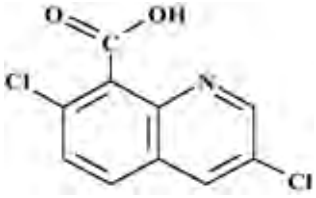
QUINCLORAC (287)

First draft was prepared by Dr Anita Stromberg, National Food Agency, Uppsala, Sweden

EXPLANATION

Quinclorac (ISO common name) is a quinone carboxylic herbicide used to control annual grass and broadleaf weed species in barley, canary seed, rape seed (canola), non-crop areas, pasture, rhubarbs cranberry, rice, sorghum and wheat. The herbicide has an auxin activity similar to that of indolylacetic acid and belongs to the auxin-type class of herbicides that includes the phenoxy-acids, benzoic acids and pyridine compounds.. The use of quinclorac results in the rupture of the cell membranes due to overstimulation of the growth of the plant. Quinclorac is mainly adsorbed via the root system and partly through foliage, mainly for the pre- and post-emergence control of *Echinocloa* spp, but also other weeds like *Aeschynomene* spp., *Sesbania* spp., and *Ipomoea* spp. occurring in direct-seeded and transplanted rice. Quinclorac was scheduled by the 46h session of the CCPR (2014) as a new compound for consideration by the 2015 JMPR.

IDENTITY

ISO common name	Quinclorac
Chemical name, IUPAC	3,7-dichloroquinoline-8-carboxylic acid
Chemical name, CA	3,7-dichloro-8-quinoline carboxylic acid
CIPAC No.	493
CAS No.	84087-01-4
Structural formula	
Molecular formula	$C_{10}H_5Cl_2NO_2$
Molecular mass	242.1 g/mol

PHYSICAL AND CHEMICAL PROPERTIES

Property	Results	Method (test material)	Reference
Appearance	Off-white powder		JMPS, Quinclorac 2002 Evaluation report 493/2002
Melting point	The melting point quinclorac pure (99.8%): 272.4-276.9 °C The melting point of quinclorac technical (purity 98.7) at atmospheric pressure is 279.9°C.	OECD 102	JMPS, Quinclorac 2002 Evaluation report 493/2002 Kroehl, T. 2010 2010/1057264
Boiling point	No boiling point of quinclorac technical (purity 99, 8%) before melting. At the end of melting gas evolution begins.	OECD 102	Daum, A. 1999 1999/11542
Relative density	Quinclorac technical (purity 99.8%): $D_4^{20} = 1.68$	EEC A3, OECD 109	Kästel, R. 2001 2001/1010797
Vapour pressure	Quinclorac technical (purity 98.7%): 4.9×10^{-11} mbar (hPa) at 25ºC 1.9×10^{-11} mbar (hPa) at 20ºC	OPPTS 830.7950	Kroehl, T. 2010, 2010/1057264
Henry´s law constant Coefficient	Henry´s law constant at 20 ºC (calculated) 3.381×10^{-13} kPa m3 / mol	Calculation	Ohnsorge, U, 2001 2001/1014896
Physical state, colour	Quinclorac, pure: white crystals	OECD 102	Daum, A. 1999

Property	Results		Method (test material)	Reference
				1999/11542
Odour	Quinclorac, pure: odourless		OECD 102	Daum, A. 1999 1999/11542
	Quinclorac technical; characteristic odour, free from visible extraneous matter and added modifying agents			JMPS, Quinclorac 2002 Evaluation report 493/2002
Solubility in water at 20ºC including effect of pH	Quinclorac, pure: 80.1 mg/L at pH 3 61.5 mg/L at PH 6.1		OECD 105 EC A.6	Daum, A. 2005 2005/1005667
	Quinclorac, (purity 99.8%) 0.072 g/l at pH 5.5 (deionized water) 75.9 g/l at pH 10.3 (NaOH, 0.1 Mol/l		EEC A8, by extrapolation	JMPS, Quinclorac 2002 Evaluation report 493/2002
Solubility in organic solvents	g/L 20 ºC:		OECD 105 EC A.6.	Daum, A. 2005 2005/1008919
	Methanol	2.7		
	Acetone	2.8		
	Ethyl acetate	0.9		
	dichloromethane	0.5		
	Toluene	0.006		
	n-heptane	0.003		
Dissociation in water	Quinclorac, pure (99.4%): Quinclorac has the character of an acid pKa = 4.34 at 20ºC pKa = 4.35 at 25ºC		OECD 112, titration method	Redeker, DC 1988 88/0137 JMPS, Quinclorac 2002 Evaluation report 493/2002
Partition coefficient n-octanol/water	Quinclorac technical (purity 99.4%): log Pow = 1.78 (at pH 4) log Pow = -0.72 (at pH 7)		OECD 117 (HPLC-method)	Daum, A. 2005 2005/1005668
	Quinclorac technical (purity 99.8%): log POW = 1.76 at 20 °C (at pH 4) log POW = -0.74 at 20 °C (at pH 7) log POW = -3.74 at 20 °C (at pH 10)		EEC A8, by extrapolation	JMPS, Quinclorac 2002 Evaluation report 493/2002
Hydrolysis rate	Half-life > 30 days at 25 °C (at pH 5, pH 7 and pH 9).		US-EPA Assessment guidelines, Subdiv. N, 161-2 (1982)	JMPS, Quinclorac 2002 Evaluation report 493/2002
Photochemical characteristics	In sterile aqueous buffer solution pH 7 using artificial light in the wavelength 300-800 nm at 25ºC. Half-life = approx. 100 days (continuous illumination) Half-life = approx. 43 days (sensitized, = 0.5% acetone),		EPA 161-2	Ellenson, JL. 2001 2001/5000828
	Half life = ca. 100 days (nonsensitized, sterile solution, calculated for continuous illumination) Half life = ca. 43 days (sensitized , sterile solution, calculated for continuous illumination) Experimental setup: solution in water (sterile), pH 7, 25°C, simulated sunlight at 805 w/m², for 660 h over 35 d (15 h light, 9 h dark, illuminated at weekends). Result: Half life > 30 days (dark control solution, non-sensitized, sterile, see hydrolysis) The results were used to extrapolate the half life values above. Half -life > 30 days (dark control solution, non-sensitized sterile)		US-EPA Assessment guidelines, Subdiv. N, 161-2 (1982)	JMPS, Quinclorac 2002 Evaluation report 493/2002

Hydrolysis of quinclorac

A hydrolysis study was carried out by Hassink, J (2005/1016370). Quinclorac at a concentration of 29.9 µg/L was investigated in aqueous solution at pH 4, 5, 7 and 9 at 25 ºC. Samples were taken 0, 2, 7, 9, 11, 14, 21 and 30 days after treatment and analysed using LC/MS.

A summary of the results is presented in the table below.

Table 1 Summary of hydrolysis of quinclorac at pH 4, pH 5, pH 7 and pH 9 at 25ºC

DAT [a]	pH4		pH5		pH7		pH9	
	µg/L	%[b]	µg/L	%[b]	µg/L	%[b]	µg/L	%[b]
0	28.8	100	28.5	100	27.6	100	27.5	100
2	28.6	99.3	27.8	97.5	27.6	100	27.7	100.7
7	29.3	101.7	28.4	99.6	28.0	101.4	28.1	102.2
9	29.1	101.0	28.2	98.9	29.3	106.2	28.7	104.4
11	31.6	109.7	30.6	107.4	29.8	108.0	30.0	109.1
14	29.3	101.7	29.1	102.1	29.0	105.1	29.5	107.3
21	28.0	97.2	29.4	103.2	29.1	105.4	28.6	104.0
30	29.4	102.1	29.3	102.8	28.7	104.0	28.7	104.4

[a] DAT = days after treatment

[b] % of initial applied test item, concentration of day 0 set to 100%

Formulations

Quinclorac is applied as a single active ingredient in different formulations.

Table 2 Available formulations of containing quinclorac as active ingredient

Formulation	Content of active ingredient
WP (wettable powder)	50% w/w
WG (wettable granules)	75% w/w
SC (suspension concentrates)	250 g/L
SL (soluble concentrates)*	180 g/L
FL (liquid flowable)*	40% w/w
DF (dry flowable)*	75% w/w

* Formulation in registered label presented to the 2015 JMPR Meeting

METABOLISM AND ENVIRONMENTAL FATE

Metabolism studies were conducted using 2, 3, 4-[^{14}C]-quinclorac (quinolone-label, Fig. 3) or 3-[^{14}C]-quinclorac (quinolone-label, Fig 2). In strawberry the [^{14}C]-quinclorac (quinolone-label, Fig. 3) was used. The position of the labels for both substances is presented in the following figures:

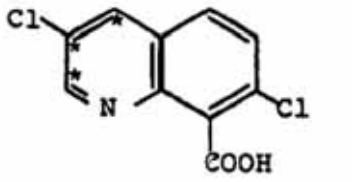


Figure 1 2, 3, 4-[^{14}C]-quinclorac

*location of the radiolabel

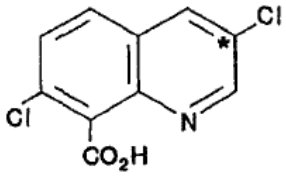


Figure 2 3-[^{14}C]-quinclorac

*location of the radiolabel

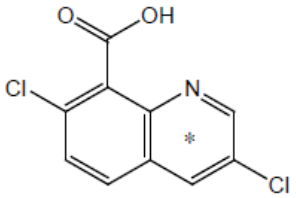
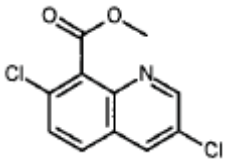
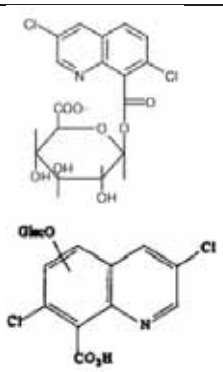
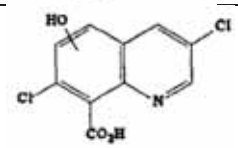


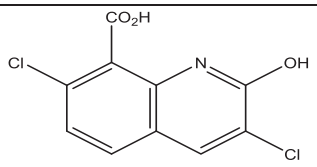
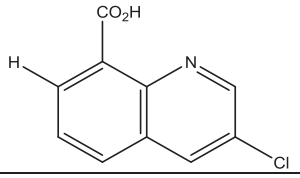
Figure 3 [^{14}C]-quinclorac

*location of the radiolabel

Chemical names, structures and code names of metabolites and degradation products of quinclorac are presented in the table below.

Table 3 Known metabolites of quinclorac from studies provided in animal, plants and soil matrices

Codes	Molecular formula and Nominal mass	Structure	Occurrence
BH 514-Me Reg. No. 161555 Quinclorac methyl ester SES218	$C_{11}H_7Cl_2NO_2$ methyl-3,7-dichloroquinoline-8-carboxylate 255		rats[1] canola sorghum rotational crops (mustard green, turnip, barley) soil (terrestrial aerial metabolism)
BAS 514 H M1 glucuronide (glucuronic acid) conjugate Quinclorac glucose conjugate	419		rat[1] goat hen wheat strawberry
Hydroxy-quinclorac	Hydroxy-quinclorac 257		wheat

Codes	Molecular formula and Nominal mass	Structure	Occurrence
BH 514-2-OH 2 -hydroxyquinclorac	$C_{10}H_5Cl_2NO_2$ 3,7-dichloro-2-hydroxyquinoline-8-carboxylic acid 258		soil (terrestrial metabolism)
BH 514-1 3-chloroquinoline-8-carboxylic acid	$C_{10}H_6ClNO_2$ 3-chloroquinoline-8-carboxylic acid 207.6		soil (aquatic metabolism)

Animal metabolism

The Meeting received metabolism studies on laboratory animals, poultry and lactating goats using the 2, 3, 4-[^{14}C]-quinclorac (quinoline label).

Laboratory animals

Rats

In rats given 2, 3, 4-[^{14}C]-quinoline labelled quinclorac orally absorption was rapid and accounted for at least 85.5% given a single administration of low and high doses (15 mg/kg and 600 mg/kg bw, respectively). The maximum plasma concentration of radioactivity was reached approximately 30 minutes after administration of the low or high dose. The half life in plasma was 3-4 hours for the low dose and 12-13 hours for the high dose. Radioactivity was widely distributed throughout the body. Elimination of radioactivity was mainly via urine (> 91%) for both female and male rates, while faecal excretion ranged from 0.7 to 3.7% of the dose. The bile was a minor route of excretion of the low dose but was found to be a significant route after administration the high dose (600mg/kg). Minor radioactivity was excreted in the faeces of intact rats dosed at this level, indicating that the greater part of the biliary excreted radioactivity was reabsorbed and eliminated via urine.

