4: Acute risk assessment according to PRIMo 2 for the representative uses of ethephon

Children		Adults	
IESTI (% ARfD)	Commodity	IESTI (% ARfD)	Commodity
21.1	Wheat	11.4	Wheat
2.6	Barley	10.6	Barley
2.5	Cattle Milk	0.3	Cattle Milk
0.3	Bovine: Kidney	0.2	Poultry: Meat
0.3	Bovine: Meat	0.1	Bovine: Kidney

CA 6.10 Other studies

CA 6.10.1 Effect on the residue level in pollen and bee products

No suitable test method for the determination of residues in pollen and bee products is listed in Commission Communication 2013/C 95/01 about the implementation of Regulation (EU) No 283/2013. Therefore, this point does not need to be addressed at the current stage.
According to the EFSA Guidance Document on the risk assessment of plant protection products on bees [EFSA Journal 2013;11(7):3295], barley and wheat do not produce nectar and in general they are considered of low attractiveness to bees for pollen although the collection of pollen cannot be excluded.
However, for the evaluation of residues in pollen and bee products for human consumption, the relevant question regarding bee attractiveness is not whether or not the crop is occasionally visited by bees, but if the crop is foraged by honey bees to an extent of economic relevance. A relevant residue level in pollen (and bee products) is only likely to occur if a significant portion of pollen (and nectar) is collected from treated cereal fields by a whole colony. The guidance Document clearly indicates that this is not the case.
It may be concluded that under normal conditions the herein supported representative uses of ethephon are very unlikely to result in significant levels of ethephon residues in pollen or other bee products.

Annex 1 Summary tables of supervised residue trials

Barley

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
13-2027 13-2027-01 [redacted] 2013 M-526906-01-1	Winter barley Duett	1) 01.10.2012 2) 07.06.2013 - 12.06.2013 3) 01.07.2013 - 31.07.2013	Spraying	0.48	300	0.16	24.05.2013	Beginning of heading	green material grain straw	6.2 0.61 0.55 0.26 0.43 0.13 0.51	0 7 14 21 24 59 59	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2027 13-2027-02 [redacted] 2013 M-526906-01-1	Winter barley Meridian	1) 28.09.2012 2) 01.06.2013 - 10.06.2013 3) 15.07.2013 - 29.07.2013	Spraying	0.512	267	0.192	22.05.2013	Beginning of heading	green material grain straw	3.2 <0.05 0.067 0.35	0 33 55 55	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
13-2027 13-2027-03 [redacted]2013 M-526906-01-1	Winter barley Malabar	1) 15.10.2012 2) 21.06.2013 - 01.07.2013 3) 22.07.2013 - 09.08.2013	Spraying	0.48	300	0.16	03.06.2013	Beginning of heading	green material grain straw	7.9 3.8 0.85 0.57 0.27 0.73 1.5	0 7 14 21 43 56 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2027 13-2027-04 [redacted] 2013 M-526906-01-1	Winter barley Cassata	1) 16.10.2012 2) 03.06.2013 - 10.06.2013 3) 26.07.2013 - 16.08.2013	Spraying	0.48	200	0.24	31.05.2013	Beginning of heading	green material grain straw	6.6 0.36 0.23 3.6	0 34 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**		**Active substance**	**: ethephon**	
Country	**: Germany**		**Crop/Crop Group**	**: Cereals**	
Content of active substance (g/kg or g/L)	**: 480 g/L**		**Page**	**: 1- B**	
Formulation (e.g. WP)	**: 480 SL**		**Indoor/outdoor**	**: Outdoor**	
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**: Ethephon SL 480**		**Residues determined as**	**: HEPA**	
Producer of commercial product	**: Bayer CropScience AG**		**Residues calculated as**	**: HEPA**	

