QUINCLORAC (287)

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EXPLANATION

Quinclorac is a systemic herbicide used with uptake through roots and foliage and used to control annual grass and broadleaf weeds. It was evaluated in the 2015 JMPR for the first time for toxicology and for residues. The 2015 JMPR allocated an ADI of 0–0.4 mg/kg bw, and an ARfD of 2 mg/kg bw. It also determined that the definition of residue for plant commodities was quinclorac plus quinclorac conjugates for compliance with MRLs and quinclorac plus quinclorac conjugate plus quinclorac methyl ester expressed as quinclorac for estimation of dietary intake, and the definition of residue for animal commodities was quinclorac plus quinclorac conjugates for compliance with MRLs and for estimation of dietary intake. It recommended maximum residue levels for cranberry and rhubarb.

Quinclorac was included on the priority list by the CCPR at the 48th Session in 2016 for the evaluation for additional MRLs by this Meeting. The current Meeting received information on analytical methods, use patterns and supervised residue trials to support estimation of maximum residue level for rice and rape seed.

RESIDUE ANALYSIS

Analytical methods

The 2015 JMPR considered that Methods D9708/1 and R0036 overestimated the level of quinclorac in samples as the extraction with acetone/0.1 M NaOH converted quinclorac methyl ester partly into quinclorac. These analytical methods were not suitable of the determination of quinclorac in oilseed rape and possibly other pulses and oilseeds, where quinclorac methyl ester could be expected to be present.

The Meeting received a new analytical method developed in 2016 for more precise accounting of quinclorac and quinclorac methyl ester in rape seed. The new analytical method D1607/01 does not allow for the partial conversion of quinclorac methyl ester back to the quinclorac.

Analytical method D1607/01

The method was validated for the determination of parent quinclorac residues and quinclorac methyl ester residues in rape seed and forage (canola) using LC-MS/MS (Sharp, 2016: 2016/7009384). The total residues of quinclorac in rape seed and forage were determined in three consecutive extraction procedures. The residues of quinclorac plus quinclorac conjugates were reported in the third extraction step in which a basic hydrolysis step was applied to release the conjugates. Total residues of quinclorac were reported as the sum from each extraction procedure. Similarly, the total residues of quinclorac methyl ester in rape seed and forage were determined in two consecutive extraction procedures. Total residues of quinclorac methyl ester were reported as the sum from each extraction procedure and also reported as the parent equivalent.

First extraction (E1): for the determination of residues of quinclorac and quinclorac methyl ester.

Seed or forage samples (5 g) first extracted (E1) twice with acetonitrile-water (50:50, v/v). Salt I [Mixture of $MgSO_4$ (4 g), NaCl (1 g), trisodium citrate dihydrate (1 g) and disodium hydrogencitrate sesquihydrate (0.5 g)] is used to separate the organic phase and further clean-up. An aliquot of the combined organic layer is diluted with acetonitrile-water (10:90, v/v) and residues of quinclorac (residues from E1) are determined using LC-MS/MS. A second aliquot of the combined organic layer is diluted with methanol-water (50:50, v/v) and residues of quinclorac methyl ester (residues from E1) are determined using LC-MS/MS.

Second extraction (E2): for the determination of residues of quinclorac and quinclorac methyl ester.

For Seed, the sample marc with the remainder of the aqueous extract from the first extraction step (E1) is then mixed with acetone-10 mM phosphate buffer at pH 7 (50:50, v/v). Additional phosphate salts [sodium dihydrogen phosphate dehydrate (8 mg) and sodium dihydrogen phosphate 12-hydrate (18 mg)] are added to adjust molarity (10mM) and pH (~7). Samples are homogenized and centrifuged. The supernatant is decanted into a volumetric flask and brought to volume with additional acetone-10 mM phosphate buffer at pH 7 (50:50, v/v).

For Forage, the sample marc with the remainder of the aqueous extract from the first extraction step (E1) is then mixed with acetone. Additional phosphate salts [sodium dihydrogen phosphate dehydrate (8 mg) and sodium dihydrogen phosphate 12-hydrate (18 mg)] are added to adjust molarity (10mM) and pH (~7). Samples are homogenized and centrifuged. The supernatant (top organic layer only) is transferred with pipet into a volumetric flask and brought to volume with acetone-10 mM phosphate buffer at pH 7 (50:50, v/v).

For seed and forage, an aliquot of the above resulting extract is concentrated at 50 °C to aqueous phase using nitrogen evaporation. A liquid-liquid partition with hexane (twice) is conducted to isolate quinclorac methyl ester residues from the sample extract. An aliquot of the combined hexane layers is evaporated to dryness at 50 °C and residues are re-dissolved in methanol-water (50:50, v/v) for determination of quinclorac methyl ester (residues from E2) using LC-MS/MS. The aqueous phase remaining after the hexane liquid-liquid partition is then acidified to pH~2 and another liquid-liquid partition with dichloromethane (twice) is performed. An aliquot of the dichloromethane phase is evaporated to dryness at 50 °C, and residues are re-dissolved in acetonitrile-water (10:90, v/v) for determination of quinclorac (residues from E2) using LC-MS/MS.

Third extraction (E3): for the determination of residues of quinclorac.

The sample marc from the second extraction step (E2) is then treated with 1 N NaOH and heated at 100 °C for one hour. After cooling to room temperature, samples are centrifuged, the supernatant is decanted into a clean tube and is then acidified to ~ pH 2. The resulting aqueous extract is saturated with NaCl and is centrifuged to separate the aqueous extract from the marc. An aliquot of this extract is then subjected to single liquid-liquid partition with dichloromethane to isolate quinclorac residues. An aliquot of the dichloromethane layer is evaporated to dryness at 50 °C, and residues are re-dissolved in acetonitrile-water (10:90, v/v) for determination of quinclorac (residues from E3) using LC-MS/MS.

After each sample extraction and clean-up, residues are determined by LC-MS/MS, monitoring ion transitions at m/z 242→224 (quantitation) and m/z 242→161 (confirmation) for quinclorac, and m/z 256→224 (quantitation) and m/z 256→161 (confirmation) for quinclorac methyl ester. The results are calculated by direct comparison of the sample peak responses to those of external standards. The LOQ for residues of quinclorac and quinclorac methyl ester in/on rape seed and forage is 0.01 mg/kg.

The method validation (MV) was performed successfully in oilseed rape matrices (seed and forage) with the LC-MS/MS ion transitions (quantitation and confirmation) available for the method, using both matrix-matched calibration standards (to determine E1 and E2 residues of quinclorac and quinclorac methyl ester) and solvent-based standards (to determine E3 residues of quinclorac). Total quinclorac residues and total quinclorac methyl ester residues were used to assess method validation recovery.

The independent laboratory validation (ILV) was also conducted using two fortification levels (0.01 and 1.0 mg/kg) for rape seed (Perez, 2016: 2016/7009386). The results of MV and ILV are summarized in Table 1 and 2.

Table 1 Summary of Method Recoveries of quinclorac from oilseed rape matrices

Commodity	Fortification mg/kg	N	m/z 242→224 (quantitation)			m/z 242→161 (confirmation)			Ref.
			Range recovery (%)	Mean recovery (%)	% RSD	Range recovery (%)	Mean recovery (%)	% RSD	
Seed	0.01	5	69–79	75	5	66–78	74	7	Sharp, 2016
	1.0	5	81–98	89	7	82–97	89	7	2016/7009384
	0.01	5	92–97	95	2	92–99	94	4	Perez, 2016
	1.0	5	95–110	102	5	97–112	104	6	2016/7009386
Forage	0.01	5	105–109	107	2	105–109	108	1	Sharp, 2016
	1.0	5	113–122	118	3	112–122	119	3	2016/7009384

Table 2: Summary of Method Recoveries of quinclorac methyl ester from oilseed rape matrices

Commodity	Fortification mg/kg	N	m/z 256→224 (quantitation)			m/z 256→161 (confirmation)			
			Range recovery (%)	Mean recovery (%)	% RSD	Range recovery (%)	Mean recovery (%)	% RSD	
Seed	0.01	5	82–87	85	3	81–87	84	3	Sharp, 2016
	1.0	5	85–95	91	5	85–96	92	6	2016/7009384
	1.0*	3	90–93	92	2	91–94	92	2	
	0.01	5	94–98	96	2	91–99	96	3	Perez, 2016
	1.0	5	107–123	117	5	110–125	119	5	2016/7009386
Forage	0.01	5	104–112	108	3	104–111	108	3	Sharp, 2016
	1.0	5	104–122	116	7	104–122	116	7	2016/7009384
	1.0*	3	110–120	116	5	111–121	117	5	

* Fortified with only quinclorac methyl ester

The Meeting also received a multi-resiude analytical method for quinclorac in plant matrices and for quinclorac methyl ester in rape seed.