Biotransformation of quinclorac was minimal. The parent and one metabolite (a glucuronide of quinclorac) was identified in the urine. The metabolism of quinclorac was characterized in the bile where > 18 minor (< 10% TRR) metabolites were identified. The metabolism is characterized by two primary reactions; nucleophilic substitution of the chlorine atom at the isocycle with glutathione and formation of an arene oxide intermediate followed by reactions with glutathione to form S-conjugates and/or by addition of water to form hydroxylated derivatives. Metabolite M1 (glucuronic acid conjugates of quinclorac) was the major metabolite identified in the liver and kidney

Livestock

Lactating goats

The kinetic behaviour and the metabolism of 2, 3, 4-[^{14}C] quinclorac was investigated by Hawkins *et al.* (1986, BASF 86/0434, 1987 BASF 86/0473).

One lactating goat (47 kg) was dosed orally daily for five days with 34 mg radiolabelled quinclorac per kg bodyweight/day (1600 mg/animal/day, equivalent to 800 ppm in the diet). The goat was sacrificed 6 hours after the last dose. Milk, plasma, urine and faeces were collected during the whole dosing period. After sacrifice liver, kidney, fat and loin muscle were sampled.

Analysis of the total radioactive residue (TRR) was carried out using combustion and or liquid scintillation counting (LSC). In total 66.7% of applied radioactivity was recovered in the experiment. The relatively low recovery of applied radioactivity is explained by unabsorbed radioactivity within gastrointestinal tract due to the termination of the sacrifice of the animal relatively early, 6 hours after the final dose. The passage time of material within the GI tract of ruminants can be up to 72 hours. The GI tract was not analysed for TRR. Excretion of radioactivity in

urine, faeces and milk accounted for 63.0%, 3.7% and 0.003%, respectively of the total dose up to 6 hours after the final dose.

The TRR found in organs and tissues were about 0.2% of the applied radioactivity, with levels being highest in kidney (10.3 mg eq/kg) followed by liver (2.13 mg eq/kg), fat (subcutaneous: 0.78 mg eq/kg, omental 0.14 mg eq/kg) and muscle (leg: 0.19 mg eq/kg, loin: 0.16 mg eq/kg). In milk the TRR level increased from 0.034 mg eq/kg directly after the first administration up to 0.055 mg eq/kg after two days, then down to 0.032 mg eq/kg at day three and back to 0.056 mg eq/kg day, a plateau level was thus not reached. The TRR levels found are summarized in Table 4. The radioactivity in milk over time is presented in table 5.

Table 4 TRR in goats milk and tissue after daily oral administration for five days with 2, 3, 4-^{14}C-quinclorac at 34 mg/kg bw/ day (equivalent to 800 ppm in the diet) 6 h after sacrifice.

Matrix	% of total (cumulative)dose administrated	TRR (mg eq/kg)
Liver	0.12	2.13
Kidney	0.10	10.3
Leg muscle	n.r.	0.19
Loin muscle	n.r	0.16
Omental fat	n.r.	0.14
Subcutaneous fat	n.r.	0.78
Total in organs and tissue	0.22	13.7
Milk 0-102h	0.003	see table 5
Urine, 0-120 h*	47.8	
cage washes	15.2	
Faeces, 0-120 h	3.7	
Total excreted in urine, cage washes, faeces	66.7	
Total excreted in organ, tissue milk, urine, cage washes .and faeces	66.92	
Bile**	n.r.	4.7
Plasma**	n.r.	2.09
Whole-blood	n.r.	1.44

* Includes cages washes

** Concentration is expressed as µg equivalents quinclorac/mL

n.r. not reported

Table 5 Concentration of radioactivity in milk during after daily oral administration of 3, 4-^{14}C-quinclorac at 34 mg/kg bw/ day (equivalent to 800 ppm in the diet) to one goat for five days

Time period (hours after first dose)	one goat TRR (mg eq/kg) milk		
	afternoon collection	morning collection*	mean concentration (total 24 h collection)
0-24	0.052	0.025	0.034
24-48	0.088	0.043	0.055
48-72	0.078	0.026	0.038
72-96	0.039		0.032
96-102	0.056		0.056

***** Refers to morning following the afternoon collection immediately prior to the next dose..

Milk (day 2, PM) was mixed with methanol to precipitate the proteins. After centrifugation the methanolic extracts were reduced by evaporation and mixed with 1 M HCl. The extract was fractionated by column chromatography (C-8, octylsilane). The column was washed sequentially with 1 M HCl and hexane followed by elution with ethyl acetate. The ethyl acetate extracts were evaporated to dryness and reconstituted in methanol.

Liver and kidney samples were homogenized and extracted with 1 M HCl/ethyl acetate (1:10, v/v) for 10-20 min followed by centrifugation. The ethyl acetate extracts were evaporated to dryness and reconstituted in methanol.

Fat and muscle samples were extracted with water/ethanol (1:9, v/v) and 1 M NaOH , followed by extraction with methanol. Both extracts were combined, concentrated by evaporation and mixed with 1 M HCl. The extract was fractionated as described for milk.

The extraction efficiency was generally > 90% TRR except in muscle where it was 83% TRR. In muscle tissue 17% TRR (mg eq/kg not given) of the residue was not extracted and attempts to further extract this solid material was not performed. Identification of the radioactivity in extracts and column fractions was done using TLC in five different solvent systems. The reference substance used was the parent quinclorac which was confirmed on TLC plates by the quenching of UV fluorescence at 254 nm.

Quinclorac is not significantly metabolized in the goat. Parent quinclorac was present at levels >80% TRR in milk, liver and kidney. The metabolite M1 (glucuronic acid conjugate of the parent) was present at levels of 4.0% TRR in milk and at 4.7% TRR in kidney. Three other unidentified fractions (R01, R03 and R05) were found at levels of 0.4–5.4% TRR in milk, liver and kidney.

Since the methods used to extract the residues included 1 M HCl, it is not clear whether parent compound represents parent only or includes parent released from conjugates and whether the M1 is the fraction of conjugates that remained uncleaved.

Table 6 Characterization and identification of compounds in milk, tissues and urine of the lactating goat after administration of 2, 3, 4-^{14}C-quinclorac at 34 mg/kg bw/day (800 ppm in the diet)

Compound/fraction	Milk day 2 PM 0.088 mg/kg eq	Loin muscle 0.16 mg/kg eq	subcu taneous fat 0.78 mg/kg eq	Liver 2.13 mg/kg eq	Kidney 10.3 mg/kg eq	Urine %TRR*	
	%TRR*	%TRR*	%TRR*	%TRR*	%TRR*	0-24 h	96-102h
Total identified	91.1			81.3	91.2	98	96.6
- Quinclorac	86.1	***	***	81.3	86.5	95.1	95.4
- M1 (R02)	4.0				4.7	2.9	1.2
Total characterized	6.9			5.6	4.4	0.19	3.4
- R01-1	1.2			1.8**	2.0	0.7	1.5
- R01-3	0.3				0.4	0.5	0.2
- R01-5	5.4			3.8	2.0	0.7	1.7
Total extracted	97.0	82.6	100.0	86.9	95.6	99.9	100
- Post extracted solids	3.7	17.4	-	13.1	4.4	0	0

* Relative % of total sample radioactivity

** Includes more than 2 regions of interest (rf 41-53)

***. not quantified because of the low levels of radioactivity; qualitatively all radioactivity co-chromatographed with parent compound

M1 is glucuronic acid conjugate of parent

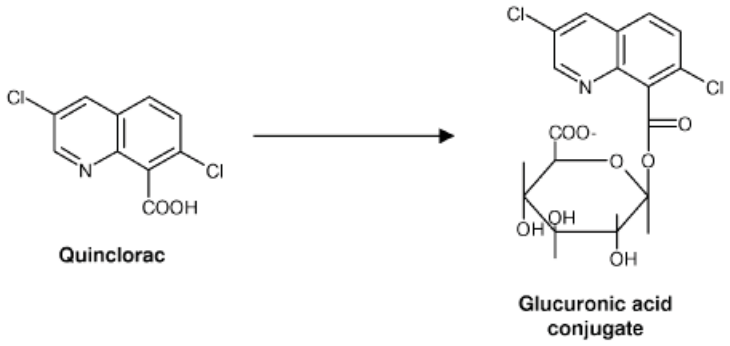


Figure 4 Metabolic pathway from available data in lactating goat

Laying hens

The kinetic behavior and the metabolism of 2, 3, 4-^{14}C-quinclorac in laying hens was investigated by Hawkins et al. (1986, BSF 1986/5003). Seven birds (366-372) were selected from a group of 15 birds based on egg laying records. These hens (1.8–2.4 kg) were orally dosed once for five days with 33–44 mg radiolabelled quinclorac per kg body weight per day (80 mg/bird/day) corresponding to 800 ppm in the diet (based on a food consumption of 100 g/day). Excreta and eggs were collected daily during the dosing period. The number of laid egg varied significantly from hen to hen. For example two birds did not lay any eggs during the study, and for two of the birds all eggs were broken and no eggs collected during the sampling time point. The birds were sacrificed 6 hours after the last dose and liver ,kidney, muscle, skin with underlying fat were collected. Blood samples were collected just prior to sacrifice and separated by centrifugation into plasma and cells.

Total radioactivity was measured in excreta, eggs and tissues using combustion and/or LSC. The TRR levels found in tissues and eggs (in concentration and per eggs) are summarized in Tables 7 and 8. Excretion of radioactivity in excreta was 87.5–95.1% of the applied radioactivity up to 6h after the final dose. The total radioactive residue (TRR) were highest in the kidney (0.77–88.98 mg eq/kg), followed by liver (0.26–10.53 mg eq/kg), plasma (0.14–13.50 mg eq/kg), whole blood (0.09–9.41 mg eq/kg), skin/fat (0.23–7.2 mg eq/kg and leg muscle (0.05–3.95 mg eq/kg). Plasma levels and tissue concentration obtained at sacrifice, 6 hours after the final dose, showed considerable inter-animal variation.

In eggs the TRR levels increased from 0.06 mg eq/kg one day after first administration up to an average plateau of 0.18–0.65 mg eq/kg after four days. Levels showed a wide variation as also found in plasma and tissue. One bird reached a plateau of 1.06 mg eq/kg after three days, while two other birds reached a plateau after two days (1.21 and 0.27 mg eq/kg.

Table 7 TRR in egg and tissue after administration of 2, 3, 4-^{14}C-quinclorac at 33-44 mg/kg bw and day (equivalent to 800 ppm in the diet) 6 h after sacrifice

Matrix	% of total dose administrated	TRR (mg eq/kg)							
		Bird number							
		366	367	368	369	370	371	372	average
Liver	n.r.	0.78	9.39	4.41	0.43	0.38	0.26	10.53	3.74
Kidney	n.r.	5.86	37.44	4.13	1.27	0.92	0.77	88.98	19.91
Breast muscle	n.r.	0.17	3.2	0.20	0.05	0.05	< 0.05	4.22	1.82
Leg muscle	n.r.	0.24	3.37	0.18	0.06	0.05	0.11	3.95	1.14
Skin/fat	n.r.	0.61	5.28	0.62	0.25	0.23	0.17	7.20	2.05
Plasma	n.r.	0.66	11.22	0.65	0.24	0.15	0.14	13.5	3.79
Whole blood	n.r.	0.48	8.38	0.41	0.19	0.12	0.09	9.41	2.73
Total in organs and tissue	-								
Excreta 0-120 h*	92.6 ± 5.6								

Table 8 Time course of total radioactive residues (mg eq/g) in eggs laid by hens, after administration of 2, 3, 4-^{14}C-quinclorac at 33-44 mg per kg body weight, for five days.

Day of collection	Bird number TRR (mg eq/kg)							Mean TRR (mg eq/kg)	**±SD**
	366	**367**	368	369	370	371	**372**		
1	ns	ns	ns	ns	< 0.06	ns	0.06	< 0.06	
2	ns	1.21	0.27	ns	B	ns	0.42	0.63	0.51
3	ns	0.44	0.15	0.20	B	B	1.06	0.46	0.42
4	ns	0.46	0.18	0.65	ns	ns	0.57	0.47	0.21
5	ns	ns	0.15	ns	0.19	ns	0.20, 0.41*	0.24	0.11

Eggs excluding shells

ns no eggs laid during this period

B eggs laid but broken by the bird and included with excreta

* Hen 272 laid two eggs on day 5

Samples of excreta, eggs, liver, breast muscle and skin/fat were further analysed for the composition of the radioactivity. Excreta were mixed with methanol and the methanolic supernatant was collected after centrifugation.