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
13-2027 13-2027-01 [redacted]2013 M-526906-01-1	Winter barley Duett	1) 01.10.2012 2) 07.06.2013 - 12.06.2013 3) 01.07.2013 - 31.07.2013	Spraying	0.48	300	0.16	24.05.2013	Beginning of heading	green material	0.091 <0.05 <0.05 <0.05 <0.05	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg
									grain	0.019	59	(h) 0.01 mg/kg day 59: 0.013 mg/kg in control sample
									straw	<0.05	59	(h) 0.05 mg/kg
13-2027 13-2027-02 [redacted] 2013 M-526906-01-1	Winter barley Meridian	1) 28.09.2012 2) 01.06.2013 - 10.06.2013 3) 15.07.2013 - 29.07.2013	Spraying	0.512	267	0.192	22.05.2013	Beginning of heading	green material	<0.05 <0.05	0 33	(g) 01429 (h) 0.05 mg/kg
									grain	<0.01	55	(h) 0.01 mg/kg
									straw	<0.05	55	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropSCience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
13-2027 13-2027-03 [redacted]2013 M-526906-01-1	Winter barley Malabar	1) 15.10.2012 2) 21.06.2013 - 01.07.2013 3) 22.07.2013 - 09.08.2013	Spraying	0.48	300	0.16	03.06.2013	Beginning of heading	green material grain straw	0.094 0.088 0.085 0.076 0.059 0.086 <0.05	0 7 14 21 43 56 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2027 13-2027-04 [redacted] 2013 M-526906-01-1	Winter barley Cassata	1) 16.10.2012 2) 03.06.2013 - 10.06.2013 3) 26.07.2013 - 16.08.2013	Spraying	0.48	200	0.24	31.05.2013	Beginning of heading	green material grain straw	0.093 <0.05 0.055 0.066	0 34 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
14-2022 14-2022-01 [redacted]2014 M-533473-01-1	Winter barley Naomie	1) 24.09.2013 2) 21.05.2014 - 24.05.2014 3) 15.07.2014 - 17.07.2014	Spraying	0.537	330	0.16	29.04.2014	Beginning of heading	green material	6.2 0.50 0.29 0.17 0.086	0 7 14 21 36	(g) 01429 (h) 0.05 mg/kg
									grain	0.031	78	(h) 0.01 mg/kg
									straw	0.64	78	(h) 0.05 mg/kg
14-2022 14-2022-02 [redacted]2014 M-533473-01-1	Winter barley Leibnitz	1) 26.09.2013 2) 05.05.2014 - 09.05.2014 3) 01.07.2014 - 15.07.2014	Spraying	0.48	300	0.16	30.04.2014	Beginning of heading	green material	7.7 0.37	0 21	(g) 01429 (h) 0.05 mg/kg
									grain	0.41	64	(h) 0.01 mg/kg
									straw	1.2	64	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropSciences AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
14-2022 14-2022-03 [redacted]2014 M-533473-01-1	Winter barley Obite	1) 03.10.2013 2) 30.04.2014 - 07.05.2014 3) 15.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	23.04.2014	Beginning of heading	green material grain straw	6.6 0.34 0.15 0.10 <0.05 0.090 0.43	0 7 14 21 28 56 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2022 14-2022-04 [redacted] 2014 M-533473-01-1	Winter barley Cassatta	1) 01.10.2013 2) 02.06.2014 - 10.06.2014 30.15.07.2014 - 08.08.2014	Spraying	0.48	200	0.24	13.05.2014	Middle of heading	green material grain straw	7.3 0.13 0.16 0.78	0 34 73 73	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg day 73: 0.088 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropSCience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
14-2022 14-2022-01 [redacted]2014 M-533473-01-1	Winter barley Naomie	1) 24.09.2013 2) 21.05.2014 - 24.05.2014 3) 15.07.2014 - 17.07.2014	Spraying	0.537	330	0.16	29.04.2014	Beginning of heading	green material grain straw	0.12 <0.05 <0.05 <0.05 <0.05 0.016 0.055	0 7 14 21 36 78 78	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2022 14-2022-02 [redacted] 2014 M-533473-01-1	Winter barley Leibnitz	1) 26.09.2013 2) 05.05.2014 - 09.05.2014 30.01.07.2014 - 15.07.2014	Spraying	0.48	300	0.16	30.04.2014	Beginning of heading	green material grain straw	0.12 <0.05 0.055 0.063	0 21 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 64: 0.054 mg/kg in control sample (h) 0.05 mg/kg day 64: 0.061 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Days) (f)	Remarks
14-2022 14-2022-03 [redacted] 2014 M-533473-01-1	Winter barley Obite	1) 03.10.2013 2) 30.04.2014 - 07.05.2014 3) 15.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	23.04.2014	Beginning of heading	green material grain straw	<0.05 <0.05 <0.05 <0.05 <0.05 0.021 <0.05	0 7 14 21 28 56 56	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2022 14-2022-04 [redacted] 2014 M-533473-01-1	Winter barley Cassatta	1) 01.10.2013 2) 02.06.2014 - 10.06.2014 3) 15.07.2014 - 08.08.2014	Spraying	0.48	200	0.24	13.05.2014	Middle of heading	green material grain straw	0.072 0.050 0.047 <0.05	0 34 73 73	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 73: 0.011 mg/kg in control sample (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Days) (f)	Remarks
13-2028 13-2028-01 [redacted] 2013 M-529491-01-1	Winter barley Cervoise	1) 28.10.2012 2) 07.05.2013 - 17.05.2013 3) 03.07.2013 - 10.07.2013	Spraying	0.48	300	0.16	25.04.2013	Flag leaf stage	green material	4.5 0.24 0.15 0.092 <0.05	0 7 12 21 39	(g) 01429 (h) 0.05 mg/kg
									grain	0.035	71	(h) 0.01 mg/kg
									straw	0.23	71	(h) 0.05 mg/kg
13-2028 13-2028-02 [redacted] 2013 M-529491-01-1	Winter barley Graphic	1) 10.12.2012 2) 05.05.2013 - 17.05.2013 3) 12.06.2013 - 30.06.2013	Spraying	0.48	400	0.12	09.04.2013	Flag leaf stage	green material	4.2 0.26	0 27	(g) 01429 (h) 0.05 mg/kg
									grain	0.21	72	(h) 0.01 mg/kg
									straw	1.7	72	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim
Country : Germany
Content of active substance (g/kg or g/L) : 480 g/L
Formulation (e.g. WP) : 480 SL