"QuEChERS" multi-residue method D1502/1

The "QuEChERS" multi-residue method D1502/1 was validated for the determination of quinclorac residues in plant matrices and for the determination of quinclorac methyl ester in rape seed by LC-MS/MS (Downs, 2016: 2015/7000570).

Parent quinclorac residues in/on homogenized plant samples (5 g each) - except dry matrices and rape seed (see below) – were extracted with acetonitrile by mechanical shaking. The residues in the extracts were cleaned-up and partitioned by shaking in the presence of a mixture of "QuEChERS" salts ($MgSO_4$, NaCl, trisodium citrate dihydrate and disodium hydrogencitrate sesquihydrate) into the organic layer, and centrifuged. The residues in an aliquot of the retained acetontrile layer were then further purified with the addition of a second "QuEChERS" salt mixture (containing $MgSO_4$ to remove residual water and C18 to remove non-polar interferences such as fats) and centrifuged. The residues in the organic phase were diluted to final volume with acetonitrile:water (10:90, v/v) and analysed by LC-MS/MS.

For dry/low-moisture content matrices (wheat grain, bean seed, rape seed), and for the separate analysis of quinclorac methyl ester in/on rape seed, the homogenized samples (5 g each) were hydrated first by the addition of water. The residues were then extracted and partitioned, as described above, and re-extracted with acetonitrile. The residues in an aliquot of the combined acetontrile extracts were further purified with the addition of the second "QuEChERS" salt mixture (described above) and centrifuged. The residues in the organic phase were diluted to final volume with acetonitrile:water (10:90, v/v) for quinclorac analyses, or with methanol-water (1:1, v/v) for quinclorac methyl ester analyses, and determined by LC-MS/MS. The validated LOQ for residues of quinclorac and quinclorac methyl ester in/on plant commodities is 0.01 mg/kg.

The independent laboratory validation (ILV) was also conducted using two fortification levels (0.01 and 1.0 mg/kg) for crop matrices (Sharp, 2015: 2015/7000966). The results of MV and ILV are summarized in Tables 3 and 4.

Table 3 Summary of Method Recoveries of quinclorac from plant matrices

Commodity	Fortification mg/kg	N	m/z 242→224 (quantitation)			m/z 242→161 (confirmation)			Ref.
			Range recovery (%)	Mean recovery (%)	% RSD	Range recovery (%)	Mean recovery (%)	% RSD	
Lettuce, leaves	0.01	5	112 – 121	116	3	110 – 122	116	4	Downs, 2016
	1.0	5	117 – 123	120	2	115 – 124	120	3	2015/7000570
	0.01	5	60 – 99	84	19	67 – 110	89	17	Sharp, 2015
	0.1	5	85 – 92	88	3	88 – 97	91	4	2015/7000966
Wheat, grain	0.01	5	105 – 113	109	3	103 – 112	108	3	Downs, 2016
	1.0	5	88 – 95	92	4	87 – 93	90	3	2015/7000570
	0.01	5	69 – 91	81	11	67 – 94	80	12	Sharp, 2015
	0.1	5	74 – 91	82	8	71 – 85	76	7	2015/7000966
Kidney bean, dried seed	0.01	5	72 – 102	85	14	71 – 103	85	15	Downs, 2016
	1.0	5	80 – 94	89	6	81 – 93	88	5	2015/7000570
	0.01	5	88 – 107	99	7	90 – 102	97	5	Sharp, 2015
	0.1	5	73 – 93	83	10	67 – 90	81	11	2015/7000966
Orange, fruit	0.01	5	116 – 122	120	2	120 – 127	123	2	Downs, 2016
	1.0	5	101 – 114	110	5	100 – 118	111	6	2015/7000570
	0.01	5	83 – 112	103	11	81 – 112	104	13	Sharp, 2015
	0.1	5	91 – 100	97	3	96 – 103	100	2	2015/7000966
Rape seed	0.01	5	79 – 90	83	5	82 – 88	84	3	Downs, 2016
	1.0	5	87 – 91	89	2	87 – 92	89	3	2015/7000570
	0.01	5	97 – 114	103	7	96 – 116	104	8	Sharp, 2015
	0.1	5	61 – 79	72	10	59 – 79	70	11	2015/7000966

Table 4 Summary of Method Recoveries of quinclorac methyl ester from oilseed rape seed

Commodity	Fortification mg/kg	N	m/z 256→224 (quantitation)			m/z 256→161 (confirmation)			
			Range recovery (%)	Mean recovery (%)	% RSD	Range recovery (%)	Mean recovery (%)	% RSD	
Rape seed	0.01	5	72 – 76	74	2	71 – 76	74	2	Downs, 2016
	1.0	5	82 – 88	86	3	82 – 88	85	3	2015/7000570
	0.01	5	72 – 81	75	5	70 – 80	73	6	Sharp, 2015
	0.1	5	76 – 87	83	5	74 – 85	82	5	2015/7000966

USE PATTERN

The Meeting received labels in Canada and the USA. The authorized uses relevant to the supervised residue trials data submitted to the current Meeting are summarized in Table 5.

Table 5 Registered uses of quinclorac relevant to the residue evaluation by the current Meeting

Crop	Country	Formulation		Application					PHI, days	notes
		Type	Conc. of quinclorac	Method	Growth stage	Rate kg ai/ha	Volume L/ha	No. max		
Cereal grains										
Rice	USA	SL	180 g/L	Ground or aerial spray	Do not apply to rice that is heading Rice must be in at least the 2-leaf stage	0.29-0.54	46.7-374	1	40	[a]
Oilseed										
Oilseed rape	Canada	SL	180 g/L	Ground spray	2-6 leaf stags	0.10	100	1	60	[b c]

[a] Do not plant any crop other than rice, spring or winter wheat, or grain sorghum for 10 months following application.

[b] Recropping interval: 10 - 22 months except wheat (spring, durum) and spring barley

[c] Grain and meal from treated oilseed rape can be fed to livestock. Do not graze or feed other portions of the treated oilseed rape to livestock.

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

The Meeting received information on quinclorac supervised field trials for the following crops.

Group	Commodity	Table No
Cereal grains	Rice	Table 6, 7
Oilseed	Rape seed	Table 8
Straw, fodder and forage of cereal grains and grasses	Rice straw and fodder, dry	Table 9, 10
Miscellaneous fodder and forage crops	Rape forage	Table 11

Quinclorac formulation was applied for ground or foliar treatment. Each of the field trial sites generally consisted of untreated control plot and treated plot. Residues, application rates and spray concentrations have generally been rounded to two significant figures.

Residue values from the trials, which have been used for the estimation of maximum residue levels, STMRs and HRs, are underlined.

Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Date of analyses and duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables except when residues were found in samples from control plots. Residue data are not corrected for percent recovery.

Conditions of the supervised residue trials were generally well reported in detailed field reports. Most field reports provided data on the sprayers used, plot size, field sample size and sampling date.

Cereal grains

Rice

A total of three field trials on rice were conducted in the USA during the 2016 growing season. The SL formulation was applied as one broadcast application at 0.57–0.58 kg ai/ha. The sprays were applied to rice 39–40 days prior to grain harvest and before heading. All applications were made in 171–186 L/ha water using ground equipment. Rice grain samples were collected 39–40 days after the last application. A minimum sample size of 1.0 kg of rice grain from each non-treated and treated plot was collected for all trials. The samples were transferred to freezers on the date of harvest (within 1.2 hours) and were shipped < 14 days later to the laboratory (Crawford, 2016: 2016/7009388).

Residues of quinclorac in rice grain samples were analysed by LC-MS/MS using the method D9708/1. Procedural recoveries of quinclorac fortified in control rice grain samples were 103 ± 12% (0.05 mg/kg), 70% (1.0 mg/kg) and 122% (10.0 mg/kg). The LOQ was 0.05 mg/kg for parent quinclorac in/on rice grain samples.

The maximum frozen storage interval from sampling to extraction for analysis was 78 days for rice grain samples. Studies investigating the freezer storage stability of quinclorac have been conducted, and residues were found to be stable in rice grain for at least 38 months when stored at freezer temperature (<-20 °C).

Table 6 Quinclorac residues on rice grain from supervised trials in the USA

Rice country, year (variety)	Application				DALA Days	Residues*, mg/kg		Ref
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
GAP, USA	*0.29-0.54*	46.7-374	*At least the 2-leaf stage but before heading*	*1*	*40*			
USA, 2016 Washington/ LA (Jupiter)	0.58	184	BBCH 41 (early boot stage)	1	39	3.3, 3.4	3.3	Sampling to analysis: 59-67 days
USA, 2016 Fisk/MO (CL111)	0.57	186	BBCH 45 (late boot stage)	1	40	1.6, 1.8	1.7	Sampling to analysis: 58-66 days
USA, 2016 East Bernard/ TX (Presidio)	0.57	171	BBCH 47 (flag leaf sheath open)	1	40	6.7, 9.2	7.9	Sampling to analysis: 70-78 days

* Quinclorac residues measured may actually include quinclorac released from conjugates.