Whole egg homogenates from birds 367 (day 2), 369 (day 4) and 372 (day 3) were mixed with methanol and the protein precipitate removed by centrifugation. The methanol extracts were reduced by evaporation and acidified with 1 M HCl. The extract was fractionated by column chromatography (C-8, octylsilane). The column was washed sequentially with 1 M HCl and hexane followed by elution with ethyl acetate. The ethyl acetate extracts were evaporated to dryness and reconstituted in methanol.

Birds 367 and 372 had the highest tissue concentration of radioactivity and were selected for extraction. Liver samples were extracted with 1M HCl/ethyl acetate (1:10, v/v). After centrifugation, the remaining solids were extracted again with ethyl acetate. Both extracts were combined. Muscle and skin/fat samples were extracted with methanol/water (1:1) with a few drops of 1 M NaOH per 10 mL. After centrifugation, the remaining solids were extracted again with methanol. Both extracts were combined, reduced by evaporation, acidified with 1 M HCl and fractionated by column chromatography as for eggs.

Identification of the radioactivity in all extracts was done using TLC in five different solvent systems. The reference substance used was the parent quinclorac which was confirmed on TLC plates by the quenching of UV fluorescence at 254 nm.

Extraction efficiency varied from bird to bird but were generally around 90% for excreta, liver, breast muscle and skin/fat (Table 9). The unextracted residues in eggs were rather high from 10.5–21.1% of TTR in the egg tissue.

Besides the parent quinclorac (levels > 78% TRR in tested matrices) the only identified metabolite was M1 (glucuronic acid conjugate of the parent). M1 co-chromatographed with the major radioactive component in the bile of rat. In the rat study this metabolite was identified as the glucuronic acid conjugate of parent by enzymatic cleavage, followed by MS analysis. The combined concentration of M1 and fractions R01-1 and R01-3 was a maximum of 3% TRR in the tissues and not detected in eggs. Another fraction R01-5was present at levels from 0.3–3.7% TRR in eggs and tissue. In eggs (excluding shells) 10.5–21.1% of the residue was not extracted.

Since the methods used to extract the residues included 1 M HCl, it is not clear whether parent compound represents parent only or includes parent released from conjugates and whether the M1 is the fraction of conjugates that remained uncleaved.

Table 9 Characterization and identification of compounds in eggs, tissues and excreta of the laying hen after administration of quinoline-2, 3, 4-^{14}C-quinclorac at 33–44 mg/kg bw and day (800 ppm in the diet).

	Eggs [a] 367, 369, 372	Breast muscle 367, 372	Skin/fat 367, 372	Liver 367, 372	Excreta 371, 372	
TRR (mg/kg eq)	1.21; 0.65; 1.06	3.2; 4.22	5.28; 7.20	9.39; 10.53		
	%TRR*	%TRR*	%TRR*	%TRR*	day 1	day 2
Quinclorac	83; 81; 78	87.0; 86.4	86.0; 87.7	91.5; 91.3	88.9-91.2	84.6-85.0
R01-1	ND; ND; 1.0	1.4; 1.2	1.1; 0.5	3.0; 2.7	0.3	0.3
M1 (R02)					1.1-1.7	1.9-4.4
R01-3					0.05-0.07	0.01-0.08
R01-5	2; 0.3; 0.9	1.8; 0.8	1.8; 2.5	3.4; 3.7	0.2-0.4	0.05-0.2
Total identified	≤ 83	≤ 88.8	≤ 90.2	≤ 95.3	≤ 93.67	≤ 96.18
Total characterized	≤ 2	≤ 1.8	≤ 2.5	≤ 3.7	≤ 2.47	≤ 4.98
Total extracted	82-90; 80-84; 79-82	90; 88	89; 91	98; 98	90.8-93.4	87.4-89.9

	Eggs [a] 367, 369, 372	Breast muscle 367, 372	Skin/fat 367, 372	Liver 367, 372	Excreta 371, 372	
TRR (mg/kg eq)	1.21; 0.65; 1.06	3.2; 4.22	5.28; 7.20	9.39; 10.53		
Unextracted	10-18; 16-20; 18-21	9.9; 11.6	11.1; 9.3	2.0; 2.4	6.7-9.2	10.1-12.6

* Relative % of total sample radioactivity

M1 is glucuronic acid conjugate of parent

nd not detected

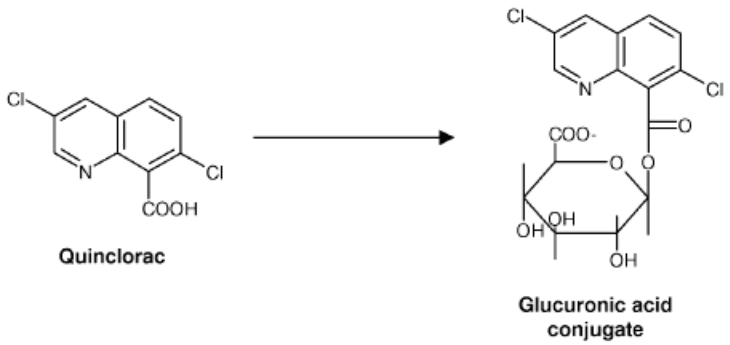


Figure 5 Metabolic pathway from available data in laying hen

Plant metabolism

The Meeting received plant metabolism studies after foliar application of ^{14}C-radiolabelled active substances to rice, wheat, rape seed (canola), sorghum and strawberry. In these studies 2, 3, 4-[^{14}C]-quinclorac (quinoline label) or 3-[^{14}C]-quinclorac (quinoline label) were used.

Rice

In a study reported by Wood (1988, Ref. BASF 88/5059) one foliar application of 2,3,4-^{14}C-quinclorac was made to paddy rice plants. The experiments were performed on plants grown in a growth chamber and in the field. These plants were treated at 1.5 kg ai/ha at the 4 leaf stage (~ BBCH 14) and were grown in pots containing a mixture of loam compost and peat moss. The field plants (variety Starbonnet) were treated at 0.84 kg ai/ha at 3-5 leaf stage (~BBCH 15-16) under unflooded conditions in a sandy loam soil. Seven days later a permanent flood was established for the field plants. Whole plants (forage) were harvested from the field plots 28 days after treatment and mature grain and straw samples were taken from the growth chamber plants (97 days after treatment) and field grown plants (118 days after treatment).

Analysis of the TRR was done using combustion and LSC. An overview of the TRR levels found in collected samples is presented in Tables 10 and 11 below. Only rice grain and straw from the growth chamber and rice forage and grain from the field treatment were analysed further.

Radioactivity in rice straw and forage was easily extracted with organic solvents. Straw samples were homogenized and 92% TRR was extracted with acetone /water (6:4, v/v). The extract was evaporated, acidified with HCl and residues were partitioned overnight between diethyl ether (87% TRR) and water (4.9% TRR). The diethyl ether fraction was analysed by TLC.

Forage samples were homogenized and 92% TRR was extracted with acetone/water (1:1, v/v) and acetone/water (6:4, v/v). The extract was evaporated and acidified with HCl. The residues in the aqueous extract were exhaustively partitioned between dichloromethane (87% TRR), ethyl acetate (2.4% TRR) and water (4.9% TRR). The dichloromethane and ethyl acetate extracts were combined, evaporated to dryness and redissolved in acetone for TLC analysis.

Radioactivity in rice grain was extracted poorly with organic solvents. When the grain was first dissolved in boiling water and then acidified or refluxed with 1 M HCl, the residues could be easily extracted with organic solvents. Grain samples from growth chambers were refluxed with water

for 2 hrs, acidified with HCl and residues were partitioned for 8 hrs into diethyl ether (97% TRR). The diethyl ether extract was partitioned with 1 M NaOH, whereby the oil remained in the diethyl ether and the residues transferred into the aqueous phase. The combined aqueous extracts were acidified with HCl and partitioned with diethyl ether. The diethyl ether extract (94% TRR) was evaporated to near dryness and then diluted with methanol for TLC analysis.

Field grain samples were first extracted with hexane (1.9% TRR) to remove the oils. Remaining solids were air dried and solubilized by reflux with 1 M HCl. Boiling acid was used to avoid frothing and to avoid emulsion problems during extraction. Residues were partitioned between diethyl ether (58% TRR), ethyl acetate (25% TRR) and water (15% TRR). The combined diethyl ether and ethyl acetate extracts were concentrated to near dryness and diluted with methanol for TLC analysis.

Organic fractions were analysed by TLC. An overview of the composition of the residue is presented in Table 11. Nearly all the radioactivity in all parts of the rice plant could be accounted for as unchanged parent up to the final harvest. Metabolites were not further characterized. The identification of the parent was performed by derivatization of quinclorac to its methyl ester and analysis with GC-MS.

Grain samples required boiling water or boiling 1 M HCl to allow extraction of the residues with organic solvents. This suggests that quinclorac is bound to the grain matrix and the quinclorac identified is actually quinclorac released from conjugates. Forage and straw were easily extracted with organic solvents, therefore the quinclorac identified in forage and straw is likely the unchanged parent compound.

Table 10 Radioactive residues in field grown rice treated after foliar application to rice with 2, 3, 4-^{14}C-quinclorac at 0.84 kg ai/ha

Matrix	Days after application	Days before harvest	mg eq/kg
Whole plant	3	115	34.60
Whole plant	14	104	5.42
Whole plant	28	90	0.49
Final harvest straw	118	0	0.10
Final harvest grain	118	0	0.12

Table 11 Extractability/mass balance of radioactivity from treated rice with 2, 3, 4-^{14}C-quinclorac

Sample	Rice straw (growth chamber) 1.5 kg ai/ha DAT 97 12.79 mg eq /kg TRR		Rice forage (field) 0.84 kg ai/ha DAT 28 0.49 mg eq/kg TRR		Rice grain (growth chamber) 1.5 kg ai/ha DAT 97 1.52 mg eq/kg TRR		Rice grain (field) 0.84 kg ai/ha DAT 118 0.12 mg eq/kg TRR	
	% TRR	mg eq/kg TRR	% TRR	mg eq/kg TRR	% TRR	mg eq/kg TRR	% TRR	mg eq/kg TRR
Quinclorac	86 a	10.99	85 a	0.42	94 b	1.43	84 b	0.11
Organosoluble	1.4	0.18	4.2	0.02	0.7	0.01	1.9	0.002
Aqueous soluble	4.9	0.63	3.9	0.02	1.2 3.0	0.02 0.05	14.6	0.02
Post extracted solids	7.6	0.98	8.2	0.04	-	-	-	-
Total	99.9		101.3		98.9		100.5	

* Final fraction containing parent compound

A extracted with acetone/water without boiling or reflux

B extracted with diethyl ether and ethyl acetate after boiling in water or reflux in 1 M HCl

Wheat

In a study reported by Ellenson, J, L (1996a, BASF 1996/5 197) one foliar application of 3-^{14}C quinclorac was applied at 3-5 leaf stage to wheat plants grown in a greenhouse at 1 × 0.125 kg ai/ha

and at 1 × 0.500 kg ai/ha. Plants (variety Katepwa) were grown in pots containing silt loam. Forage was sampled at 37 DAT when plants were in early to late boot stage and mature wheat grain and straw were sampled at 92 DAT.

Analysis of the TRR was carried out using combustion and LSC. The TRRs found in the samples collected amounted to 3.26 and 13.14 mg eq/kg at the two application rates in forage. In the straw 1.86 mg eq/kg was detected at the low application rate and 8.16 mg eq/kg at the high application rate. TRR for the grain were 1.13 mg eq/kg at the low application rate and 3.94 mg eq/kg at the high application rate samples. An overview of the TRR levels found in collected samples is presented in Table 12.

In forage, straw and grain 85–95% TRR was extracted with acetone/water (2:1, v/v). A further 3.3–12% TRR could be released by hydrolysis with 0.1 M NaOH. Identification of residues in the acetone/water fraction in straw was based upon retention time comparison with known standards and/or determination with HPLC-MS. Separation and isolation of specific radioactive residues from the straw samples was accomplished using semi-preparative and analytical HPLC methods coupled with fraction collection. Identification and characterization of residues in forage and grain acetone/water fractions were derived from HPLC retention time comparison with residues isolated from the higher application straw. An aliquot of the acetone/water extract was treated by base hydrolysis (pH 13, 100 °C, 2 hrs) to cleave any conjugates present in the extract and the extract was re-analysed by HPLC-MS.