Commercial product (name) : Ethephon SL 480
Producer of commercial product : Bayer CropScience AG

Active substance : ethephon

Crop/Crop Group : Cereals
Page : 2- A
Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content) :
Residues determined as : ethephon
Residues calculated as : ethephon

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
13-2028 13-2028-03 [redacted] 2013 M-529491-01-1	Winter barley Quench	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 15.06.2013 - 15.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material grain straw	5.9 0.44 0.087 0.078 0.051 0.041 0.39	0 7 14 21 24 62 62	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2028 13-2028-04 [redacted] 2013 M-529491-01-1	Winter barley Federal	1) 07.11.2012 2) 30.04.2013 - 10.05.2013 3) 25.06.2013 - 05.07.2013	Spraying	0.48	350	0.137	24.04.2013	Flag leaf stage	green material grain straw	3.5 <0.05 0.021 0.24	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Plt) (days) (f)	Remarks
13-2028 13-2028-01 [redacted]2013 M-529491-01-1	Winter barley Cervoise	1) 28.10.2012 2) 07.05.2013 - 17.05.2013 3) 03.07.2013 - 10.07.2013	Spraying	0.48	300	0.16	25.04.2013	Flag leaf stage	green material	0.053 <0.05 <0.05 <0.05 <0.05	0 7 12 21 39	(g) 01429 (h) 0.05 mg/kg
									grain	<0.01	71	(h) 0.01 mg/kg
									straw	<0.05	71	(h) 0.05 mg/kg
13-2028 13-2028-02 [redacted]2013 M-529491-01-1	Winter barley Graphic	1) 10.12.2012 2) 05.05.2013 - 17.05.2013 3) 12.06.2013 - 30.06.2013	Spraying	0.48	400	0.12	09.04.2013	Flag leaf stage	green material	0.058 <0.05	0 27	(g) 01429 (h) 0.05 mg/kg day 0: 0.081 mg/kg in control sample
									grain	0.069	72	(h) 0.01 mg/kg day 72: 0.023 mg/kg in control sample
									straw	0.17	72	(h) 0.05 mg/kg day 72: 0.17 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
13-2028 13-2028-03 [redacted] 2013 M-529491-01-1	Winter barley Quench	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 15.06.2013 - 15.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material grain straw	0.051 <0.05 <0.05 <0.05 <0.05 0.012 0.054	0 7 14 21 24 62 62	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
13-2028 13-2028-04 [redacted] 2013 M-529491-01-1	Winter barley Federal	1) 07.11.2012 2) 30.04.2013 - 10.05.2013 3) 25.06.2013 - 05.07.2013	Spraying	0.48	350	0.137	24.04.2013	Flag leaf stage	green material grain straw	<0.05 <0.05 0.070 <0.05	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 64: 0.060 mg/kg in control sample (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
14-2020 14-2020-01 [redacted] 2014 M-533463-01-1	Winter barley Limpid	1) 13.10.2013 2) 22.04.2014 - 29.04.2014 3) 17.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	08.04.2014	Flag leaf stage	green material	5.6 3.0 3.0 0.38 0.095	0 7 14 21 42	(g) 01429 (h) 0.05 mg/kg
									grain	0.14	72	(h) 0.01 mg/kg
									straw	1.1	72	(h) 0.05 mg/kg
14-2020 14-2020-02 [redacted] 2014 M-533463-01-1	Winter barley Graphic	1) 20.11.2013 2) 20.04.2014 - 27.04.2014 30.10.06.2014 - 10.07.2014	Spraying	0.411	342	0.12	08.04.2014	Mid boot stage	green material	6.6 0.36	0 29	(g) 01429 (h) 0.05 mg/kg
									grain	0.039	64	(h) 0.01 mg/kg
									straw	0.97	64	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	:	**Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	:	**480 g/L**	**Page**	:	**2- A**
Formulation (e.g. WP)	:	**480 SL**	**Indoor/outdoor**	:	**Outdoor**
			Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	**Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	:	**Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
14-2020 14-2020-03 [redacted] 2014 M-533463-01-1	Winter barley Lutece	1) 04.11.2013 2) 17.04.2014 - 27.04.2014 3) 05.06.2014 - 15.06.2014	Spraying	0.48	400	0.12	10.04.2014	Flag leaf stage	green material	3.3 1.2 0.34 0.10 <0.05	0 6 14 20 29	(g) 01429 (h) 0.05 mg/kg
									grain	0.047	64	(h) 0.01 mg/kg
									straw	0.39	64	(h) 0.05 mg/kg
14-2020 14-2020-04 [redacted] 2014 M-533463-01-1	Winter barley Mucho	1) 23.10.2013 2) 29.04.2014 - 03.05.2014 3) 12.06.2014	Spraying	0.48	300	0.16	08.04.2014	Flag leaf stage	green material	8.2 <0.05	0 48	(g) 01429 (h) 0.05 mg/kg
									grain	0.034	63	(h) 0.01 mg/kg
									straw	0.35	63	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**	**Active substance**	**: ethephon**
Country	**: Germany**	**Crop/Crop Group**	**: Cereals**
Content of active substance (g/kg or g/L)	**: 480 g/L**	**Page**	**: 1- B**
Formulation (e.g. WP)	**: 480 SL**	**Indoor/outdoor**	**: Outdoor**
		Other a.s. in formulation (common name and content)	**:**
Commercial product (name)	**: Ethephon SL 480**	**Residues determined as**	**: HEPA**
Producer of commercial product	**: Bayer CropScience AG**	**Residues calculated as**	**: HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
14-2020 14-2020-01 [redacted] 2014 M-533463-01-1	Winter barley Limpid	1) 13.10.2013 2) 22.04.2014 - 29.04.2014 3) 17.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	08.04.2014	Flag leaf stage	green material grain straw	0.069 0.055 0.055 <0.05 <0.05 0.026 <0.05	0 7 14 21 42 72 72	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2020 14-2020-02 [redacted]2014 M-533463-01-1	Winter barley Graphic	1) 20.11.2013 2) 20.04.2014 - 27.04.2014 30.10.06.2014 - 10.07.2014	Spraying	0.411	342	0.12	08.04.2014	Mid boot stage	green material grain straw	0.14 <0.05 0.013 0.080	0 29 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	:	**Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	:	**480 g/L**	**Page**	:	**2- B**
Formulation (e.g. WP)	:	**480 SL**	**Indoor/outdoor**	:	**Outdoor**
			Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	**Ethephon SL 480**	**Residues determined as**	:	**HEPA**
Producer of commercial product	:	**Bayer CropScience AG**	**Residues calculated as**	:	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
14-2020 14-2020-03 [redacted] 2014 M-533463-01-1	Winter barley Lutece	1) 04.11.2013 2) 17.04.2014 - 27.04.2014 3) 05.06.2014 - 15.06.2014	Spraying	0.48	400	0.12	10.04.2014	Flag leaf stage	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 6 14 20 29	(g) 01429 (h) 0.05 mg/kg
									grain	<0.01	64	(h) 0.01 mg/kg
									straw	<0.05	64	(h) 0.05 mg/kg
14-2020 14-2020-04 [redacted] 2014 M-533463-01-1	Winter barley Mucho	1) 23.10.2013 2) 29.04.2014 - 03.05.2014 3) 12.06.2014	Spraying	0.48	300	0.16	08.04.2014	Flag leaf stage	green material	0.14 <0.05	0 48	(g) 01429 (h) 0.05 mg/kg
									grain	0.014	63	(h) 0.01 mg/kg
									straw	<0.05	63	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Wheat