Fourteen field trials were conducted in the principal rice growing regions of the USA. The data from these trials were submitted to the 2015 JMPR. Each trial consisted of an untreated control plot and a treated plot that received a single postemergence, broadcast spray application of the DF formulation at the target rate of 0.56 kg ai/ha, 40 days before normal harvest to flooded rice. Duplicate samples were collected for each matrix from each plot. At least twelve sub-samples were collected and combined to form each replicate sample of at least 2.0 kg for grain. All control and treated samples were placed into separate coolers with ice and transferred to separate freezers within 4 hours of collection (Zehr, 1997: 97/5051).

All samples were analysed for quinclorac residues by the method A8902 using GC-ECD. Control samples were fortified with a solution of quinclorac at a level of 0.05, 5.0 and 10.0 mg/kg, and analysed concurrently with the treated and control samples. Average recoveries of quinclorac were 80 ± 18% (n=13, 0.05 mg/kg fortification level), 84 ± 6.6% (n=7, 5.0 mg/kg fortification level) and 85 ± 12% (n=6, 10.0 mg/kg fortification level). The LOQ for method A8902 for rice grain was 0.05 mg/kg.

A maximum of 6 months lapsed between harvest and analysis of the samples for quinclorac. Storage stability data for rice grain has been collected and stability of quinclorac during frozen storage was demonstrated for 38 months. Therefore, no deterioration of quinclorac residues was expected to have occurred from the time of harvest until they were analysed.

Table 7 Quinclorac residues on rice grain from supervised trials in the USA (See JMPR 2015 Quinclorac Evaluation, Table 54)

Rice country, year (variety)	Application				DALA Days	Residues*, mg/kg		Trial
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
GAP, USA	*0.29-0.54*	46.7-374	*At least the 2-leaf stage but before heading*	*1*	*40*			
USA, 1996	0.56	94	Booting	1	34 37 40 43 46	0.37, 0.44 0.35, 0.39 0.37, 0.40 0.34, 0.35 0.31, 0.43	0.40 0.37 0.38 0.35 0.37	96152
USA, 1996	0.56	96	Booting	1	40	1.7, 1.9	1.8	96154
USA, 1996	0.56	94	Heading	1	34 37 41 43 46	3.2, 4.1 4.2, 4.5 3.7, 3.8 3.0, 3.6 3.7, 4.3	3.6 4.4 3.8 3.3 4.0	96155
USA, 1996	0.58	96	Heading	1	40	0.33, 0.37	0.35	96156
USA, 1996	0.57	94	Early boot	1	40	0.48, 0.63	0.56	96157
USA, 1996	0.56	97	Early boot	1	40	0.71, 0.82	0.77	96158

Rice country, year (variety)	Application				DALA Days	Residues*, mg/kg		Trial
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
USA, 1996	0.56	99	Early boot	1	40	0.43, 0.55	0.49	96159
USA, 1996	0.57	100	Early boot	1	41	0.25, 0.27	0.26	96160
USA, 1996	0.56	94	Three inch panicle	1	40	0.66, 0.91	0.79	96161
USA, 1996	0.57	95	2 inch panicle in the sheath	1	40	1.1, 1.1	1.1	96162
USA, 1996	0.56	102	Panicle initiation to three inch panicle	1	40	0.083, 0.14	0.11	96163
USA, 1996	0.58	96	Heading	1	40	1.5, 2.0	1.7	96164
USA, 1996	0.58	102	Full boot to 1% headed	1	40	0.68, 0.74	0.71	96166

* Quinclorac residues measured may actually include quinclorac released from conjugates.

Oilseeds

Rape seed

A total of nine field trials on oilseed rape (canola) were conducted in Canada and the USA during the 2016 growing season. The SL formulation was applied as one broadcast application at 0.10–0.11 kg ai/ha. The sprays were applied as a foliar broadcast to canola at the 2–6 leaf stage and 60 days prior to crop cutting for seed harvest. All applications were made in 100–105 L/ha of water using ground equipment (Crawford, 2016: 2016/7009389).

Canola was cut for seed samples 60 days after the least application (DALA). A minimum sample size of 1 kg of canola seed from each non-treated and treated plot was collected for all trials. Some seeds were not quite mature at the 60 DALA harvest interval, so additional seed samples were collected at seed maturity for trials SK, MB and ID. The canola samples were transferred to freezers (< 4.5 hours to long-term freezer storage) on the date of sample collection and were shipped < 22 days later to the laboratory.

Residues of quinclorac in canola samples were analysed by LC-MS/MS using the method D1607/01. Procedual recoveries of quinclorac and quinclorac methyl ester fortified in control canola seed samples were 74 ± 11% (quinclorac) and 96 ± 11% (quinclorac methyl ester) at 0.01 mg/kg, and 79 ± 20% (quinclorac) and 107% (quinclorac methyl ester) at 1.0 mg/kg. The LOQ for both analytes were 0.01 mg/kg.

The maximum frozen storage interval from sampling to extraction for analysis was 145 days for canola samples. Studies investigating the freezer storage stability of quinclorac and quinclorac methyl ester have been conducted, and resiudes were found to be stable for 22 months for canola seed when stored at freezer temperatures (<-20 °C).

Table 8 Quinclorac and quinclorac methyl ester residues on rape seed from supervised trials in Canada and the USA

Rape seed country, year (variety)	Application				DALA Days	Residues, mg/kg			Storage interval
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac [a]	Quinclorac methyl ester	Quinclorac methyl ester eq.[b]	
GAP, Canada	*0.10*	*100*	*2-6 leaf stage*	*1*	*60*				
USA, 2016 Northwood/ ND (L252)	0.10	101	BBCH 15-16	1	60	0.021, 0.023 mean 0.022	0.080, 0.094	0.076, 0.089 mean 0.082	Sampling to analysis 80-145 days
USA, 2016 Carrington/ ND (L252)	0.10	100	BBCH 15	1	60	0.033, 0.033 mean 0.033	0.14, 0.14	0.13, 0.13 mean 0.13	Sampling to analysis: 84-144 days
Canada, 2016 Branchton/ ON (Pioneer 46H75)	0.10	100	BBCH 16	1	60	0.054, 0.055 mean 0.055	0.20, 0.20	0.19, 0.19 mean 0.19	Sampling to analysis: 83-139 days

Rape seed country, year (variety)	Application				DALA Days	Residues, mg/kg			Storage interval
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac [a]	Quinclorac methyl ester	Quinclorac methyl ester eq.[b]	
Canada, 2016 Portage la Prairie/MB (Dekalb 74-44 BL)	0.10	104	BBCH 14	1	60	< 0.01, 0.010 mean 0.01	0.024, 0.023	0.023, 0.022 mean 0.022	Sampling to analysis: 88-145 days
Canada, 2016 Hanley/SK (Liberty Link L130 Invigor)	0.10	100	BBCH 14-15	1	60	0.014, 0.015 mean 0.015	0.050, 0.056	0.047, 0.053 mean 0.050	Sampling to analysis: 66-141 days
					83	< 0.01,< 0.01 mean < 0.01	0.052, 0.054	0.049, 0.051 mean 0.050	
Canada, 2016 Okanagan Falls/BC (Liberty Link Invigor)	0.10	102	BBCH 15-16	1	60	0.099, 0.11 mean 0.10	0.12, 0.12	0.11, 0.11 mean 0.11	Sampling to analysis: 71-123 days
Canada, 2016 Neepawa/MB (Dekalb 74-44 BL)	0.10	101	BBCH 14	1	60	0.012, 0.017 mean 0.015	0.024, 0.038	0.023, 0.036 mean 0.029	Sampling to analysis: 85-142 days
Canada, 2016 Brandon/MB (L252)	0.10	105	BBCH 12	1	60	< 0.01,< 0.01 mean < 0.01	< 0.01, 0.010	< 0.01,< 0.01 mean < 0.01	Sampling to analysis: 62-136 days
					85	< 0.01,< 0.01 mean < 0.01	< 0.01, < 0.01	< 0.01,< 0.01 mean < 0.01	
USA, 2016 American Falls/ID (Hyclass 930)	0.11	104	BBCH 13	1	60	0.016, 0.017 mean 0.017	0.069, 0.062	0.065, 0.059 mean 0.062	Sampling to analysis: 74-142 days
					77	< 0.01,< 0.01 mean < 0.01	0.040, 0.042	0.038, 0.040 mean 0.039	

[a] Quinclorac + quinclorac conjugate

[b] Quinclorac methyl ester equivalent to parent (mg/kg): 0.945 × quinclorac methyl ester

Straw, fodder and forage of cereal grains and grasses

Rice straw

A total of three field trials on rice were conducted in the USA during the 2016 growing season. The SL formulation was applied as one broadcast application at 0.57–0.58 kg ai/ha. The sprays were applied to rice 39–40 days prior to grain harvest and before heading. All applications were made in 171–186 L/ha water using ground equipment. Rice straw samples were collected 39–40 days after the last application. A minimum sample size of 0.5 kg of rice straw from each non-treated and treated plot was collected for all trials. The samples were transferred to freezers on the date of harvest (within 1.2 hours) and were shipped < 14 days later to the laboratory (Crawford, 2016: 2016/7009388).