In forage, parent residues accounted for 24% TRR (0.78 mg eq/kg) in the low application rate and 45% TRR (5.92 mg eq/kg) in the high rate samples. A total of 9.8% TRR (0.32 mg eq /kg) in the low application rate and 6.4% TRR (0.84 mg/kg) in the high application rate forage were associated with hydroxyquinclorac conjugates. Other metabolites identified at levels <5% TRR were quinclorac conjugates and hydroxyquinclorac. Unidentified components were <5% TRR (0.16 mg/kg) for the low application rate or 6.93%TRR (0.91 mg/kg) for the high application rate.

In grain, parent residues accounted for 62% TRR (0.69 mg eq/kg) in the low application rate grain, and 68% TRR (2.68 mg eq/kg) in the high rate samples. A total of 4% TRR (0.14 mg eq/kg) in the high application rate grain was assigned to hydroxyquinclorac conjugates. Unidentified components were none > 2.11% TRR (0.024 mg eq/kg) for the low application rate or 3.47%TRR (0.14 mg eq/kg) for the high application rate.

In straw, parent accounted for 12% TRR (0.22 mg eq/kg) in the low application rate samples and 22% TRR (1.83 mg eq/kg) in the high application rate samples. Additional residues at 13.7% TRR (0.26 mg eq/kg) in the low application rates samples and 12.6% TRR (1.02 mg eq/kg) in the high application rate were assigned to hydroxyquinclorac conjugates. Unidentified compounds were none > 7.07% TRR (0.13 mg eq/kg) for the low application rate samples or 7.71%TRR (0.63 mg eq/kg) for the high application rate.

A more detailed fractionation of the high application rate straw were generally in agreement with the simpler profile determined by HPLC analysis of the soluble residues only. Individual residues identified during analysis of the high application rate straw sample included the parent 23% TRR, a glucose conjugate of hydroxyquinclorac (~6% TRR), and hydroxyquinclorac (~3% TRR). The hydroxyquinclorac was not the 2-OH quinclorac identified in the soil degradation studies. Mass spectral analysis also indicated the presence of small (<1% TRR) amounts of possible malonate esters of parent and/or hydroxyquinclorac. A relatively large portion of TRR (20% or 1.6 mg/kg in the 4× sample) was associated with high molecular weight species that are presumed to be natural products.

Base hydrolysis (pH 13, 100 °C, 2 hrs) of the entire homogenized forage, straw and grain samples did not release any compounds beyond what was already identified.

The results indicate that the residues in wheat primarily consist of unchanged parent compound. Low levels of hydroxyquinclorac are formed by oxidative hydroxylation of the ring structure of the parent compound. Both quinclorac and hydroxyquinclorac can be metabolized to glucose conjugates. A less prevalent metabolic pathway may involve esterification of the parent at the carboxyl group.

Table 12 Extractability from wheat forage, straw and grain treated with 3-^{14}C-quinclorac

Sample	Forage 0.125 kg ai/ha DAT 37 TRR= 3.26 mg/kg eq		Forage 0.50 kg ai/ha DAT 37 TRR = 13.14 mg/kg eq		Straw 0.125 kg ai/ha DAT 92 TRR= 1.86 mg/kg eq		Straw 0.50 kg ai/ha DAT 92 TRR = 8.16 mg/kg eq		Grain 0.125 kg ai/ha DAT 92 TRR = 1.13 mg/kg eq		Grain 0.50 kg ai/ha DAT 92 TRR = 3.94 mg/kg eq	
	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg	%TRR	mg/kg
Acetone/water	87.8	2.86	93.4	12.3	84.6	1.57	87.0	7.09	93.8	1.06	95.3	3.75
- Quinclorac	24.0	0.78	45.1	5.92	11.7	0.22	22.4	1.83	61.6	0.69	68.0	2.68
- Quinclorac glucose conjugates a	4.6	0.15	6.9	0.91	-	-	-	-	-	-	-	-
- Hydroxy quinclorac	3.0	0.098	-	-	-	-	-	-	-	-	-	-
- Hydroxy quinclorac glucose conjugates b	6.8	0.22	6.4	0.84	13.7	0.26	12.6	1.02	4.0	0.05	3.7	0.14
-Unidentified compounds	42.7 c	1.39[c]	38.4 c	5.01 [c]	44.8 d	0.83 d	45.1 d	3.68 d	15.0 e	0.17 e	17.2 e	0.68 e
Unidentified fraction released by 0.1 M NaOH	10.3	0.34	5.6	0.74	12.4	0.23	10.9	0.09	3.34	0.04	3.97	0.16
PES	1.87	0.06	0.43 0.44	0.06 0.06	3.27	0.06	1.02 0.59	0.08 0.05	0.33	0.004	1.10	0.043
Total	100.0		99.9		100.3		99.5		97.5		100.4	

A 419 dalton quinclorac glucose conjugate

B Conjugates which released a hydroxyquinclorac exocon with molecular weight 257, when the acetone/water extract was treated by base hydrolysis (pH 13, 100 °C, 2hrs).

C 23 chromatographic regions, none > 4.96 TRR (0.16 mg/kg) for 1X or 6.93%TRR (0.91 mg/kg) for 4X

d 20 chromatographic regions, none > 7.07 TRR (0.13mg/kg) for 1X or 7.71%TRR (0..63 mg/kg) for 4X

e 19 chromatographic regions, none > 2.11 TRR (0.024mg/kg) for 1X or 3.47%TRR (0.14 mg/kg) for 4X

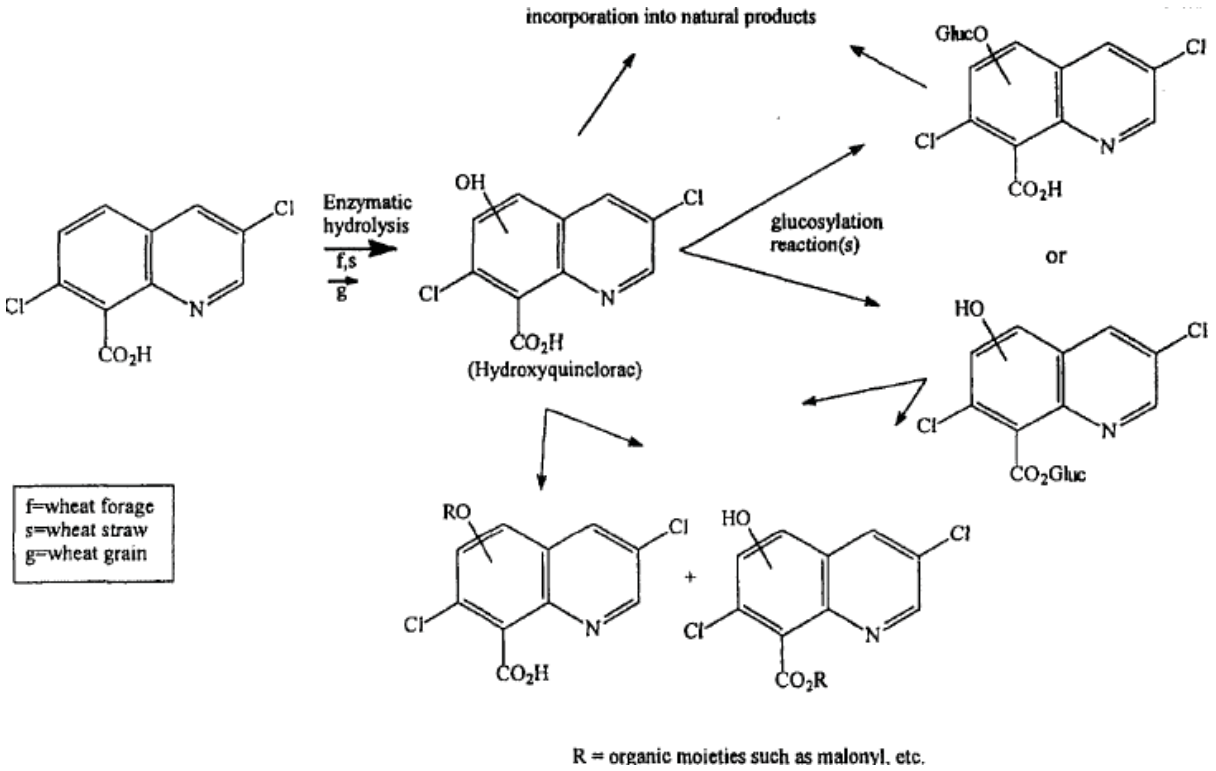


Figure 6 Proposed metabolic pathway of quinclorac in wheat

Sorghum

In a metabolism study reported by Ellenson J, L, (1993, Ref 1993/5088) 3-^{14}C-quinclorac was applied pre-emergent outdoors to the soil followed by a post-emergence treatment when sorghum plants were 15–25 cm tall. The pre-emergence treatment was 0.525 kg ai/ha and the post-emergence was 0.504 kg ai /ha (total 1.03 kg ai/ha) with an interval of 25 days. The plants (variety G820) were grown in a field plot with loamy sand soil in North Carolina, USA.

Analysis of the TRR was carried out using combustion and LSC. Residue analysis was done on forage sampled 25 days after the last treatment and on grain and fodder sampled 95 days after the last treatment. The TRRs for these samples amounted to 4.01 mg eq/kg in forage, 0.87 mg eq/kg in fodder and 0.83 mg eq/kg in grain.

Sorghum forage was extracted with acetone/water and the filtrate was further extracted with ethyl acetate. Sorghum fodder samples were extracted with acetone/water and the filtrate was subsequently extracted with hexane, dichloromethane and ethyl acetate. Sorghum grain samples were extracted with acetone/water and the filtrate was subsequently extracted with hexane, dichloromethane and ethyl acetate and refluxed with HCl.

Remaining solids were subjected to refluxing with NaCl solution (10 g/L) for 2 hr to determine radioactivity incorporated into water soluble polysaccharides, boiling with EDTA (5 g/L) for 1 hr to determine incorporation in peptic polysaccharides, with 1.25 M NaOH (50 g/L) for 6 hr at 80 °C to determine incorporation in hemicellulose I, with sodium chlorite ($NaClO_3$, 10 g/L at room temperature) for 3 hr to determine incorporation in lignin and with 6 M NaOH (240 g/L) for 6 hr to determine incorporation in hemicellulose II.

Extracts were analysed by radio TLC. Quinclorac was confirmed using methylation to its methyl ester and determined by GC-ECD. The presence of quinclorac methyl ester was also separately confirmed by two dimensional TLC.

An overview of the TRR levels found in collected samples and the composition of the residue is presented in Tables 13–15. In all samples unchanged quinclorac was the major residue being present at levels of 73.4% TRR in forage, 21.5% TRR in fodder and 73.5% in grain. This residue included the parent compound that was released from remaining solids (4% in grains to 9% TRR in forage and fodder). The only other metabolite identified was quinclorac methyl present at 3.6% TRR in forage, 5.9% in fodder and 1.7% in grain. In spite of substantial alkaline extraction procedure, a large amount of unidentified residues was present in forage and fodder in organic and aqueous fractions, maximum 18.7% TRR (0.75 mg eq/kg in forage and 52.4% TRR (0.46 mg eq/kg) in fodder. The majority of the released residue from the remaining solids was in the polysaccharide fraction ($NaCl/H_2O$) or the hemicellulose fraction (1 M NaOH).

The results indicate that extraction with acetone/water is very effective for the sorghum forage and grain, but less so for the fodder. An additional 24% TRR could be extracted from the remaining fodder solids after addition of NaOH. The current analytical method incorporates an alkaline extraction step.