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim
Country : Germany
Content of active substance (g/kg or g/L) : 480 g/L
Formulation (e.g. WP) : 480 SL

Commercial product (name) : Ethephon SL 480
Producer of commercial product : Bayer CropScience AG

Active substance : ethephon

Crop/Crop Group : Cereals
Page : 1- A
Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content) :
Residues determined as : ethephon
Residues calculated as : ethephon

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
13-2029 13-2029-01 [redacted] 2013 M-529493-01-1	Soft wheat Winnetou	1) 29.10.2012 2) 17.06.2013 - 24.06.2013 3) 10.08.2013 - 31.08.2013	Spraying	0.48	300	0.16	10.06.2013	Beginning of heading	green material	3.3 0.46 0.21 0.17 0.17	0 7 14 21 23	(g) 01429 (h) 0.05 mg/kg
									grain	0.059	75	(h) 0.01 mg/kg
									straw	0.36	75	(h) 0.05 mg/kg
13-2029 13-2029-03 [redacted]2013 M-529493-01-1	Soft wheat Matrix	1) 20.10.2012 2) 18.06.2013 - 03.07.2013 30.05.08.2013 - 12.08.2013	Spraying	0.48	300	0.16	12.06.2013	Beginning of heading	green material	3.1 0.16 0.11 0.11 0.11	0 8 14 21 29	(g) 01429 (h) 0.05 mg/kg
									grain	0.059	61	(h) 0.01 mg/kg
									straw	0.66	61	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	:	**Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	:	**480 g/L**	**Page**	:	**2- A**
Formulation (e.g. WP)	:	**480 SL**	**Indoor/outdoor**	:	**Outdoor**
			Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	**Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	:	**Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
13-2029 13-2029-04 [redacted] 2013 M-529493-01-1	Soft wheat Claire	1) 10.10.2012 2) 17.06.2013 - 24.06.2013 3) 01.08.2013 - 16.08.2013	Spraying	0.48	200	0.24	07.06.2013	Beginning of heading	green material grain straw	7.5 0.32 0.11 1.3	0 38 74 74	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropSCience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**1- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Plt) (days) (f)	Remarks
13-2029 13-2029-01 [redacted]2013 M-529493-01-1	Soft wheat Winnetou	1) 29.10.2012 2) 17.06.2013 - 24.06.2013 3) 10.08.2013 - 31.08.2013	Spraying	0.48	300	0.16	10.06.2013	Beginning of heading	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 23	(g) 01429 (h) 0.05 mg/kg
									grain	0.027	75	(h) 0.01 mg/kg
									straw	0.050	75	(h) 0.05 mg/kg
13-2029 13-2029-03 [redacted]2013 M-529493-01-1	Soft wheat Matrix	1) 20.10.2012 2) 18.06.2013 - 03.07.2013 3) 05.08.2013 - 12.08.2013	Spraying	0.48	300	0.16	12.06.2013	Beginning of heading	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 8 14 21 29	(g) 01429 (h) 0.05 mg/kg
									grain	0.029	61	(h) 0.01 mg/kg
									straw	<0.05	61	(h) 0.05 mg/kg