Residues of quinclorac in rice straw samples were analysed by LC-MS/MS using the method D9708/1. Procedural recoveries of quinclorac fortified in control rice straw samples were 89% (0.05 mg/kg) and 107% (1.0 mg/kg). The limit of quantitation was 0.05 mg/kg for parent quinclorac in/on rice straw samples.

The maximum frozen storage interval from sampling to extraction for analysis was 78 days for rice straw samples. Studies investigating the freezer storage stability of quinclorac have been conducted, and residues were found to be stable in rice straw for at least 38 months when stored at freezer temperature (<-20 °C).

Table 9 Quinclorac residues on rice straw from supervised trials in the USA

Rice straw country, year (variety)	Application				DALA Days	Residues*, mg/kg		Ref
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
GAP, USA	*0.29-0.54*	46.7-374	*At least the 2-leaf stage but before heading*	*1*	*40*			
USA, 2016 Washington/ LA (Jupiter)	0.58	184	BBCH 41 (early boot stage)	1	39	2.4, 2.5	2.5	Sampling to analysis: 59-67 days
USA, 2016 Fisk/MO (CL111)	0.57	186	BBCH 45 (late boot stage)	1	40	2.8, 3.9	3.4	Sampling to analysis: 58-66 days
USA, 2016 East Bernard/ TX (Presidio)	0.57	171	BBCH 47 (flag leaf sheath open)	1	40	3.9, 4.8	4.4	Sampling to analysis: 70-78 days

* Quinclorac residues measured may actually include quinclorac released from conjugates.

Fourteen field trials were conducted in the principal rice growing regions of the USA. The data from these trials were submitted to the 2015 JMPR. Each trial consisted of an untreated control plot and a treated plot that received a single postemergence, broadcast spray application of the DF formulation at the target rate of 0.56 kg ai/ha, 40 days before normal harvest to flooded rice. Duplicate samples were collected for each matrix from each plot. At least twelve sub-samples were collected and combined to form each replicate sample of at least 1.0 kg for straw. All control and treated samples were placed into separate coolers with ice and transferred to separate freezers within 4 hours of collection (Zehr, 1997: 97/5051).

All samples were analysed for quinclorac residues by the method A8902 using GC-ECD. Control samples were fortified with a solution of quinclorac at a level of 0.05, 5.0 and 10.0 mg/kg, and analysed concurrently with the treated and control samples. Average recoveries of quinclorac were 82 ± 18% (n=12, 0.05 mg/kg fortification level), 84 ± 8.1% (n=7, 5.0 mg/kg fortification level) and 88 ± 12% (n=5, 10.0 mg/kg fortification level). The LOQ for method A8902 for rice straw was 0.05 mg/kg.

A maximum of 5 months lapsed between harvest and analysis of the samples for quinclorac. Storage stability data for rice straw has been collected and stability of quinclorac during frozen storage was demonstrated for 38 months. Therefore, no deterioration of quinclorac residues was expected to have occurred from the time of harvest until they were analysed.

Table 10 Quinclorac residues on rice straw from supervised trials in the USA (See JMPR 2015 Quinclorac Evaluation, Table 62)

Rice straw country, year (variety)	Application				DALA Days	Residues*, mg/kg		Ref
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
GAP, USA	*0.29-0.54*	46.7-374	*At least the 2-leaf stage but before heading*	*1*	*40*			
USA, 1996	0.56	94	Booting	1	34 37 40 43 46	0.26, 0.42 0.23, 0.33 0.28, 0.44 0.17, 0.35 0.22, 0.38	0.34 0.28 0.36 0.26 0.30	96152
USA, 1996	0.56	96	Booting	1	40	1.7, 1.8	1.8	96154
USA, 1996	0.56	94	Heading	1	34 37 41 43 46	1.5, 1.6 1.4, 2.4 1.2, 1.3 1.7, 2.0 1.3, 1.3	1.6 1.9 1.2 1.9 1.3	96155
USA, 1996	0.58	96	Heading	1	40	0.11, 0.13	0.12	96156
USA, 1996	0.57	94	Early boot	1	40	0.87, 1.1	0.96	96157

Rice straw country, year (variety)	Application				DALA Days	Residues*, mg/kg		Ref
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac	Mean	
USA, 1996	0.56	97	Early boot	1	40	1.1, 1.2	1.2	96158
USA, 1996	0.56	99	Early boot	1	40	0.62, 0.77	0.70	96159
USA, 1996	0.57	100	Early boot	1	41	1.2, 1.2	1.2	96160
USA, 1996	0.56	94	Three inch panicle	1	40	0.66, 1.6	1.1	96161
USA, 1996	0.57	95	2 inch panicle in the sheath	1	40	1.2, 1.4	1.3	96162
USA, 1996	0.56	102	Panicle initiation to three inch panicle	1	40	0.31, 0.47	0.39	96163
USA, 1996	0.58	96	Heading	1	40	1.9, 3.5	2.7	96164
USA, 1996	0.58	102	Full boot to 1% headed	1	40	0.76, 0.93	0.84	96166

* Quinclorac residues measured may actually include quinclorac released from conjugates.

Miscellaneous fodder and forage crops

Rape forage

A total of nine field trials on oilseed rape (canola) were conducted in Canada and the USA during the 2016 growing season. The SL formulation was applied as one broadcast application at 0.10–0.11 kg ai/ha. The sprays were applied as a foliar broadcast to canola at the 2–6 leaf stage and 60 days prior to crop cutting for seed harvest. All applications were made in 100–105 L/ha of water using ground equipment (Crawford, 2016: 2016/7009389).

Canola forage samples were collected 10–25 days after the last application. A minimum sample size of 1 kg of canola forage from each non-treated and treated plot was collected for all trials. The canola samples were transferres to freezers (< 4.5 hours to long-term freezer storage) on the date of sample collection and were shipped < 22 days later to the laboratory.

Residues of quinclorac in canola samples were analysed by LC-MS/MS using the method D1607/01. Procedual recoveries of quinclorac and quinclorac methyl ester fortified in control canola forage samples were 87 ± 8.1% (quinclorac) and 109 ± 8.5% (quinclorac methyl ester) at 0.01 mg/kg, and 97 ± 5.8% (quinclorac) and 113 ± 10% (quinclorac methyl ester) at 1.0 mg/kg. The LOQ for both analytes were 0.01 mg/kg.

The maximum frozen storage interval from sampling to extraction for analysis was 145 days for canola samples. Studies investigating the freezer storage stability of quinclorac and quinclorac methyl ester have been conducted, and resiudes were found to be stable for 22 months for canola seed when stored at freezer temperatures (<-20 °C).

Table 11 Quinclorac and quinclorac methyl ester residues on rape forage from supervised trials in Canada and the USA

Rape forage country, year (variety)	Application				DALA Days	Residues, mg/kg			Storage interval
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac [a]	Quinclorac methyl ester	Quinclorac methyl ester eq.[b]	
GAP, Canada	*0.10*	*100*	*2-6 leaf stage*	*1*					
USA, 2016 Northwood/ ND (L252)	0.10	101	BBCH 15-16	1	13	0.30, 0.33 mean 0.32	0.019, 0.023	0.018, 0.022 mean 0.020	Sampling to analysis 80-145 days
USA, 2016 Carrington/ ND (L252)	0.10	100	BBCH 15	1	10	0.30, 0.42 mean 0.36	0.014, 0.016	0.013, 0.015 mean 0.014	Sampling to analysis: 84-144 days
Canada, 2016 Branchton/ ON (Pioneer 46H75)	0.10	100	BBCH 16	1	15	0.18, 0.24 mean 0.21	0.014, 0.018	0.013, 0.017 mean 0.015	Sampling to analysis: 83-139 days
Canada, 2016 Portage la Prairie/MB	0.10	104	BBCH 14	1	17	0.071, 0.072 mean 0.072	< 0.01, < 0.01	< 0.01,< 0.01 mean < 0.01	Sampling to analysis: 88-145 days