Table 13 Fractionation, characterization and identification of radioactive residues in sorghum forage after treatment with 3-^{14}C-quinclorac

Sample	Sorghum forage DALT=25 TRR =4.01 mg/kg eq			quinclorac		quinclorac methyl ester		unidentified			
								organo soluble		aqueous soluble	
Acetone/water extract		%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg
	EtOAc, pH 2	71.3	2.86	64.5	2.585	3.6	0.145	3.2	0.130	-	-
86%TRR	aqueous	14.6	0.58					-	-	14.6	0.58
3.44 mg/kg eq	subtotal	85.9	3.44	64.5	2.58	3.6	0.145	3.2	0.13	14.6	0.58
Solids	$NaCl/H_2O$	5.8	0.23								
	EtOAc			4.1	0.163	-	-	0.3	0.012		
14% TRR	Aqueous					-	-			1.1	0.05
0.57 mg/kg eq	EDTA	0.8	0.03								
	EtOAc			0.5	0.020	-	-	1.0	0.040		
	Aqueous					-	-			2.8	0.111
	NaOH	7.6	0.29								
	EtOAc			3.9	0.156	-	-	0.1	0.007		
	Aqueous			-	-	-	-			0.2	0.009
	$NaClO_3$	1.2	0.05								
	EtOAc			0.4	0.014	-	-				
	Aqueous			-	-						
	NaOH	0.3	0.01								
	Residuum	0.1	0.004								
	subtotal	15.8	0.614	8.9	0.353	-			1.4		
	overall total	**102**	**4.10**	**73.4**	**2.93**	**3.6**	**0.145**	**4.7**	**0.188**	**18.7**	**0.750**

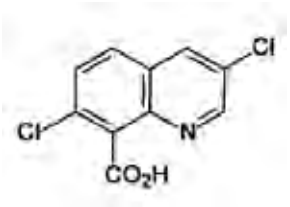
Table 14 Fractionation, characterization and identification of radioactive residues in sorghum fodder after treatment with 3-^{14}C-quinclorac

Sample	Sorghum fodder DALT = 95 0.87 mg/kg eq			quinclorac		quinclorac methyl ester		unidentified			
								organo soluble		aqueous soluble	
Acetone/water extract	Partition	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg
	Hexane, pH 8	2.7	0.023	-	-	2.7	0.023	-	-	-	-
52%TRR	DCM, pH 8	3.0	0.026	-	-	3.0	0.026	-	-	-	-
0.45 mg/kg eq	EtOAc, pH 8	1.8	0.016	-	-	-	-	1.8	0.016	-	-
	Hexane, pH 2	0.8	0.007	0.5	0.004	0.2	0.002	0.1	0.001	-	-
	DCM, pH 2	10.7	0.093	7.3	0.063	-	-	3.4	0.030	-	-
	EtOAc, pH 2	9.3	0.081	3.2	0.028	-	-	6.1	0.053	-	-
	Aqueous	23.5	0.204	-	-	-	-	-	-	23.5	0.204
	Subtotal	51.8	0.45	11.0	0.095	5.9	0.051	11.4	0.1	23.5	0.204
Post extracted	$NaCl/H_2O$	18.5	0.160								

Sample	Sorghum fodder DALT = 95 0.87 mg/kg eq			quinclorac		quinclorac methyl ester		unidentified			
								organo soluble		aqueous soluble	
solids	EtOAc			5.2	0.045	-	.	2.2	0.019		
	Aqueous									10.0	0.087
	EDTA	1.6	0.014								
49%TRR	EtOAc			0.4	0.003	-	-	0.4	0.003	-	-
0.42 ppm	Aqueous									0.6	0.005
	NaOH 1	24.3	0.211								
	EtOAc			3.8	0.033	-	-	4.6	0.04	-	-
	Aqueous					-	-	-	-	13.3	0.116
	$NaClO_3$	2.8	0.024								
	EtOAc			0.9	0.008	-	-	0.4	0.004	-	-
	Aqueous					-	-	-	-	4.5	0.039
	NaOH II	1.3	0.011								
	EtOAc			0.2	0.002	-	-	0.4	0.003	-	-
	Aqueous									0.5	0.004
	subtotal	48.5	0.42	10.5	0.09			8.0	0.069	28.9	0.25
	overall total	**100**	**0.08**	**21.5**	**0.186**	**5.9**	**0.051**	**19.4**	**0.169**	**52.4**	**0.455**

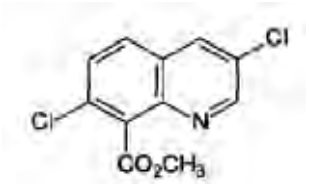
Table 15 Fractionation, characterization and identification of radioactive residues in sorghum grain with 3-^{14}C-quinclorac

Sample	Sorghum grain DALT=95 TRR=0.83 mg/kg eq			quinclorac		quinclorac methyl ester		unidentified			
								organo soluble		aqueous soluble	
Acetone/water extract	Partition	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg	%TRR	mg eq/kg
	Hexane, pH 2	7.7	0.064	5.9	0.049	1.7	0.014	0.1	0.001		-
15% TRR	DCM, pH 2	62.6	0.520	60.7	0.504			1.9	0.016		
0.09 mg/kg eq	EtOAc, pH 2	3.8	0.032	1.0	0.008			2.8	0.023		
	Aqueous	10.6	0.088	2.1	0.017					2.1	0.017
	Subtotal	84.7	0.704	69.7	0.578	1.7	0.014	4.8	0.040	2.1	0.017
Post extracted solids	$NaCl/H_2O$	7.5	0.062								
	EtOAc			3.8	0.032			0.6	0.005		
	Aqueous									2.4	0.020
12% TRR	EDTA	0.6	0.004								
0.1 mg/kg eq	NaOH	4.1	0.034								
	EtOAc							1.2	0.010		
	Aqueous									0.4	0.003
	subtotal	12.2	0.1	3.8	0.032			1.8	0.015	3.4	0.027
	overall total	**96.9**	**0.804**	**73.5**	**0.610**	**1.7**	**0.014**	**6.6**	**0.055**	**5.5**	**0.044**



Quinclorac BAS H (parent compound)

↓



Quinclorac methyl ester BH 514 ME

Figure 7 Proposed metabolic pathway of quinclorac in sorghum

Rape seed (canola)

In a study reported by Parker 1998a (BASF 1998/5180) one foliar application of 3-^{14}C quinclorac was made post emergence (30 days after sowing at 5th true leaf stage) at 0.2 kg ai/ha. The experiment was performed in a growth chamber on a *brassica rapa v*ariety "Horizon" grown on a sandy loam. By simulation of a North American climate during summer it was possible to cultivate oil seed within 90 days. Whole plants were harvested 1 and 29 days after treatment. Seed and straw were harvested 60 days after treatment.

Analysis of the TRR was carried out using combustion and SC. An overview of the TRR levels found in collected samples is presented in Table 16. Forage was not further characterized.

Homogenized samples of oilseed rape seeds or straw were subsequently extracted with acetone/phosphate buffer pH 7 (50:50, v/v). Rape seeds were further extracted with 0.1 M NaOH at room temperature (mild alkaline hydrolysis) and 0.1 M NaOH at 100 °C (harsh alkaline hydrolysis). Organic solvents extracted 84–87% TRR from seed and straw, while an additional 6.9% and 5.2% TRR could be extracted from the seeds by mild and harsh alkaline hydrolysis (Table 17). After centrifugation, each extract was partitioned between an aqueous and organo-soluble fraction (Table 18). Extracts and solids were analysed by (combustion) LSC.

Table 16 Total radioactive residues of quinclorac in rape seed grown in a growth chamber after foliar treatment with 3-^{14}C-quinclorac at 0.2 kg ai /ha.

Matrix	Combustion TRR mg eq/kg	Extraction TRR mg eq/kg
Plants Pre-treatment	0.001	-
Plants, 1 DAT*	9.952	-
Forage, 29 DAT	0.676	-
Straw, 60 DAT	0.645	0.637
Seed, 60 DAT	0.469	0.475

* DAT - Days after treatment

Table 17 Extractability of radioactive residues of quinclorac in rape seed after foliar treatment with 3-^{14}C-quinclorac at 0.2 kg ai /ha

Matrix	TRR [a]		Solvent extraction [b]		Mild hydrolysis [c]		Harsh hydrolysis [d]		Total extracted [e]		PES [f]	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Seed	0.475	100	0.402	84.5	0.033	6.9	0.025	5.2	0.459	96.6	0.013	2.7
Straw	0.637	100	0.560	87.8	-		-		-		0.078	12.2

[a] Combustion TRR

[b] Solvent extraction by 50:50% acetone:pH 7 phosphate buffer

[c] Mild hydrolysis by 0.1 M NaOH at room temperature

[d] Harsh hydrolysis by 0.1 M NaOH at 100°C temperature

[e] Total extracted represents the total extracted residues; i.e. the sum of solvents 1-3

[f] PES represents the residues in the post extracted solids

Table 18 Extractability of radioactive residues of quinclorac in rape seed and straw after foliar treatment with 3-^{14}C-quinclorac at 0.2 kg ai/ha

Commodity	Description	Organo-soluble		Aqueous soluble	
		mg eq/kg	% TRR	mg eq/kg	% TRR
Oilseed rape seed	50:50 acetone:buffer	0.359	75.6 [a]	0.037	7.7
	Mild base hydrolysis	0.030	6.2 [b]	0.005	1.1
	Hard base hydrolysis	0.023	4.8 [c]	0.002	0.4
	Total extracted	0.412	86.6	0.044	9.2
Oilseed rape straw	50:50 acetone:buffer	0.338	53.0 [c]	0.193	30.2

[a] Partitioned into hexane at pH 7 (37.1% TRR quinclorac methyl) and into dichloromethane at pH 2 (38.5%, contains 37.1% TRR quinclorac parent)

[b] Partitioned into ethyl acetate at pH 2

[c] Partitioned into dichloromethane at pH 2

Identification and characterization of residues in rape seed was based upon retention time comparison with standards for parent and quinclorac methyl and by confirmation using HPLC-MS/MS. An overview of the composition of the residues in collected samples is presented in Table 19.

In rape seed a total of 37.1% TRR (0.176 mg eq/kg) was identified as the parent quinclorac and 37.1% TRR (0.176 mg eq/kg) was identified as a methyl ester. Quinclorac methyl, in the acetone/phosphate buffer extract partitioned into hexane at pH 7, while the quinclorac parent partitioned into dichloromethane at pH 2. The remainder of the extracts (17.4% TRR) represents a multitude of minor discrete residues and was characterized as organo soluble or aqueous-soluble. The post extraction solids accounted for 2.7% TRR (0.013 mg eq/kg).

For straw, the organo soluble fractions consisted of two major fractions containing quinclorac and quinclorac methyl ester, and at least two minor fractions. A minor peak at approximately 25 min. corresponded to a minor peak seen in the seed samples. No quantitative data are indicated in the report. The post extraction solids from straw containing 12.2% TRR (0.078 mg eq/kg) were not further analysed as it was concluded that rape seed straw not is a feed item.

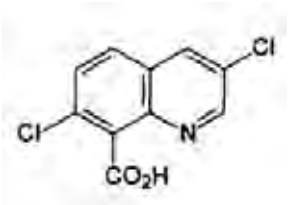
Table 19 Degree of identification/characterization of radioactive residues of quinclorac in rape seed after foliar treatment with 3-^{14}C-quinclorac at 0.2 kg ai /ha.

Degree of identification	Designation	Oilseed rape seeds mg eq/kg	Oilseed rape seeds % TRR
TRR	Total [c]	0.475	
Identified	Quinclorac (parent)	0.176	37.1
	Quinclorac methyl ester	0.176	37.1
	Subtotal	0.352	74.2
Characterized	Aqueous soluble residues	0.042 [a]	8.7 [a]
	Organo soluble residues	0.041 [a]	8.6 [a]
	Subtotal	0.083	17.4
Post-extraction solids	PES	0.013 [b]	2.7 [b]
	Subtotal	0.013	2.7
Total	Total	0.448	94.2

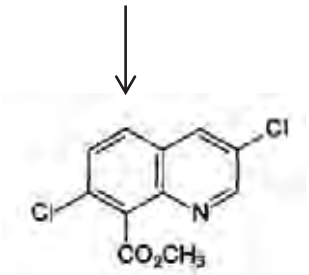
[a] Fractionated after solvent extraction and hydrolysis by 0.1 M NaOH at room temperature and at 100 C.

[b] Remains after hydrolysis

[c] TRR based on sum of extracts



Quinclorac BAS 514 H (parent compound)



Quinclorac methyl ester BH 514 ME

Figure 8 Proposed metabolic pathway of quinclorac in rape seed (canola) following foliar post-emergence application of 3-^{14}C-quinclorac

Strawberry

In a study reported by Walsh, K (2015, BASF/029602-1, report 029602-1) mature strawberry plants were individually treated with one foliar spray application of ^{14}C-quinclorac at 1.120 kg ai/ha at growth stage BBCH 73 61 days prior to the third sampling. The fruits were harvested 21, 37 and 61 days after treatment (DAT). All mature fruit was collected and approximately 2-3 leaves from each plant. At the third and final harvest, all the remaining leaves and immature green strawberry fruits were collected.