(a) **According to Codex (or other e.g. EU) Classification/Guide.**
(b) **Only if relevant.**
(c) **High or low volume spraying, spreading, dusting etc. overall broadcast.**
(d) **Year must be indicated.**
(e) **BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).**
(f) **DALT : Days after last treatment.**
(g) **Reference to analytical method.**
(h) **Limit of quantification**
(i) **Dosage of a.s. or water given as...**
(-) **Missing data in the above columns occurs where the information is not available in the original report.**

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**		**Active substance**	**:**	**ethephon**
Country	**: Germany**		**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**: 480 g/L**		**Page**	**:**	**2- B**
Formulation (e.g. WP)	**: 480 SL**		**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**: Ethephon SL 480**		**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**: Bayer CropScience AG**		**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment			Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg) (f)	DALT (Pfl (days) (f)	Remarks
				kg a.s./ha	Water (L/ha)	kg a.s./hL						
13-2029 13-2029-04 [redacted] 2013 M-529493-01-1	Soft wheat Claire	1) 10.10.2012 2) 17.06.2013 - 24.06.2013 3) 01.08.2013 - 16.08.2013	Spraying	0.48	200	0.24	07.06.2013	Beginning of heading	green material grain straw	0.076 0.050 0.080 0.083	0 38 74 74	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**: Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**: 480 g/L**	**Page**	**:**	**1- A**
Formulation (e.g. WP)	**: 480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
		Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**: Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**: Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT PHI (days) (f)	Remarks
14-2018 14-2018-01 [redacted] 2014 M-532267-01-1	Winter wheat Winnetou	1) 02.10.2013 2) 30.05.2014 - 12.06.2014 3) 25.07.2014 - 15.08.2014	Spraying	0.48	300	0.16	22.05.2014	Beginning of heading	green material grain straw	4.9 0.28 0.29 0.23 0.22 0.083 0.44	0 8 14 21 29 71 71	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2018 14-2018-02 [redacted] 2014 M-532267-01-1	Winter wheat Tobak	1) 30.09.2013 2) 26.05.2014 - 02.06.2014 3) 15.07.2014 - 15.08.2014	Spraying	0.48	300	0.16	21.05.2014	Beginning of heading	green material grain straw	7.0 0.23 0.14 1.2	0 26 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**2- A**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
14-2018 14-2018-03 [redacted] 2014 M-532267-01-1	Winter wheat Solstice	1) 10.10.2013 2) 04.06.2014 - 20.06.2014 3) 28.07.2014 - 15.08.2014	Spraying	0.48	200	0.24	25.05.2014	Beginning of heading	green material grain straw	7.0 0.39 0.27 0.17 0.12 0.23 1.2	0 7 15 22 36 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2018 14-2018-04 [redacted] 2014 M-532267-01-1	Winter wheat Rustic	1) 20.10.2013 2) 15.05.2014 - 25.05.2014 3) 01.07.2014 - 20.07.2014	Spraying	0.48	300	0.16	30.04.2014	Beginning of heading	green material grain straw	7.2 0.071 0.052 0.57	0 35 77 77	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**3- A**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
14-2018 14-2018-05 [redacted]2014 M-532267-01-1	Winter wheat Touareq	1) 01.11.2013 2) 10.06.2014 - 20.06.2014 3) 20.07.2014 - 01.08.2014	Spraying	0.48	400	0.12	30.05.2014	Beginning of heading	green material grain straw	5.9 0.23 0.31 1.5	0 32 54 54	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**	**Active substance**	**: ethephon**
Country	**: Germany**	**Crop/Crop Group**	**: Cereals**
Content of active substance (g/kg or g/L)	**: 480 g/L**	**Page**	**: 1- B**
Formulation (e.g. WP)	**: 480 SL**	**Indoor/outdoor**	**: Outdoor**
		Other a.s. in formulation (common name and content)	**:**
Commercial product (name)	**: Ethephon SL 480**	**Residues determined as**	**: HEPA**
Producer of commercial product	**: Bayer CropScience AG**	**Residues calculated as**	**: HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Days) (f)	Remarks