Rape forage country, year (variety)	Application				DALA Days	Residues, mg/kg			Storage interval
	kg ai/ha	water, L/ha	Growth Stage	no.		Quinclorac [a]	Quinclorac methyl ester	Quinclorac methyl ester eq.[b]	
(Dekalb 74-44 BL)									
Canada, 2016 Hanley/SK (Liberty Link L130 Invigor)	0.10	100	BBCH 14-15	1	10	0.15, 0.17 mean 0.16	< 0.01, < 0.01	< 0.01,< 0.01 mean < 0.01	Sampling to analysis: 66-141 days
Canada, 2016 Okanagan Falls/BC (Liberty Link Invigor)	0.10	102	BBCH 15-16	1	10	0.61, 0.62 mean 0.62	0.037, 0.041	0.035, 0.039 mean 0.037	Sampling to analysis: 71-123 days
Canada, 2016 Neepawa/MB (Dekalb 74-44 BL)	0.10	101	BBCH 14	1	15	0.057, 0.087 mean 0.072	< 0.01, < 0.01	< 0.01,< 0.01 mean < 0.01	Sampling to analysis: 85-142 days
Canada, 2016 Brandon/MB (L252)	0.10	105	BBCH 12	1	25	< 0.01,0.010 mean < 0.01	< 0.01, < 0.01	< 0.01,< 0.01 mean < 0.01	Sampling to analysis: 62-136 days
USA, 2016 American Falls/ID (Hyclass 930)	0.11	104	BBCH 13	1	14	0.24, 0.29 mean 0.27	0.013, 0.015	0.012, 0.014 mean 0.013	Sampling to analysis: 74-142 days

[a] Quinclorac + quinclorac conjugate

[b] Quinclorac methyl ester equivalent to parent (mg/kg): 0.945 × quinclorac methyl ester

FATE OF RESIDUES IN STORAGE AND PROCESSING

In Processing

The 2015 JMPR has received information on the fate of quinclorac and its metabolite quinclorac methyl ester during processing of rice, wheat, and sorghum and rape seed. Since the current Meeting received the information to estimate maximum residue levels for rice and rape seed, the processing studies of rice and rape seed are shown below.

Rice

In one field trial conducted in the USA rice samples were taken from field plots treated with a single foliar application of 1.68 kg ai/ha (3 × GAP rate) and a PHI of 79 days (Single, 1989: 1989/5003). The samples were harvested at normal maturity and then processed into hulls and brown rice which was further processed into bran and white milled rice indicating that it is polished milled rice.

The milling process was designed to simulate commercial processing. The rough rice was shelled to remove hulls. The remaining brown rice was milled to remove the bran and to yield white milled rice. The processed fractions were homogenized and stored frozen. Rough rice was analysed 12 months after storage followed by the processed fraction 13 months after harvest.

All samples (10 g) were analysed for quinclorac according to method A8902. The method is designed to determine residues of quinclorac equivalents. The LOQ was 0.05 mg/kg. Spiked samples were run concurrently and the overall average recovery was 82 ± 11% (n=23). In the following table the residues found in the processed commodities are summarized.

Table 12 Residues of quinclorac in rice and rice processed products

country, year	Application		DALA Days	Commodity	Residues, mg/kg	Processing factor
	kg ai/ha	no.				
USA, 1989 TX	1.68	1	79	Grain (Rough rice) Hulls Husked rice (Brown rice) Bran (unprocessed) Polished rice (Milled rice)	0.43, 0.46 mean 0.45 0.45, 0.50 mean 0.48 0.45, 0.47 mean 0.46 1.2, 1.3, 1.4, 1.5 mean 1.35 0.33, 0.35 mean 0.34	 1.07 1.02 3 0.76

Residues in the hulls have been corrected for the control baseline. None of the other results were corrected for control or recovery values.

Rape seed

In two independent field trials in rape seed one conducted in Canada and the other in the USA samples of rape seed were taken from plots treated with 0.1 kg ai/ha (1 × GAP rate), 0.5 kg ai/ha (5 × GAP rate) and control plots (Guirguis, 1998: 1998/5093). The application was a broadcast spray made to the crop 60 days, before the rape seed was harvested and then processed.

The rape seed was dried at 54–71 °C to a moisture content of 7–10%. After aspiration separating light impurities, the sample is screened to separate large and small foreign particles (screenings) from the rape seed. The conditioned and cleaned oil seeds were flaked and pressed yielding crude oil, press cake (meal), refined oil and soap stock.

Whole seed were flaked with a gap setting of 4–5 mm. The flakes were heated to 82–99 °C and pressed to liberate most of the crude oil. Residual crude oil remaining in the solid material (press cake) exiting the expeller was extracted with the solvent hexane.

The press cake was placed in stainless steel batch extractors and submerged in 43–52 °C solvent (hexane). After 30 minutes, the hexane was drained and fresh hexane added to repeat the cycle two more times. After the final draining, warm air was forced through the extracted press cake to remove residual hexane.

The miscella (crude oil and hexane) was passed through a Precision Scientific Recovery unit to separate the crude oil and hexane. The crude oil was heated to 73–90 °C for hexane removal. The crude oil recovered from the expeller and solvent extraction was combined and refined. Before refining the crude oil was pre-treated with phosphoric acid. Refining is performed according to AOCS method Ca9a52. After refining, the refined oil and soap stock are collected.

Residues of quinclorac and quinclorac methyl ester were determined in rape seed, meal and refined oil. Samples (duplicate) were analysed for quinclorac according to method D9708/1 (LC-MS/MS) and for quinclorac methyl ester by the method D9806 (LC-MS/MS). The LOQ was 0.05 mg/kg for each analyte. Spiked samples were run concurrently for each analyte and the recovery for each of them ranged in rape seed, meal, and oil from 69–110%. In the following table the residues found processed products are summarized.

Table 13 Residues of quinclorac and quinclorac methyl ester in rape seed, meal and refined oil

country, year (variety)	Application			DALA Days	Commodity	Quinclorac + Quinclorac conjugate (A)		Quinclorac methyl ester (B)	For dietary intake estimation (A) + 10 × (B)	
	kg ai/ha	water, L/ha	no.			mg/kg	PF	mg/kg	mg/kg	PF
Canada, 1997 Lacombe/ Alberta (Quanturn)	0.10	50.7	1	60	seed meal refined oil	0.13 0.28 < 0.05	 2.2 < 0.39	0.24 < 0.05 0.29	2.53 0.78 2.95	 0.31 1.2
	0.51	50.6	1	60	seed meal refined oil	0.36 0.58 0.08	 1.6 0.22	1.0 0.082 1.36	10.36 1.40 13.68	 0.14 1.3

country, year (variety)	Application			DALA Days	Commodity	Quinclorac + Quinclorac conjugate (A)		Quinclorac methyl ester (B)	For dietary intake estimation (A) + 10 × (B)	
	kg ai/ha	water, L/ha	no.			mg/kg	PF	mg/kg	mg/kg	PF
USA, 1997 Northwood/ ND (Hyola 308)	0.099	51.4	1	60	seed meal refined oil	0.05 < 0.05 < 0.05	 <1 <1	0.054 < 0.05 0.055	0.59 < 0.55 0.60	 < 0.93 1.0
	0.50	51.6	1	60	seed meal refined oil	0.19 0.07 < 0.05	 0.36 < 0.26	0.30 0.45 0.20	3.19 4.57 2.05	 1.4 0.64

PF: Processing factor

RESIDES IN ANIMAL COMMODITES

Farm animal feeding studies

For the estimation of residues of quinclorac in animal matrices lactating cow and laying hen feeding studies was submitted to the 2015 JMPR.

Lactating cow

Residues in lactating cows were investigated by Mayer F (1989: 1989/5025). Fifteen lactating Friesian dairy cows, three cows/treatment group, were dosed orally, via capsule, for 28 consecutive days with quinclorac either 0 ppm (control), 1 ppm (1 × dose group), 10 ppm (10 × dose group), 50 ppm (50 × dose group) or 500 ppm (500 × dose group) corresponding to approximately 0.002 mg/kg bw, 0.02 mg/kg bw, 0.09 mg/kg bw and 0.9 mg/kg bw, respectively.

Milk was collected twice daily. On day 29 after the administration of the first dose, the animals were sacrificed and liver, kidney, muscle, peritoneal fat, and subcutaneous fat were collected for analysis. The maximum storage time under frozen conditions was for milk 31 days, subcutaneous fat 58 days, peritoneal fat 56 days and muscle 51 days.

Milk and tissues were analysed for the quinclorac using Method 268. The LOQ was 0.05 mg/kg. The LOD was 0.01 mg/kg.

Quinclorac residues in milk are presented in the following table. No residues greater than LOQ (0.05 mg/kg) were found in any milk samples, regardless of dose.