Foliage was surfaced washed with ethanol prior to homogenization. Homogenized samples of both fruits and foliage were extracted with ethanol/water. The post extracted solids (PES) were combusted and further extracted using a Soxhlet apparatus. Acid hydrolysis of pooled extracts was done with 12 N hydrochloric acid and 2 hours incubation at 37 °C. Extracts and PES were analysed by LSC, and concentrated extracts were analysed on HPLC to determine the TRR and the nature of major terminal residues. The identity was confirmed by LC-MS/MS. An overview of the residues and fractions found in collected samples is presented in tables below.

In foliage, parent quinclorac accounted for 67.4% TRR (10.43 mg eq/kg) at first harvest 21 DAT and at 57.4% TRR (4.36 mg eq/kg) at the last harvest 61 DAT. Conjugated quinclorac (M1) released by acid hydrolysis was identified from 26.8%TRR (4.19 mg eq/kg) at first harvest and at 28.6%TRR (2.27 mg eq/kg) in the last harvest. As the parent is an acid it is possibly a glucose ester conjugate. A minor polar metabolite was present from 1.8% (0.27 mg eq/kg) at first harvest 21DAT to 5.8% TRR (0.47 mg eq/kg) at last harvest 61 DAT. Post extracted (non-characterized) solids went from 4.5% TRR (0.7 mg eq/kg) at the first harvest to 8.1% TRR (0.67 mg eq/kg) at the last harvest. Quinclorac methyl ester was not detected in the foliage.

In fruit, parent quinclorac accounted for 78.8% TRR (9.13 mg eq/kg) at first harvest and at 50.8% TRR (1.69 mg eq/kg) at third harvest. Conjugated quinclorac (M1) released by acid hydrolysis went from 10.7%TRR (1.26 mg eq/kg) at first harvest to 47.3%TRR (1.57 mg eq/kg) in the last harvest. Quinclorac methyl ester accounted for 9.6% TRR (1.13 mg eq/kg) at first harvest, to 4.9% TRR (0.42 mg eq/kg) at second harvest and was not detected at the last harvest. Level of post extracted (non-characterized) solids was below 10% TRR throughout the study.

Table 20 Characterization of total radioactive residues detected in strawberry fruit after foliar application of ^{14}C-quinclorac

	Quinclorac methyl ester		Quinclorac		Quinclorac conjugates (M1)		PES		Total	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Harvest 1 (21 DAT)										
Solvent extract	1.09	9.3	8.97	76.4	1.22	10.4	-	-	11.29	96.2
Soxhlet extract	0.04	0.3	0.16	1.4	0.04	0.3	-	-	0.24	2.0
PES							*0.22*	*1.8*	*0.22*	*1.8*
Total	1.13	9.6	9.13	77.8	1.26	10.7	0.22	1.8	11.75	100
Harvest 2 (37 DAT)										
Solvent extract	0.39	4.5	6.78	77	1.27	14.5	-	-	8.44	96
Soxhlet extract	0.03	0.4	0.15	1.8	0.03	0.3	-	-	0.21	2.5
PES							*0.14*	*1.6*	*0.14*	*1.6*
Total	0.42	4.9	6.93	78.8	1.3	14.53	0.14	1.6	8.79	100
Harvest 3 (61 DAT)										
Solvent extract	nd	nd	1.53	46	1.57	47.3	-	-	3.10	93.3
Soxhlet extract	nd	nd	0.16	4.8	-	-	-	-	0.16	4.8
PES	-	-	-	-	-	-	*0.06*	*1.9*	*0.06*	*1.9*
Total	nd	nd	1.69	46	1.57	47.3	0.06	1.9	3.32	100

*approximate times, nd not detected

** M1 the portion of the radioactive residue in the conjugated form

PES = post extracted solids

DAT = days after treatment

*** Quinclorac total = quinclorac parent +quinclorac methyl ester

Table 21 Characterization of total radioactive residues detected in strawberry foliage after foliar application of ^{14}C-quinclorac

	4.5 minutes* peak retention minutes		Quinclorac		Quinclorac conjugates (M1)		Post extracted solids (PES)		Total	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Harvest 1 (21 DAT)										
Surface wash	nd	nd	5.33	34.7	0.24	1.5	-	-	5.57	35.7
Solvent extract	nd	nd	4.02	25.8	3.79	24.3	-	-	7.81	50.1
Soxhlet extract	0.27	1.8	1.08	6.9	0.16	1.0	-	-	1.51	9.7
PES							0.7	4.5	0.7	4.5
Total	0.27	1.8	10.43	67.4	4.19	26.8	0.7	4.5	15.59	100
Harvest 2 (37 DAT)										
Surface wash	nd	nd	3.01	17.1	0.15	0.9	-	-	3.16	18.0
Solvent extract	nd	nd	7.67	45.6	1.79	10.7	-	-	9.46	56.3
Soxhlet extract	0.548	3.3	1.38	8.2	0.34	2.0	-	-	2.268	13.5
PES							1.89	11.3	1.89	11.3
Total	0.548	3.3	12.06	70.9	2.28	13.6	1.89	11.3	16.78	99.1
Harvest 3 (61 DAT)										
Surface wash	nd	nd	0.34	8.3	0.08	1.8	-	-	0.42	10.1
Solvent extract	nd	nd	2.86	34.9	2.19	26.8	-	-	5.05	61.7

	4.5 minutes* peak retention minutes		Quinclorac		Quinclorac conjugates (M1)		Post extracted solids (PES)		Total	
	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR
Soxhlet extract	0.47	5.8	1.16	14.2	-	-	-	-	1.63	20.0
PES							0.67	8.1	0.67	8.1
Total	0.47	5.8	4.36	57.4	2.27	28.6	0.67	8.1	7.77	99.9

*approximate times, nd not detected

** M1 the portion of the radioactive residue in the conjugated form.

PES = post extracted solids

DAT = days after treatment

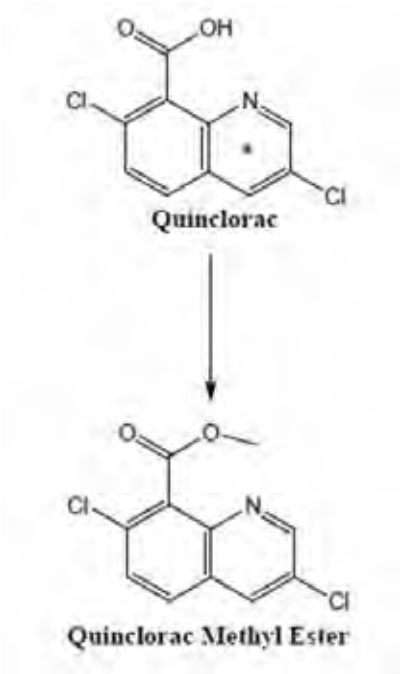


Figure 9 Proposed metabolic pathway of quinclorac in strawberry following foliar post-emergence application of ^{14}C-quinclorac

Environmental fate in soil

For the investigation of the environmental fate of quinclorac the Meeting received one study on hydrolysis, one on photolysis, two on terrestrial and aquatic soil metabolism and one on field dissipation. In the studies, 2, 3, 4-[^{14}C]-quinclorac (quinoline label) or 3-[^{14}C]-quinclorac (quinoline label) were used.

The characteristics of the soils used in the experiments are presented in the table below.

Table 22 Characteristics of soils used for laboratory and field dissipation studies

Study	Clark J.R BASF1987/5040; Clark J.R. BASF 1988/5046 Wood & Winkler BASF 1991/5005	Clark, J R BASF1987/5040 Clark J.R BASF 1988/5046			Goetz A, BASF /1993/5074		Jackson, S et al . BASF 1996/5205
Remark	non-GLP	non-GLP	non-GLP	non-GLP	GLP, Lab	GLP, Lab	GLP, field
Location	Savoy, IL, USA	Greenville,	Davis, CA,	Greenville,	Leland, MS,	Holly	Kingman

Study	Clark J.R BASF1987/5040; Clark J.R. BASF 1988/5046 Wood & Winkler BASF 1991/5005	Clark, J R BASF1987/5040 Clark J.R BASF 1988/5046			Goetz A, BASF /1993/5074		Jackson, S et al . BASF 1996/5205
		MS, USA	USA	MS, USA	USA	Springs, NC, USA	County, KA, USA
Soil name	Soil	Soil	Aquatic/ sediment	Aquatic/ sediment	-	-	-
% sand	14.8	20.8	11.2	9.2	28.5	81.0	84
% silt	65.2	65.2	48.8	48.8	30.0	13.0	10
% clay	20.2	14.0	40.0	42.0	41.5	6.0	6
Texture Class (USDA)	Silt loam*	Silt loam*	Silty Clay Loam	Silty Clay	Clay	Loamy sand	Loamy sand
organic matter %OM	2.5	0.6	2.1	2.5	1.6	1.2	0.7
pH in water	6.4	6.2	7.1	7.1	6.9	6.8	6.7
Cation Exchange Capacity (CEC)	24.8	10.6	33.5	34.2	21.4	3.3	7.3
Water holding capacity at 1/3 bar	29.6	21.3	34.5	21.9	33.0	6.2	7.3

*Soil classification system not stated

Photolysis on soil

The photodegradation of quinclorac was investigated by Wood, N and Winkler, V (1991, BASF 1991/5005) with 3-[^{14}C]-quinclorac in soil (15% sand, 65% silt and 20% clay). Irradiated soil layers were exposed to light from a xenon lamp, filtered to remove light with wavelengths < 290 nm, in a 12 hour light/ 12 hour dark cycle. Test systems were maintained at 26ºC during irradiated periods and 18 ºC during dark periods. The test system was continually aerated with a stream of moistened, CO_2 free, air, and the outgoing air connected to traps for the collection of $^{14}CO_2$. Total recoveries were generally in the range of 93–106% of the % AR.

Under the conditions of the test quinclorac degraded slowly in irradiated samples, with a half-life (DT_{50}) of 162 days; polar metabolites were identified but each to an extent less than 10% AR. In dark control samples the degradation of quinclorac was very slow, with DT_{50} of 529 days.

Soil metabolism

The aerobic soil metabolism was investigated in aquatic and terrestrial soil systems using quinoline [2, 3, 4-^{14}C]- or [3-^{14}C] labelled quinclorac.

In the terrestrial and aquatic soil metabolism study conducted by Clark, J (1987, BASF 1987/5040) [2,3,4-^{14}C]- quinclorac was applied to two silt loam soils from Savoy, IL (USA) and Greenville, MS (USA) and two aquatic water and soil systems from rice fields near Davis, CA, USA and Greenville, MS, USA, see Table 22. The studies were performed prior to GLP being required, but were performed in accordance with US EPA guideline 162-1. Applications were made at a concentration of 0.5 mg/kg, and 5.0 mg/kg corresponding to field application rates of 0.375 kg ai/ha and 3.750 kg ai/ha respectively.

The terrestrial soil test systems were maintained in the dark at 23 ºC, and the moisture adjusted at the start of the study to 40% of the maximum water holding capacity (mWHC). Reaction

flasks with gas outlets to allow CO_2 free air to pass into the bottom and out at the top of the cylinders were used in the experiment. Soil, 500 g for the 0.5 ppm rate and 200 g for the 5 ppm rate. was placed in the flasks and an acetone solution (0.4 mg/g of soil) of quinclorac was added.

The aquatic soil test systems were conducted in a growth chamber in the dark (temperature not given). 250 mL flasks contained approximately 100 g of sediment and 100 mL of water collected from the rice field simultaneously with the sediment. The flasks were connected via tubing to allow the flasks to receive a stream of CO_2 free air and an exit containing scintillation cocktail to capture $^{14}CO_2$. In both the aerobic and the anaerobic experiments, the application of 0.5 mg/kg and 5 mg/kg of quinclorac was added to the water and the water added to each flask containing the sediment.

The individual test systems were continually aerated with a stream of moistened, CO_2 free air, and the outgoing air connected to traps for the collection of $^{14}CO_2$. Single samples for the 0.5 mg/ kg studies were taken after application and at seven further sample times including at the study termination 12 months after application. For the 5 mg/kg studies samples were collected at 5 sample times from 1 month to 12 months after application. In the aerobic aquatic soil studies water was decanted and analysed by LSC. Soil samples were frozen at -20 ºC following collection until they were analysed.

Soil samples were extracted at room temperature with water and 0.1 N NaOH. The aqueous extracts were partitioned with ethyl acetate. The extracted soil was then refluxed with 0.1 N NaOH, neutralized with HCl, and partitioned with ethyl acetate.

All extracts were radio-assayed, with residual soil combusted and analysed by LSC to determine radioactive mass balances. TLC was used for identification and quantification, with confirmation by HPLC using eight synthetized standards.

An overview of radioactive residues extracted from terrestrial and aquatic soil systems are presented in tables below.