14-2018 14-2018-01 [redacted] 2014 M-532267-01-1	Winter wheat Winnetou	1) 02.10.2013 2) 30.05.2014 - 12.06.2014 3) 25.07.2014 - 15.08.2014	Spraying	0.48	300	0.16	22.05.2014	Beginning of heading	green material grain straw	0.085 <0.05 <0.05 <0.05 <0.05 0.031 <0.05	0 8 14 21 29 71 71	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 71: 0.013 mg/kg in control sample (h) 0.05 mg/kg
14-2018 14-2018-02 [redacted] 2014 M-532267-01-1	Winter wheat Tobak	1) 30.09.2013 2) 26.05.2014 - 02.06.2014 3) 15.07.2014 - 15.08.2014	Spraying	0.48	300	0.16	21.05.2014	Beginning of heading	green material grain straw	0.078 <0.05 0.040 0.15	0 26 68 68	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg day 68: 0.23 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**: Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**: Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**: 480 g/L**	**Page**	**:**	**2- B**
Formulation (e.g. WP)	**: 480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
		Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**: Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**: Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT/ PHI (days) (f)	Remarks
14-2018 14-2018-03 [redacted] 2014 M-532267-01-1	Winter wheat Solstice	1) 10.10.2013 2) 04.06.2014 - 20.06.2014 3) 28.07.2014 - 15.08.2014	Spraying	0.48	200	0.24	25.05.2014	Beginning of heading	green material grain straw	0.073 <0.05 <0.05 <0.05 <0.05 0.089 0.055	0 7 15 22 36 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 64: 0.043 mg/kg in control sample (h) 0.05 mg/kg
14-2018 14-2018-04 [redacted]2014 M-532267-01-1	Winter wheat Rustic	1) 20.10.2013 2) 15.05.2014 - 25.05.2014 3) 01.07.2014 - 20.07.2014	Spraying	0.48	300	0.16	30.04.2014	Beginning of heading	green material grain straw	0.087 <0.05 0.019 <0.05	0 35 77 77	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**3- B**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**HEPA**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT / PHI (days) (f)	Remarks
14-2018 14-2018-05 [redacted]2014 M-532267-01-1	Winter wheat Touareq	1) 01.11.2013 2) 10.06.2014 - 20.06.2014 3) 20.07.2014 - 01.08.2014	Spraying	0.48	400	0.12	30.05.2014	Beginning of heading	green material grain straw	0.062 <0.05 0.046 <0.05	0 32 54 54	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	:	**Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	:	**Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	:	**480 g/L**	**Page**	:	**1- A**
Formulation (e.g. WP)	:	**480 SL**	**Indoor/outdoor**	:	**Outdoor**
			Other a.s. in formulation (common name and content)	:	
Commercial product (name)	:	**Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	:	**Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT / PHI (days) (f)	Remarks
13-2030 13-2030-01 [redacted]2013 M-529488-01-1	Soft wheat Hystar	1) 23.10.2012 2) 18.05.2013 3) 10.07.2013 - 25.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material	5.7 0.50 0.31 0.24 0.16	0 7 14 21 45	(g) 01429 (h) 0.05 mg/kg
									grain	0.049	80	(h) 0.01 mg/kg
									straw	0.86	80	(h) 0.05 mg/kg
13-2030 13-2030-02 [redacted]2013 M-529488-01-1	Soft wheat Artur Nick	1) 28.12.2012 2) 15.04.2013 - 30.04.2013 30.01.06.2013 - 30.06.2013	Spraying	0.515	322	0.160	02.04.2013	Flag leaf stage	green material	17 0.21	0 43	(g) 01429 (h) 0.05 mg/kg
									grain	0.057	64	(h) 0.01 mg/kg
									straw	0.84	64	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**2- A**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Days) (f)	Remarks
13-2030 13-2030-03 [redacted]2013 M-529488-01-1	Soft wheat Quality	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 20.06.2013 - 31.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material	6.9 0.48 0.17 0.19 0.16	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg
									grain	0.13	63	(h) 0.01 mg/kg
									straw	1.7	63	(h) 0.05 mg/kg
13-2030 13-2030-04 [redacted]2013 M-529488-01-1	Soft wheat Serio	1) 07.11.2012 2) 06.05.2013 - 13.05.2013 30.01.07.2013 - 10.07.2013	Spraying	0.48	350	0.137	02.05.2013	Flag leaf stage	green material	5.6 0.050	0 25	(g) 01429 (h) 0.05 mg/kg