Table 14 Residues of quinclorac in milk after daily oral administration of quinclorac for 28 days

Days	Residues* in mg quinclorac-equivalents per kg			
	1 ppm	10 ppm	50 ppm	500 ppm
-1	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)
1	< 0.01 (3)			0.01, 0.014, 0.016 mean 0.013
2	< 0.01 (3)			< 0.01, 0.011, 0.035 mean 0.019
3	< 0.01 (3)			0.016, 0.026, 0.033 mean 0.025
4	< 0.01 (3)			0.032, 0.027, 0.038 mean 0.032
5	< 0.01 (3)			0.016, 0.018, 0.030 mean 0.021
6	< 0.01 (3)			0.018, 0.026, < 0.01 mean 0.018
7	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	0.013, 0.023, 0.024 mean 0.020
10	< 0.01 (3)			0.012, 0.014, 0.017 mean 0.014
12	< 0.01 (3)			0.01, 0.016, 0.02 mean 0.015
14	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01 (2), 0.013 mean 0.011
18	< 0.01 (3)			< 0.01, 0.011, 0.019 mean 0.013
21	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01 (2), 0.01 mean 0.01
23	< 0.01 (3)			< 0.01 (2), 0.01 mean 0.01
25	< 0.01 (3)			< 0.01 (3)
28	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01 (2), 0.012 mean 0.011

*based on limit of detection (LOD: 0.01 mg/kg), LOQ is 0.05 mg/kg

For lactating cow residues of quinclorac found in tissue after the end of the dosing period are presented in the table below.

Table 15 Residues of quinclorac in tissues from lactating cows after daily oral administration of quinclorac for 28 days

Tissue	Residues* in mg quinclorac-equivalents per kg			
	1 ppm	10 ppm	50 ppm	500 ppm
Fat, subcutaneous	< 0.01, < 0.01, 0.013 mean 0.005	< 0.01 (3)	< 0.01, 0.01 (2)	1.4, 0.11, 0.12 mean 0.54
Fat, peritoneal	< 0.01 (3)	< 0.01 (2), 0.023 mean 0.008	< 0.01 (2), 0.014 mean 0.005	0.25, 0.27, 0.20 mean 0.24
Muscle	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	0.037, 0.010, 0.033 mean 0.027
Kidney	0.010, 0.016, < 0.01 mean 0.012	0.082, 0.062, 0.074 mean 0.073	0.19, 0.17, 0.14 mean 0.17	2.6, 1.2, 1.5 mean 1.8
Liver	< 0.01 (2), 0.010 mean 0.010	0.014, 0.010, 0.020 mean 0.015	0.029, 0.026, 0.022 mean 0.026	0.33, 0.19, 0.28 mean 0.26

*based on limit of detection (LOD: 0.01 mg/kg), LOQ is 0.05 mg/kg

Laying hen

The residue of quinclorac has been studies in laying hens by Mayer, F (1989, 1989/5024). Adult hens (15 birds per diet group divided in 3 subgroups with five birds each, one control with four to three birds) were exposed for 28 consecutive days to levels of 1 ppm (1 × dose group), 10 ppm (10 × dose group) and 100 ppm feed/day (100 × dose group) corresponding to approximately (0.07, 0.7 and 7 mg/kg bw/day).

Eggs were collected during the whole dosing period. At sacrifice (day 28) samples of muscles, skin and subcutaneous fat, heart, gizzard, liver and kidney were sampled.

Eggs and tissues were analysed for the parent using Method 268. The LOQ was 0.05 mg/kg for the parent. The limit of detection was (LOD) was 0.01 mg/kg. The maximum storage time under frozen conditions was 90 days for eggs and 74 days for tissues.

In the following table the residues from eggs are summarized. No residues greater than LOQ (0.05 mg/kg) were found in any egg samples, regardless of the dose.

Table 16 Residues of quinclorac in eggs of laying hens after daily administration of quinclorac for 28 days

Days	Residues* in mg quinclorac-equivalents per kg		
	1 ppm	10 ppm	100 ppm
-1	< 0.01 (2)	< 0.01 (2)	< 0.01 (2)
1	< 0.01 (2)		< 0.01, 0.011
2	< 0.01 (2)		0.016, 0.013 mean 0.015
3	< 0.01 (2)		0.020, 0.023 mean 0.022
4	< 0.01 (2)		0.011, 0.019 mean 0.015
5	< 0.01 (2)		0.017, < 0.01 mean 0.014
6	< 0.01 (2)		0.024, 0.025 mean 0.025
7	< 0.01 (2)	< 0.01 (2)	0.032, 0.033 mean 0.033
10	< 0.01 (2)		0.016, 0.025 mean 0.021
12	< 0.01 (2)		0.021, 0.032 mean 0.027
14	< 0.01 (2)	< 0.01, 0.01	0.030, 0.019 mean 0.025
18	< 0.01 (2)		0.013, 0.016 mean 0.015
21	< 0.01 (2)	< 0.01 (2)	0.015, 0.033 mean 0.024
23	< 0.01 (2)		0.013, 0.031 mean 0.022
25	< 0.01 (2)		0.036, 0.041 mean 0.039
28	< 0.01 (2)	< 0.01 (2)	0.036, 0.024 mean 0.030

*based on limit of detection (LOD: 0.01 mg/kg), LOQ is 0.05 mg/kg

For laying hen tissue residues of quinclorac found in tissue after end of dosing period are presented in the following table.

Table 17 Residues of quinclorac in tissues of laying hens after daily administration of quinclorac for 28 days

Tissue	Residues* in mg quinclorac-equivalents per kg		
	1 ppm	10 ppm	100 ppm
Skin and subcutaneous fat	< 0.01, 0.013, 0.018 mean 0.014	0.012, 0.013, 0.017 mean 0.014	0.475, 0.760, 0.122 mean 0.45
Muscle dark	< 0.01 (3)	< 0.01 (3)	0.045, 0.022, 0.025 mean 0.031
Muscle light	< 0.01 (3)	< 0.01 (3)	0.068, 0.039, 0.018 mean 0.042
Kidney	< 0.01, 0.021, < 0.01 mean 0.014	0.015, 0.011, < 0.01 mean 0.012	0.558, 0.235, 0.456 mean 0.42
Liver	< 0.01 (3)	0.012, < 0.01, 0.013 mean 0.012	0.128, 0.042, 0.054 mean 0.075

*based on limit of detection (LOD: 0.01 mg/kg), LOQ is 0.05 mg/kg

APPRAISAL

Quinclorac is a systemic herbicide used with uptake through roots and foliage and used to control annual grass and broadleaf weeds. It was evaluated by the 2015 JMPR for the first time for toxicology and for residues. The 2015 JMPR allocated an ADI of 0–0.4 mg/kg bw, and an ARfD of 2 mg/kg bw. It also determined that the definition of residue for plant commodities was quinclorac plus quinclorac conjugates for compliance with MRLs and quinclorac plus quinclorac conjugate plus quinclorac methyl ester expressed as quinclorac for estimation of dietary intake, and the definition of residue for animal commodities was quinclorac plus quinclorac conjugates for compliance with MRLs and for estimation of dietary intake. It recommended maximum residue levels for cranberry and rhubarb.

Quinclorac was included on the priority list by the CCPR at the 48th Session in 2016 for evaluation for additional uses by the current Meeting. The current Meeting received information on analytical methods, use patterns and supervised residue trials to support estimation of maximum residue levels for rice and rape seed.

Methods of analysis

The Meeting received a new analytical method D1607/01 developed in 2016 for more precise accounting of quinclorac and quinclorac methyl ester in rape seed. The method D1607/01 did not convert quinclorac methyl ester back into quinclorac.

The total residues of quinclorac in rape seed and forage were determined in three consecutive extraction procedures. For the 1st extraction, samples were extracted with acetonitrile/water (1/1). Parent quinclorac and quinclorac methyl ester were determined using LC-MS/MS. For the 2nd extraction, the seed and forage marc with aqueous phase from the 1st extraction were extracted with acetone/10 mM phosphate buffer at pH 7 (1/1) and with acetone, respectively. Parent quinclorac and quinclorac methyl ester were determined using LC-MS/MS. For the 3rd extraction, the marc from the 2nd extraction was treated with 1N NaOH at 100 °C for 1 hour. This harsh hydrolysis to release quinclorac conjugates was used in the plant metabolism study for rape seed. Quinclorac and quinclorac conjugates were determined as quinclorac using LC-MS/MS. After each sample extraction and clean-up, residues are determined by LC-MS/MS, monitoring ion transitions at m/z 242→224 (quantitation) and m/z 242→161 (confirmation) for quinclorac, and m/z 256→224 (quantitation) and m/z 256→161 (confirmation) for quinclorac methyl ester. Total residues of quinclorac were reported as the sum from each extraction procedure. Similarly, the total residues of quinclorac methyl ester

were determined in two consecutive extraction procedures and reported as the sum from each extraction procedure. The LOQ for residues of quinclorac and quinclorac conjugates was 0.01 mg/kg, and the LOQ for residues of quinclorac methyl ester was 0.01 mg/kg in/on rape seed and forage.

The Meeting also received a multi-residue analytical method D1502/1 for quinclorac in plant matrices and for quinclorac methyl ester in rape seed.