Table 23 Recovery of radioactivity (% AR) during aerobic terrestrial degradation of 0.5 mg/kg from 2, 3, 4-^{14}C- quinclorac

Soil	Days after treatment	H_2O wash	0.1N NaOH extract	0.1 N NaOH reflux	Unextracted residues	$^{14}C0_2$ trapped	Total recovery
Savoy, IL, USA Silt loam	14	55.7	39.7	12.1	1.5	-	109.0
	180	49.6	26.0	20.2	3.9	-	95.8
	360	47.1	21.3	15.7	11.3	0.05	95.45
Greenville, MS,USA Silt loam	14	74.8	16.4	9.7	0.7	-	101.8
	180	62	20.4	18.8	2.4	-	113.6
	360	58.8	17.2	22.1	2.5	0.08	100.68

Table 24 Recovery of radioactivity (% AR) during aerobic aquatic degradation of 0.5 and 5 mg/kg from 2, 3, 4-^{14}C- quinclorac

Soil	Days after treatment	H_2O wash	0.1N NaOH extract	0.1 N NaOH reflux	Unextracted residues	$^{14}C0_2$ trapped	Total recovery
Davis, CA USA Silty clay loam 0.5 mg/kg	30	88.4	3.3	5.4	5.1	0.03	102.2
	180	74.4	7.7	8.0	3.6	3.9	97.5
	360	56.7	10.7	12.3	4.8	5.4	89.9
Greenville, MS, USA Silt loam 0.5 mg/kg	30	84.0	11.0	5.6	1.4	0.02	102.0
	180	74.5	13.5	6.8	3.3	6.9	105.0
	360	41.6	15.0	17.9	14.9	8.8	98.2
Greenville,	120	58.0	20.0	9.5	3.5	-	91.0

Soil	Days after treatment	H_2O wash	0.1N NaOH extract	0.1 N NaOH reflux	Unextracted residues	$^{14}C0_2$ trapped	Total recovery
MS, USA Silt loam 5.0 mg/kg	180	30.0	27.0	20.0	12.0	-	89.0
	360	20.2	24.4	23.1	21.5	-	89.2

Table 25 Recovery of radioactivity (% AR) 180 days after treatment in analysis of fractions during aerobic and anaerobic aquatic degradation in a silt loam* of 0.5 mg/kg from 2, 3, 4-^{14}C- quinclorac

Conditions	Supernatant + wash	0.1 N NaOH extract	0.1 N NaOH reflux	Unextracted residues	$^{14}C0_2$ trapped	Total recovery
Anaerobic	85.7	2.5	2.1	2.0	0.04	92.3
Aerobic	74.4	7.6	8.0	3.6	5.1	98.7

* Silt loam soil from Greenville, MS, USA

Table 26 Characterization of total extracted radioactive residues (% AR) in the aerobic aquatic soil degradation in a silt loam after application of 5 mg/kg from 2, 3, 4-^{14}C-quinoline labelled quinclorac

Soil	Days after treatment	Quinclorac	BH 514-1	Unk-2	Unk-3	Unk-4
Greenville, MS, USA Silt loam 5.0 mg/kg	120	55.8	31.7	0.0	0.0	0.0
	180	5.7	55.7	5.0	3.4	0.9
	360	7.6	30.8	5.0	7.6	6.9

*3-chloro-8-quinolilne carboxylic acid

Quantified characterization data of extracted residues is not presented in the reports. It is stated with regard to the terrestrial soil samples that the TLC profiles on total extracted residues in both soils indicated no degradation of quinclorac 120 days after treatment. After one year incubation, traces of metabolite BH 514-1 (3-chloro-8-quinolilne carboxylic acid) was reported to have been observed in the soil.

In the aquatic anaerobic and aerobic systems (Table 25) extraction data 180 days after the application of quinclorac show small differences in the distribution of residues in the different fractions.

In the aerobic aquatic system, with an application rate of 0.5 mg/kg, it is stated in the report that samples displayed mainly unchanged quinclorac after 1 year. In the same system (Table 26) at an application rate (AR) of 5 mg/kg (corresponding to 3.75 kg ai/ha) to sediment and water of a silty loam (rice field) quinclorac degraded slowly to the metabolite BH 514-1 (3-chloro-8-quinolilne carboxylic acid) at a maximum concentration of 55.7% AR 180 days after treatment. Three additional metabolites were detected each present at less than 10% AR and not further characterized. The half-life (DT_{50}) of quinclorac in this system was 4.7 months and for the metabolite BH 514-1 7.4 months. Under anaerobic conditions at the 5 mg/kg level, the same metabolites were formed but at a slower rate, there was a 50% conversion of quinclorac to BH 514-1 within one year.

In an aerobic soil metabolism study conducted by Goetz AJ (1993, BASF 1993/5074) [3-^{14}C]-quinclorac was applied to a clay soil from Holly Springs, NC, USA, and to a loamy sand soil from Leland, MS, USA (Table 22 beginning of chapter). Applications were made at concentrations of 5.3 mg/kg dry soil to the clay soil, and 5.5 mg/kg dry soil to the loamy sand soil, corresponding to field application rates of 3.975 kg ai/ha and 4.125 kg ai/ha respectively. Soil samples from loamy sand and a clay soil were extracted by shaking and/ or refluxing borate buffer and additionally by refluxing in sodium hydroxide if required.

Radioactivity in the extracts was quantified by LSC, with residual soil combusted and analysed by LSC. HPLC was used for characterization and quantification of extracted radioactivity. Analytical standards were used for quinclorac, BH 514-1 (3-chloro-8-quinolilne carboxylic acid), BH 514-2-OH (2-hydroxyquinclorac) and BH 514-Me (quinclorac methyl ester).

The extractability and characterization of the extracted residues in the organic extracts is presented in tables below. Additional residues present in the sodium hydroxide fractions are presented in brackets.

Table 27 Extractability and distribution of radioactive residues after incubation of 5.5 mg/kg (corresponding to 3.98 kg ai/ha) of [3-^{14}C quinclorac dry loamy sand soil (81.0% sand, 13.0% silt, 6.0% clay)

Fraction	Residues (% of applied radioactivity) at days after treatment										
	0	3	7	14	30	61	90	149	210	273	364
Borat buffer	90.9	84.2	83.0	92.8	89.9	76.6	84.6	73.9	77.9	72.4	81.1
Aqueous	0.4	-	-	0.8	1.9	1.0	2.9	2.5	4.6	4.6	5.3
1 N NaOH	-	-	-	-	4.1	-	6.3	-	9.1	13.5	10.7
Humic	-	-	-	-	0.3		0.5		0.8	1.0	1.1
Unextracted residue	1.0	5.6	10.4	1.8	0.4	9.0	0.7	10.8	0.8	1.2	1.2
Volatile organic radioactivity	-	0.1	0.2	0.4	0.5	2.0	3.2	4.2	5.2	5.6	7.5
Total *recovery	97.1	89.9	93.6	101.7	95.7	85.7	90.5	88.9	89.9	89.3	99.9
Identification and characterization											
Quinclorac**	95.7	-	-	94.8	74.5 (3.3)	64.2	60.2 (4.9)	52.9	53.5 (6.3)	45.7 (10.9)	51.5 (6.6)
Met-1	0.0	-	-	1.3	3.9 (0.4)	3.0	4.8 (0.7)	5.0	2.5 (1.2)	4.1 (1.5)	9.1 (0.8)
Met-2	0.2	-	-	0.2	2.2	0.0	2.1	1.7	1.6	1.9	0.0 (1.2)
BH 514-2-OH	0.0	-	-	0.8	3.6	2.6	5.3	5.5	6.7	7.6 (0.4)	8.1 (0.3)
BH 514-Me	0.0	-	-	1.6	4.7	3.9	5.2	5.6	7.1	4.8	7.8
Other	0.0	-	-	1.2	0.0	0.0	0.0	0.0	0.0	0.0	0.3

***** The radioactivity found in the different fraction reported does not always add up to exact TTR

** Additional residues from the extraction with methanol/ammonium hydroxide following reflux in sodium hydroxide are presented in brackets.

Table 28 Extractability and distribution of radioactive residues after incubation of 5.3 mg/kg (corresponding to 4.1 kg ai/ha) [3-^{14}C] quinclorac to dry clay soil (28.5% sand, 30.0% silt, 41.5% clay)

Fraction	Residues (% of applied radioactivity) at days after treatment										
	0	3	7	14	30	61	91	150	210	274	364
Borat buffer	96.7	84.2	80.6	90.2	86.2	61.2	66.0	55.4	61.2	55.6	54.5
Aqueous	0.2	-	0.5	2.5	4.4	9.1	6.6	10.8	13.6	5.8	11.6
1 N NaOH	-	-	-	6.2	10.6	18.0	20.2	22.1	23.1	28.6	26.1
humic	-			1.5	1.6	2.2	2.9	2.3	3.0	6.0	5.5
Unextracted residue	4.4	14.1	16.6	0.9	1.8	3.0	3.7	4.0	4.5	4.7	3.9
Volatile organic radioactivity	-	0.1	0.1	0.2	0.3	1.4	2.6	3.0	4.4	5.4	6.1
Total *recovery	96.8	98.4	93.1	102.6	94.4	82.8	94.2	90.6	94.2	91.7	89.4
Identification and characterization											
Quinclorac**	92.2	-	-	88.9 (4.3)	73.8 (4.7)	43.9 (12.8)	44.1 17.1)	33.7 (13.1)	32.6 (14.2)	25.5 (15.8)	19.2 (11.8)
Met-1	0.0	-	-	1.2	0.0	1.4	1.2	4.4	1.5	3.3	4.2

Fraction	Residues (% of applied radioactivity) at days after treatment										
	0	3	7	14	30	61	91	150	210	274	364
				(0.3)	(0.4)	(1.6)	(2.4)	(3.1)	(3.2)	(2.8)	(3.9)
Met-2	0.0	-	-	0.8 (0.1)	0.0 (0.2)	0.6	0.8 (0.2)	1.4 (0.2)	1.8 (0.9)	2.4 (0.8)	2.2 (0.6)
BH 514-2-OH	0.0	-	-	0.7	3.8 (0.2)	3.4 (0.8)	7.2 (1.2)	8.2 (1.0)	10.0 (0.3)	12.4 (2.7)	12.4 (2.5)
BH 514-Me	0.0	-	-	0.5	2.3	1.7	3.1	4.0	2.3	2.5	3.0
Other	0.0	-	-	0.3 (0.1)	0.0 (0.2)	0.0	0.0	0.0	0.0	0.0	0.0

***** The radioactivity found in the different fraction reported does not always add up to exact TTR

** Additional residues from the extraction with methanol/ammonium hydroxide following reflux in sodium hydroxide are presented in brackets.

The radioactive residues extracted from soil by refluxing with sodium hydroxide solution are considered bound. The residues associated with the humic material increased with time and at 364 days after treatment accounted for 1.1 and 5.5% TRR in the loamy sand and clay soil. The majority of the residues extracted from the humic material by sodium hydroxide were quinclorac.

The residues extracted from the borate buffer solution are considered as available residues**.** Under the condition of the study quinclorac degraded with half-lives (DT_{50}) of 391 days in a loamy sand and 168 days in a clay, forming the metabolites BH 514-2 –OH (2-hydroxyquinclorac) at a maximum concentration of 12% AR and the metabolite BH 514-Me (quinclorac methyl ester) at a maximum of 7.8% AR. Other metabolites were identified at levels well below 10% AR throughout the study and not further characterized.

Field dissipation study

The dissipation of quinclorac in a loamy sand soil was investigated at one site in Kansas USA by Jackson, S *et al* (1997, BASF 1996/5205). Quinclorac was applied with two applications of 2.8 kg ai/ha to bare soil. One application of was made in autumn (October 1994) and the other at summer (June 1995).

Soil samples were taken at day 0 to approximately 540 days after the first application at a maximum depth of 1.22 m. Samples were separated into 15 cm segments (table below) and three samples were analysed per segment. The samples were extracted with 0.1 N NaOH followed by acidification and partitioning with methylene chloride/ ethyl acetate. An aliquot of the organic extract was dried and reconstituted in HPLC mobile phase and analysed by LC/MS/MS. The LOQ for the summed residue was 0.01 mg/kg. Quinclorac methyl ester was extracted from soil with methylene chloride, ethyl acetate and methanol. The extract was dried, re-constituted in HPLC mobile phase, and analysed by LC/MS/MS.

Soil characteristics and residue concentrations of quinclorac and the metabolites BH 514-2-OH and BH 514-Me are presented in tables below.