									grain	0.010	62	(h) 0.01 mg/kg
									straw	0.30	62	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**1- B**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**HEPA**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT / PHI (days) (f)	Remarks
13-2030 13-2030-01 [redacted] 2013 M-529488-01-1	Soft wheat Hystar	1) 23.10.2012 2) 18.05.2013 3) 10.07.2013 - 25.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material grain straw	0.27 <0.05 <0.05 <0.05 <0.05 0.037 0.051	0 7 14 21 45 80 80	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg day 80: 0.017 mg/kg in control sample (h) 0.05 mg/kg
13-2030 13-2030-02 [redacted] 2013 M-529488-01-1	Soft wheat Artur Nick	1) 28.12.2012 2) 15.04.2013 - 30.04.2013 3) 01.06.2013 - 30.06.2013	Spraying	0.515	322	0.160	02.04.2013	Flag leaf stage	green material grain straw	0.24 <0.05 0.029 <0.05	0 43 64 64	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropSCience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- B**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**HEPA**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
13-2030 13-2030-03 [redacted]2013 M-529488-01-1	Soft wheat Quality	1) 08.01.2013 2) 02.05.2013 - 13.05.2013 3) 20.06.2013 - 31.07.2013	Spraying	0.48	300	0.16	23.04.2013	Flag leaf stage	green material	<0.05 <0.05 <0.05 <0.05 <0.05	0 7 14 21 24	(g) 01429 (h) 0.05 mg/kg
									grain	0.044	63	(h) 0.01 mg/kg
									straw	0.12	63	(h) 0.05 mg/kg
13-2030 13-2030-04 [redacted]2013 M-529488-01-1	Soft wheat Serio	1) 07.11.2012 2) 06.05.2013 - 13.05.2013 30.01.07.2013 - 10.07.2013	Spraying	0.48	350	0.137	02.05.2013	Flag leaf stage	green material	0.11 <0.05	0 25	(g) 01429 (h) 0.05 mg/kg
									grain	0.014	62	(h) 0.01 mg/kg
									straw	0.058	62	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**1- A**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**ethephon**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
14-2019 14-2019-01 [redacted] 2014 M-532272-01-1	Winter wheat Soléhio	1) 25.10.2013 2) 14.05.2014 - 22.05.2014 3) 09.07.2014 - 20.07.2014	Spraying	0.48	300	0.16	23.04.2014	Flag leaf stage	green material grain straw	7.1 0.27 0.16 0.12 <0.05 0.025 0.29	0 7 14 21 41 77 77	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg
14-2019 14-2019-02 [redacted]2014 M-532272-01-1	Winter wheat Don Pedro	1) 17.12.2013 2) 05.04.2014 - 15.04.2014 30.01.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	17.03.2014	Flag leaf stage	green material grain straw	6.4 <0.05 0.011 0.21	0 39 72 72	(g) 01429 (h) 0.05 mg/kg (h) 0.01 mg/kg (h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	**:**	**Bayer CropScience AG, Monheim**	**Active substance**	**:**	**ethephon**
Country	**:**	**Germany**	**Crop/Crop Group**	**:**	**Cereals**
Content of active substance (g/kg or g/L)	**:**	**480 g/L**	**Page**	**:**	**2- A**
Formulation (e.g. WP)	**:**	**480 SL**	**Indoor/outdoor**	**:**	**Outdoor**
			Other a.s. in formulation (common name and content)	**:**	
Commercial product (name)	**:**	**Ethephon SL 480**	**Residues determined as**	**:**	**ethephon**
Producer of commercial product	**:**	**Bayer CropScience AG**	**Residues calculated as**	**:**	**ethephon**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (days) (f)	Remarks
14-2019 14-2019-03 [redacted]2014 M-532272-01-1	Winter wheat Mieti	1) 04.11.2013 2) 24.04.2014 - 05.05.2014 3) 25.06.2014 - 05.07.2014	Spraying	0.48	400	0.12	16.04.2014	Flag leaf stage	green material	10 0.82 0.30 0.30 0.26	0 7 14 21 30	(g) 01429 (h) 0.05 mg/kg
									grain	0.10	58	(h) 0.01 mg/kg
									straw	1.2	58	(h) 0.05 mg/kg
14-2019 14-2019-04 1 2005-019 [redacted] [redacted]2014 M-532272-01-1	Winter wheat Artur Nick 2	1) 04.11.2013 2) 20.03.2014 - 05.04.2014 30.10.06.2014 - 10.07.2014	Spraying	0.48	300	0.16	21.02.2014	Flag leaf stage	green material	16 0.075	0 60	(g) 01429 (h) 0.05 mg/kg
									grain	0.043	110	(h) 0.01 mg/kg
									straw	0.44	110	(h) 0.05 mg/kg