Parent quinclorac residues in/on homogenized plant samples (5 g each) - except dry matrices and rape seed – were extracted with acetonitrile and cleaned-up by a mixture of "QuEChERS" salts ($MgSO_4$, NaCl, trisodium citrate dihydrate and disodium hydrogen citrate sesquihydrate). The residues in the organic phase were diluted with acetonitrile/water (10/90, v/v) and analysed by LC-MS/MS. For dry/low-moisture content matrices (wheat grain, bean seed, rape seed), and for the separate analysis of quinclorac methyl ester in/on rape seed, the homogenized samples (5 g each) after hydration with water were extracted and partitioned, as described above, and re-extracted with acetonitrile. The residues in an aliquot of the combined acetontrile extracts were further purified with the addition of the second "QuEChERS" salt mixture (described above). The residues in the organic phase were diluted with acetonitrile/water (10/90, v/v) for quinclorac analyses, or with methanol/water (1/1, v/v) for quinclorac methyl ester analyses, and determined by LC-MS/MS. The LOQ for residues of quinclorac and quinclorac methyl ester in/on plant commodities is 0.01 mg/kg.

The methods are suitable for the analysis of quinclorac and quinclorac methyl ester residues in rape seed and forage.

Stability of residues in stored analytical samples

The freezer storage stability studies were reported on rice (grain and straw) and rape seed samples to the 2015 JMPR. Storage stability results indicated that quinclorac residues were stable for at least 38 months in rice (grain and straw) and at least 22 months in rape seed, and quinclorac methyl ester residues were stable for at least 22 months in rape seed. The periods of storage stability studies generally cover the sample storage intervals of residue trials.

Residues resulting from supervised residue trials on crops

The Meeting received supervised trial data for the broadcast spray application of quinclorac on rice and oilseed rape from the USA.

Labels were available from Canada and the USA describing the registered uses of quinclorac.

The 2015 JMPR noted that quinclorac methyl ester has a toxicological potency up to 10 times that of quinclorac. In calculating residue values for dietary intake estimation the Meeting agreed to use the following formula: residues = (quinclorac + quinclorac conjugate) + 10 × quinclorac methyl ester.

The 2015 JMPR also noted quinclorac methyl ester in cereals at levels up to 10 percent of quinclorac in the metabolism study and agreed to use to the following formula to estimate levels for use in dietary intake calculations:

HR/STMR = (quinclorac + quinclorac conjugate) + 10 × 0.1 (quinclorac + quinclorac conjugate)

= 2 × (quinclorac + quinclorac conjugate)

Rice

The supervised trials were conducted on rice in the USA during the 1996 (submitted to the 2015 JMPR) and 2016 growing seasons.

The GAP on rice in the USA is one broadcast application at a maximum rate of 0.50 kg ai/ha from at least the 2-leaf stage to before heading with a PHI of 40 days.

Quinclorac residues (quinclorac + quinclorac conjugate) in rice grains from independent trials in the USA matching GAP for maximum residue level estimation were (n=12): 0.11, 0.26, 0.38, 0.49, 0.56, 0.71, 0.77, 1.1, 1.7, 1.8, 3.3 and 7.9 mg/kg.

Based on the quinclorac residues for rice grains from trials in the USA, the Meeting estimated a maximum residue level of 10 mg/kg and a median residue value for livestock feed of 0.74 mg/kg for quinclorac in rice.

Residues for dietary intake estimation (2 × (quinclorac + quinclorac conjugate)) in rice grains were (n=12): 0.22, 0.52, 0.76, 0.98, 1.1, 1.4, 1.5, 2.2, 3.4, 3.6, 6.6 and 16 mg/kg.

Based on the residues for dietary intake estimation in rice grains, the Meeting estimated an STMR value of 1.45 mg/kg for rice.

Rape seed

Data were available from supervised trials on oilseed rape in Canada and the USA. Residues of quinclorac and quinclorac methyl ester in oilseed rape samples were analysed using the new analytical method D1607/1.

The GAP on oilseed rape of Canada is one broadcast application at rate of 0.10 kg ai/ha and a PHI of 60 days.

Quinclorac residues (quinclorac + quinclorac conjugate) in rape seeds from independent trials in Canada and the USA matching GAP for a maximum residue level estimation were (n=9): < 0.01, 0.01, 0.015 (2), 0.017, 0.022, 0.033, 0.055 and 0.10 mg/kg.

Based on the quinclorac residues for rape seeds from trials in Canada and the USA, the Meeting estimated a maximum residue level of 0.15 mg/kg and a median residue value for livestock feed of 0.017 mg/kg for quinclorac in rape seed.

Quinclorac methyl ester residues expressed as quinclorac equivalents in rape seeds from independent trials in Canada and the USA matching GAP were (n=9): < 0.01, 0.022, 0.029, 0.050, 0.062, 0.082, 0.13, 0.11 and 0.19 mg/kg.

Residues for dietary intake estimation ((quinclorac + quinclorac conjugate) + 10 × quinclorac methyl ester) in rape seeds were (n=9): < 0.11, 0.23, 0.31, 0.52, 0.64, 0.84, 1.2, 1.3 and 2.0 mg/kg.

Based on the residues for dietary intake estimation in rape seeds, the Meeting estimated an STMR value of 0.64 mg/kg for rape seed.

Animal feedstuffs

Rice straw and fodder, dry

Data were available from supervised trials on rice in the USA during the 1996 (submitted to the 2015 JMPR) and 2016 growing seasons.

The GAP on rice of the USA is one broadcast application at a maximum rate of 0.50 kg ai/ha from at least the 2-leaf stage to before heading and a PHI of 40 days.

Quinclorac residues (quinclorac + quinclorac conjugate) in rice straw (as received) from independent trials in the USA matching GAP were (n=12): 0.36, 0.39, 0.70, 0.84, 0.96, 1.2 (2), 1.3, 1.8, 2.5, 3.4 and 4.4 mg/kg.

Based on the quinclorac residues for rice straw, the Meeting estimated a median residue value of 1.2 mg/kg and a highest residue value of 4.4 mg/kg on an “as received” basis and after correction for an average 90% dry matter content, estimated a maximum residue level of 8 mg/kg for quinclorac in rice straw.

Rape forage

Data were available from supervised trials on oilseed rape in Canada and the USA.

The GAP on oilseed rape in Canada is one broadcast application at a rate of 0.10 kg ai/ha and a PHI of 60 days. Grain and meal from treated oilseed rape can be fed to livestock, while other portions of the treated oilseed rape must not be grazed or fed to livestock.

Since the Canadian GAP does not allow grazing or feeding rape forage to livestock, the Meeting agreed not to estimate a median residue value and a highest residue value for rape forage.

Fate of residues during processing

Residues in processed commodities

The 2015 JMPR received information on the fate of incurred residues of quinclorac during the processing of rice and rape seed. Residues of quinclorac and quinclorac methyl ester were determined in rape seed, meal and refined oil using analytical method D9708/1 (quinclorac) and D9806 (quinclorac methyl ester). Method D9708/1 is not suitable of the determination of quinclorac in rape seed because extraction with acetone/0.1 M NaOH converts quinclorac methyl ester partly into parent quinclorac. However, since the ratios of the residues in processed commodities were estimated as processing factors, the results of the study using method D9708/1 were acceptable.

Estimated processing factors and the derived STMR-Ps are summarized in the Table below.

Processing factors, STMR-P for food and feed

Raw agricultural commodity (RAC)	Processed commodity	Calculated processing factor	RAC STMR or median residue (mg/kg)	STMR-P (mg/kg)	Median residue (mg/kg)
Rice	Husked rice	1.0	1.45 (STMR)	1.45	-
	Polished rice	0.76		1.1	-
	Husked rice	1.0	0.74 (median residue)	-	0.74
	Hulls	1.1		-	0.81
	Bran, unprocessed	3		-	2.2

Raw agricultural commodity (RAC)	Processed commodity	Processing factor (PF)				**RAC**	
		Quinclorac + quinclorac conjugate		(Quinclorac + quinclorac conjugate) + 10 × quinclorac methyl ester		STMR (mg/kg)	median residue (mg/kg)
		Calculated [a]	PF [b]	Calculated [a]	PF [b]		
Rape seed	Meal	0.36, <1, 1.6, 2.2	1.3	-	-	-	0.017
	Refined oil	-	-	0.64, 1.0, 1.2, 1.3	1.1	0.64	-

[a] Each value represents a separate study. The factor is the ratio of the residue in the processed commodity divided by the residue in the RAC.

[b] Mean or best estimate

The Meeting estimated a maximum residue level of 10 mg/kg (10 × 1.0 = 10 mg/kg) for husked rice and 8 mg/kg (10 × 0.76 = 7.6 mg/kg) for polished rice.

The Meeting estimated an STMR value of 0.70 mg/kg (0.64×1.1 = 0.70 mg/kg) for rape seed refined oil and a median residue value of 0.022 mg/kg (0.017×1.3 = 0.022 mg/kg) for rape seed meal.

Residue in animal commodities

Farm animal dietary burden

The Meeting estimated the dietary burden of quinclorac in farm animals on the basis of the diets listed in Appendix IX of the FAO Manual third edition, 2016. Calculations from the highest residue, STMR (some bulk commodities) and STMR-P values provide levels in feed suitable for estimating MRLs, while calculations using STMR and STMR-P values for feed are suitable for estimating STMR values for animal commodities. The percentage dry matter is taken as 100% when the highest residue levels and STMRs are already expressed on a dry weight basis.

Estimated maximum and mean dietary burdens of farm animals

The calculations were made according to the animal rations from US-Canada, EU, Australia and Japan in the Table (Appendix IX of the FAO manual).

Potential feed items include: rice grains, rice hulls, rice bran, rice straw and rape seed meal.

Livestock dietary burden, quinclorac, ppm of dry matter diet								
	US-Canada		EU		Australia		Japan	
	Max	Mean	Max	Mean	Max	Mean	Max	Mean
Beef cattle	0.535	0.535	0.494	0.138	**3.91**[a]	**1.78**[b]	3.18	1.23
Dairy cattle	0.535	0.535	0.736	0.558	**2.13**[c]	**1.42**[d]	1.47	0.584
Poultry – broiler	0.413	0.413	0.244	0.244	0.911	0.911	0.123	0.123
Poultry – layer	0.413	0.413	0.125	0.125	**0.911**[e]	**0.911**[f]	0.493	0.493

[a] Highest maximum beef cattle dietary burden suitable for MRL estimates for mammalian meat, fat and edible offal

[b] Highest mean beef cattle dietary burden suitable for STMR estimates for mammalian meat, fat and edible offal

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

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

[e] Highest maximum layer poultry dietary burden suitable for MRL estimates for poultry meat, fat, edible offal and eggs

[f] Highest mean layer poultry dietary burden suitable for STMR estimates for poultry meat, fat, edible offal and eggs

Farm animal feeding studies

The 2015 JMPR received lactating dairy cow and laying hen feeding studies using quinclorac, which provided information on likely residues resulting in animal commodities and milk from quinclorac residues in the animal diet.

Animal commodities maximum residue levels

For MRL estimation, the residue in the animal commodities is quinclorac and quinclorac conjugates.

Residues in tissues and milk at the expected dietary burden for beef and dairy cattle are shown in the Table below. Residues of quinclorac in milk were only detected at levels of 500 ppm in the diet.

	Feed level (ppm) for milk residues	Residues (mg/kg) in milk	Feed level (ppm) for tissue residues	Residues (mg/kg) in			
				Muscle	Liver	Kidney	Fat
MRL beef or dairy cattle							
Feeding study	1 10	< 0.05 < 0.05	1 10	< 0.05 < 0.05	< 0.05 < 0.05	< 0.05 0.082	< 0.05 < 0.05
Dietary burden and residue estimate	2.13	< 0.05	3.91	< 0.05	< 0.05	0.060	< 0.05
STMR beef or dairy cattle							
Feeding study	1 10	< 0.05 < 0.05	1 10	< 0.05 < 0.05	< 0.05 < 0.05	< 0.05 0.073	< 0.05 < 0.05
Dietary burden and residue estimate	1.42	< 0.05	1.78	< 0.05	< 0.05	0.052	< 0.05

Based on the highest estimated residue in milk (< 0.05 mg/kg), the Meeting estimated a maximum residue level of 0.05 (*) mg/kg in milk.

Based on the highest estimated residue in fat (< 0.05 mg/kg), the Meeting estimated a maximum residue level of 0.05 (*) mg/kg in mammalian fat and meat (fat).

Based on the highest estimated residue in kidney (0.060 mg/kg), the Meeting estimated a maximum residue level of 0.1 mg/kg in mammalian edible offal.

Based on the highest estimated residues in tissues, the Meeting estimated HR values of 0 mg/kg in mammalian muscle, 0.060 mg/kg in mammalian edible offal and 0.05 mg/kg in mammalian fat.

Based on the mean estimated residues in tissues and milk, the Meeting estimated STMR values of 0 mg/kg in milk, 0 mg/kg in mammalian muscle, 0.052 mg/kg in mammalian edible offal and 0.05 mg/kg in mammalian fat.

Residues in tissues and eggs at the expected dietary burden for broiler and layer poultry are shown in the Table below.

	Feed level (ppm) for egg residues	Residues (mg/kg) in eggs	Feed level (ppm) for tissue residues	Residues (mg/kg) in			
				Muscle	Liver	Kidney	Skin & Fat
MRL broiler or layer poultry							
Feeding study	1	< 0.05	1	< 0.05	< 0.05	< 0.05	< 0.05
Dietary burden and residue estimate	0.911	< 0.05	0.911	< 0.05	< 0.05	< 0.05	< 0.05
STMR broiler or layer poultry							
Feeding study	1	< 0.05	1	< 0.05	< 0.05	< 0.05	< 0.05
Dietary burden and residue estimate	0.911	< 0.05	0.911	< 0.05	< 0.05	< 0.05	< 0.05

Based on the highest estimated residue in eggs (< 0.05 mg/kg), the Meeting estimated a maximum residue level of 0.05 (*) mg/kg in eggs.

Based on the highest estimated residue in fat (< 0.05 mg/kg), the Meeting estimated a maximum residue level of 0.05 (*) mg/kg in poultry fat and meat (fat).

Based on the highest estimated residue in kidney (< 0.05 mg/kg), the Meeting estimated a maximum residue level of 0.05 (*) mg/kg in poultry edible offal.

Based on the highest estimated residues in tissues and eggs, the Meeting estimated HR values of 0 mg/kg in eggs, 0 mg/kg in poultry muscle, 0.05 mg/kg in poultry edible offal and 0.05 mg/kg in poultry fat.

Based on the mean estimated residues in tissues and eggs, the Meeting estimated STMR values of 0 mg/kg in eggs, 0 mg/kg in poultry muscle, 0.05 mg/kg in poultry edible offal and 0.05 mg/kg in poultry fat.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting concluded that the residue levels listed below are suitable for estimating maximum residue limits and for IEDI and IESTI assessment.

Definition of the residue (for compliance with the MRL) for plant commodities: *Quinclorac plus quinclorac conjugates*

Definition of the residue (for estimation of dietary intake) for plant commodities: *Quinclorac plus quinclorac conjugates plus quinclorac methyl ester expressed as quinclorac*

Definition of the residue (for compliance with the MRL and for estimation of dietary intake for animal commodities): *Quinclorac plus quinclorac conjugates*

The residue is fat soluble

Commodity		Recommended MRL, mg/kg	STMR or STMR-P, mg/kg	HR or HR-P, mg/kg
CCN	Name	New		
MO 0105	Edible offal (mammalian)	0.1	0.052	0.060
PE 0112	Eggs	0.05*	0	0
MF 0100	Mammalian fats (except milk fats)	0.05*	0.05	0.05
MM 0095	Meat (from mammals other than marine mammals)	0.05* (fat)	0.05 fat 0 muscle	0.05 fat 0 muscle
ML 0106	Milks	0.05*	0	
PO 0111	Poultry, Edible offal of	0.05*	0.05	0.05
PF 0111	Poultry fats	0.05*	0.05	0.05
PM 0110	Poultry meat	0.05* (fat)	0.05 fat 0 muscle	0.05 fat 0 muscle
SO 0495	Rape seed	0.15	0.64	-
GC 0649	Rice	10	1.45	-
CM 0649	Rice, husked	10	1.45	-
CM 1205	Rice, polished	8	1.1	-
AS 0649	Rice straw and fodder, dry	8 (DW)	1.2 (as received)	4.4 (as received)

* at or about the LOQ.

Table of additional STMR and HR values for use in dietary intake estimation

Commodity name	STMR or STMR-P, mg/kg	Median residue, mg/kg
Rape seed meal	0.022	-
Rape seed oil, edible	0.70	-
Rice bran, unprocessed	-	2.2
Rice grain	-	0.74
Rice hulls	-	0.81
Rice, husked	-	0.74

DIETARY RISK ASSESSMENT

Long-term dietary exposure

The International Estimated Daily Intakes (IEDIs) of quinclorac were calculated for the 17 GEMS/Food cluster diets using STMRs/STMR-Ps estimated by the 2015 and the current Meeting (Annex 3). The ADI is 0–0.4 mg/kg bw and the calculated IEDIs were 0–1% of the maximum ADI (0.4 mg/kg bw). The Meeting concluded that the long-term dietary exposures to residues of quinclorac, resulting from uses considered by the JMPR, are unlikely to present a public health concern.

Short-term dietary exposure

The International Estimated Short-Term Intakes (IESTI) of quinclorac were calculated for food commodities and their processed commodities using HRs/HR-Ps or STMRs/STMR-Ps estimated by the current Meeting (Annex 4). The ARfD is 2 mg/kg bw and the calculated IESTIs were a maximum of 1% of the ARfD for the general population and 2% of the ARfD for children. The Meeting concluded that the short-term dietary exposure to residues of quinclorac, when used in ways that have been considered by the current JMPR, is unlikely to present a public health concern.

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