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address)	: **Bayer CropScience AG, Monheim**	**Active substance**	:	**ethephon**
Country	: **Germany**	**Crop/Crop Group**	:	**Cereals**
Content of active substance (g/kg or g/L)	: **480 g/L**	**Page**	:	**1- B**
Formulation (e.g. WP)	: **480 SL**	**Indoor/outdoor**	:	**Outdoor**
		Other a.s. in formulation (common name and content)	:	
Commercial product (name)	: **Ethephon SL 480**	**Residues determined as**	:	**HEPA**
Producer of commercial product	: **Bayer CropScience AG**	**Residues calculated as**	:	**HEPA**

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT (Pre Harvest Interval) (days) (f)	Remarks
14-2019 14-2019-01 [redacted]2014 M-532272-01-1	Winter wheat Soléhio	1) 25.10.2013 2) 14.05.2014 - 22.05.2014 3) 09.07.2014 - 20.07.2014	Spraying	0.48	300	0.16	23.04.2014	Flag leaf stage	green material	0.13 <0.05 <0.05 <0.05 <0.05	0 7 14 21 41	(g) 01429 (h) 0.05 mg/kg
									grain	0.019	77	(h) 0.01 mg/kg day 77: 0.015 mg/kg in control sample
									straw	0.079	77	(h) 0.05 mg/kg
14-2019 14-2019-02 [redacted]2014 M-532272-01-1	Winter wheat Don Pedro	1) 17.12.2013 2) 05.04.2014 - 15.04.2014 3) 01.06.2014 - 30.06.2014	Spraying	0.48	300	0.16	17.03.2014	Flag leaf stage	green material	0.087 <0.05	0 39	(g) 01429 (h) 0.05 mg/kg
									grain	0.019	72	(h) 0.01 mg/kg day 72: 0.023 mg/kg in control sample
									straw	0.092	72	(h) 0.05 mg/kg day 72: 0.12 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.

Document MCA: Section 6 Residues in or on treated products, food and feed
Ethephon

RESIDUE DATA FROM SUPERVISED TRIALS (SUMMARY)

(Application on agricultural and horticultural crops)

Responsible body for reporting (name and address) : Bayer CropScience AG, Monheim
Country : Germany
Content of active substance (g/kg or g/L) : 480 g/L
Formulation (e.g. WP) : 480 SL

Commercial product (name) : Ethephon SL 480
Producer of commercial product : Bayer CropScience AG

Active substance : ethephon

Crop/Crop Group : Cereals
Page : 2- B
Indoor/outdoor : Outdoor
Other a.s. in formulation (common name and content) :
Residues determined as : HEPA
Residues calculated as : HEPA

1	2	3	4	5			6	7	8	9	10	11
Study Trial No.; Plot Location incl. postal code Year of Trial	Commodity / Variety (a)	Date of 1) Sowing or planting 2) Flowering 3) Harvest 4) Transplanting (b)	Method of treatment (c)	Application rate per treatment kg a.s./ha	Water (L/ha)	kg a.s./hL	Dates of treatment(s)/ Application interval or no. of treatments and last date/ (d)	Growth stage at last treatment (e)	Portion analysed (a)	Residues (mg/kg)	DALT / PHI (days) (f)	Remarks
14-2019 14-2019-03 [redacted]2014 M-532272-01-1	Winter wheat Mieti	1) 04.11.2013 2) 24.04.2014 - 05.05.2014 3) 25.06.2014 - 05.07.2014	Spraying	0.48	400	0.12	16.04.2014	Flag leaf stage	green material	0.12 <0.05 <0.05 <0.05 <0.05	0 7 14 21 30	(g) 01429 (h) 0.05 mg/kg
									grain	0.042	58	(h) 0.01 mg/kg
									straw	<0.05	58	(h) 0.05 mg/kg
14-2019 14-2019-04 1 2005-019 [redacted] [redacted]2014 M-532272-01-1	Winter wheat Artur Nick 2	1) 04.11.2013 2) 20.03.2014 - 05.04.2014 3) 10.06.2014 - 10.07.2014	Spraying	0.48	300	0.16	21.02.2014	Flag leaf stage	green material	0.21 <0.05	0 60	(g) 01429 (h) 0.05 mg/kg
									grain	0.031	110	(h) 0.01 mg/kg day 110: 0.029 mg/kg in control sample
									straw	0.084	110	(h) 0.05 mg/kg day 110: 0.061 mg/kg in control sample

(a) According to Codex (or other e.g. EU) Classification/Guide.
(b) Only if relevant.
(c) High or low volume spraying, spreading, dusting etc. overall broadcast.
(d) Year must be indicated.
(e) BBCH Monograph, Growth Stages of Plants, 1997, (Blackwell, ISBN 3-8263-3152-4).
(f) DALT : Days after last treatment.
(g) Reference to analytical method.
(h) Limit of quantification
(i) Dosage of a.s. or water given as...
(-) Missing data in the above columns occurs where the information is not available in the original report.

Note: All entries to be filled in as appropriate. Date format dd.mm.yyyy.