Table 29: Soil characteristics for soil used for a field dissipation study for quinclorac

Soil characteristic	Soil depth (cm)						
	0-15	15-30	30-45	45-61	61-76	76-91	91-107
% sand	84	84	88	94	94	94	90
90% silt	10	08	04	0	02	02	02
% clay	06	08	08	06	04	04	08
% organic matter	0.7	0.9	0.4	0.5	0.4	0.4	0.2
pH	6.4	6.3	6.6	6.9	7.1	7.2	6.8
% moister 1/3 bar	7.3	8.6	6.9	4.3	4.0	3.5	6.1
CEC (m eq/kg soil)	7.3	9.7	8.6	5.1	5.5	3.6	6.7
texture	loamy soil	loamy soil	loamy soil	sand	sand	sand	sand

Residue values were determined at each sampling interval in (15 cm) segments to a depth of up to 121 cm. Based on the distribution and magnitude of concentrations, ca. 89% of the quinclorac was observed in the topsoil (0–30cm) with 74% in the 0–15 cm segment and 15% in the 15–30 inch segment. At the exaggerated use rate of this study (2 × 2.8 kg ai/ha) some movement to lower depth segments was observed with 7% in the 30-46 cm segment, 2% in the 46-61 cm segment, 1% in the 61-76 cm segment, and < 1% in all lower depths. Metabolite BH 514-2-OH was observed primarily in the topsoil (91%) with 32% in the 0–15 cm segment and 59% in the 15-30 cm segment. The remainder (9%) was observed in the 30–46 cm segment. Metabolite BH 514-Me was only observed in topsoil with ca. 84% in the 0–15 cm segment and 16% in the 15–30 cm segment.

Table 30 below shows total residues from quinclorac during the 540 day study detected from samples taken to a maximum depth of 1.22 m.

Table 30 Total residue concentration of quinclorac, metabolite BH 514-2-OH and BH 514-Me following application of 5.6 kg ai/ha quinclorac to bare soil in Kansas USA

Time	Total residue of all depths (mg/kg)		
Days after treatment (DAT)	quinclorac	BH 514-2 -OH	BH 514-Me
0 Treatment 1	0.836	0	0
1	0.918	0	0
3	0.801	0	0
5	0.816	0	0
7	0.774	0	0
14	0.757	0	0
21	0.617	0	0
30	0.582	0	0
60	0.499	0	0.003
90	0.539	0.017	0.007
120	0.414	0	0
180	0.421	0.020	0.010
240 Treatment 2	0.799	0	0
241 (1 DAT 2)	0.840	0	0
243 (3 DAT 2)	0.769	0	0.007
245 (5 DAT 2)	0.591		0
247 (7 DAT 2)	0.583	0.003	0
254 (14 DAT 2)	0.545	0.003	0
261 (21 DAT 2)	0.330	0.025	0.007
300 (60 DAT 2)	0.004	0.033	0
330 (90 DAT 2)	0	0.013	0
420 (180 DAT 2)	0	0.014	0
540 (300 DAT 2)	0	0.019	0.009

The maximum observed concentrations of the two metabolites were 3.6% for BH 514-2-OH (2-hydroxyquinclorac quinclorac) and 1.1% for BH 514-Me (quinclorac methyl ester). DT_{50} and DT_{90} for quinclorac were 126 days and > 360 days following the first application (winter), and 8 days and 26 days following the second application (summer).

Long-term soil accumulation studies were not submitted to the Meeting.

Confined rotational crop studies

The metabolism of [2, 3, 4-^{14}C]-quinclorac was investigated by Winkler, V and Brown M (1987, BASF 1987/5037) in the rotational crops wheat, mustard greens, turnips, sorghum and soya bean from two consecutive (first (120 days after treatment) and second (360 days after treatment) rotations. A replanting of a crop just after harvest (30 days) was not considered necessary as in good agricultural practice a new crop is never planted 30 days after harvesting of a rice crop. The first (autumn) rotational crops were wheat, mustard green and turnips, the second (annual) rotational crops were sorghum, mustard green, soya beans and turnip.

Quinclorac was applied to flooded and non-flooded rice (primary crop) at a rate of 0.84 kg ai/ha in Mississippi, USA. Rice was planted approximately one month prior to application.

The formulation was applied to one plot under flooded conditions and to another plot under non-flooded conditions; seven days later, permanent flood conditions were established on this plot. After mature harvest of rice, the soil was “worked and prepared” before first rotational crops were planted less than one month after the rice harvest (120 DAT) followed by the second rotational crops 360 DAT. The study was ended 474 days after the application of quinclorac.

Table 31 Physiochemical properties of the soil

Soil type	pH	OM%	Sand %	Silt	Clay	Field moisture	CEC meq/100g
Silty clay	6.5	2.2	9.6	40.4	50.0	21.69	33.18

Soil and plant samples were collected. Soil samples were extracted with distilled water following centrifugation. Residual soil was re-suspended in 0.1N NaOH and refluxed, centrifuged and analysed by combustion to determine $^{14}CO_2$ content. Plant samples were extracted with aqueous acetone, concentrated into the aqueous phase, acidified and extracted with ethyl ether. Soya bean and wheat seeds were defatted with hexane, hydrolysed with 1N HCl and extracted with ethyl ether. Soya bean was also further extracted by 1% NaCl reflux, EDTA reflux, 5% NaOH extraction and finally 1% sodium chlorite treatment for three hours at 80 °C. The extracted residues were derivatized using diazomethane before TLC analysis using authentic standards for parent quinclorac and the metabolite BH 514-1 (3-chloro-8-quinoline carboxylic acid) which was found as a major metabolite (55.7% AR) in the aquatic soil degradation systems.

The non-flooded treatment gave the highest residues in soil and in crops. In the following table the TRRs found in soil samples (silty clay) in the first 1–10 cm from non-flooded treatments are summarized.

Table 32 Total radioactive residues (mg/kg ^{14}C-quinclorac equivalents) in the first 10 cm of a silty clay soil (non-flooded)

Days after treatment	Total TRR	Water extract	0.1N NaOH Extract	Unextracted	Unextracted % TRR	% material balance
0	0.424	0.365	0.094	0.022	5	116
1	0.056	0.031	0.031	0.011	20	107
3	0.029	0.004	0.013	0.013	45	103
4	0.033	0.007	0.015	0.012	36	102
6	0.051	0.003	0.009	0.017	33	58
326	0.123	0.026	0.067	0.034	27	103
385	0.043	0.002	0.010	0.024	65	94
474	0.059	0.005	0.025	0.028	45	99

Water extracted residues is considered as free and available to the plant, while generally sodium hydroxide extracts are ionic and covalent bound residues**.** The total radioactive residues decreased from an initial level of 0.4 ppm to 0.056 ppm one day after application, and remained relatively constant at that level through the 474 days study.

The table below summarizes the uptake of radioactive residues in different rotational crops and their matrixes.

Table 33 Total radioactive residue (mg/kg ^{14}C-quinclorac equivalents) in first (autumn) and second (annual) rotational crops

Crop *In brackets days from application to harvest is stated*	First rotation**,** planted 120 days after treatment		Second rotation**,** planted 360 days after treatment	
	Non-flooded	Flooded	Non-flooded	Flooded
Leafy vegetable				
Mustard top (158)	0.015	0.006	0.014 (0.016,0.012)	0.003 (0.002, 0.003)
Mustard plant (40)	0.028	0.009		
Small grain				

Crop *In brackets days from application to harvest is stated*	First rotation, planted 120 days after treatment		Second rotation, planted 360 days after treatment	
	Non-flooded	Flooded	Non-flooded	Flooded
Wheat seed (205)	0.025	0.013	n.a.*	n.a.*
Wheat straw (205)	0.021	0.016-	n.a.*	n.a.*
Wheat plant (40d)	0.019	0.029	n.a.*	n.a.*
Soya bean seed (82)	n.a.*	n.a.*	0.017	0.009
Soya bean stalk (82)	n.a.*	n.a.*	0.025	0.013
Soya bean plant (50)	n.a.*	n.a.*	0.006 (< 0.002, 0.009)	0.004 (0.005 0.003)
Sorghum seed (171)	n.a.*	n.a.*	< 0.002	0.006
Sorghum heads (171)	n.a.*	n.a.*	< 0.002	0.028
Sorghum tops (23)	n.a.*	n.a.*	0.03 (0.038, 0.023)	0.006
Sorghum plants (65)	n.a.*	n.a.*	-	0.003
Sorghum stalk (171)	n.a.*	n.a.*	0.013	0.006
Root and tuber vegetable				
*Turnip plant**(40-50)*	0.012	0.004	0.008	0.003
*Turnip root** (82-172)*	0.008 (0.013,0.003)	0.006 (0.009, 0.002)	0.02 (0.042,0.005)	0.002
Soil mean values				
0-10 cm	0.041	0.012	0.065	0.017
10-20	0.034	0.016	0.023	0.014
20-30 cm	0.021	0.014	0.023	0.018

*The first (fall) rotational crops were wheat, mustard green and turnips, the second (annual) rotational crops were sorghum, mustard green, soya beans and turnip.

**sampling days for first and second rotational crop

In the first rotational crops as well as the second rotational crops, the residues found were higher from crops grown under non-flooded conditions. Uptake of residues was observed in both first and second rotational crops. For the first rotational crops maximum uptake was 0.028 mg eq/kg for leafy vegetable (mustard plant), for small grain (wheat seed) 0.025 mg eq/kg and for root and tuber vegetable (turnip plant) 0.012 mg eq/kg. For the second rotational crops maximum uptake was 0.014 mg eq/kg for leafy vegetable (mustard top) for small grain (soya bean seed) 0.017 mg eq/kg and for root and tuber vegetable (turnip root) 0.02 mg eq/kg.

The methylated extracted residues were identified as mainly total quinclorac and trace amounts of the metabolite BH 514-1 (3-chloro-8-quinoline carboxylic acid).

The table below quantifies the total radioactive residues found in the different rotational crops and their matrixes.

Table 34 Extraction of ^{14}C-quinclorac from mustard, wheat and soya bean samples

Crop	days after treatment	TRR (quinclorac equivalents)*	
		mg/kg TRR	% TRR
Mustard top	147		
total		0.015	(100)
acidic ether		0.005	31
aqueous acidic		-	0
Marc		0.004	23
Wheat seed	147		
total		0.025	(100)
hexane		-	
acidic ether		0.017	67
aqueous acidic		0.007	42
Marc		0.005	19
Mustard top	303		
total		0.012	(100)
acidic ether		0.003	27
aqueous acidic		-	0
Marc		0.004	32
Soya bean seed	303		
total		0.017	(100)

Crop	days after treatment	TRR (quinclorac equivalents)*	
		mg/kg TRR	% TRR
hexane		0.004	25
acidic ether		0.003	17
aqueous acidic		-	0
Marc		0.010	62
Soya bean hay	303		
Total		0.025	(100)
acetone/water		0.002	7
1N HCL		0.002	6
Marc		0.018	73

Quinclorac was the only major residue (>10% TRR but less than 0.05 mg eq/kg) detected in the examined rotated crops. The metabolism of quinclorac by soya bean was different from mustard and wheat due to that as much as 62% TRR (0.01 mg eq/kg) was found in soya bean seed as insoluble residues in the marc. Further extraction of the marc revealed radioactive residues in protein, carbohydrate and lignin fractions according to table below.

Table 35: Characterization of ^{14}C-quinclorac residues in soya bean

Fraction	soya bean seed	soya bean hay
	% TRR	
Hexane	8	
Pellet (insoluble debris)	37	
Protein	34	
Carbohydrate soluble	35	
Acetone extract		15.8
Polysaccharides water soluble		11.7
Pectic polysaccharides		21.8
Hemicellulose I		36.8
Lignin		11.8
Hemicellulose II		10.5

The metabolism of [3-^{14}C]-quinclorac was investigated by Nelsen, J (1992, BASF 1992/5044) in rotational crops mustard green, turnip and barley from one rotational interval (120 days). 3-^{14}C-quinclorac was applied as a spray pre-emergence and 25 days later post-emergence to sorghum plants. Treatment levels were 0.527 kg ai/ha pre-emergence and 0.504 kg ai/ha post-emergence. Sorghum plants were harvested 95 days after the post-emergence treatment. Approximately 120 days after the post-emergence treatment, mustard, turnip and barley seed were planted. Rotational crops were harvested at maturity. Barely forage was harvest 205 days after treatment.

Crop samples were treated with 0.1N NaOH or 0.1N NH_4OH and then extracted with acetone. The filtrate was subsequently acidified, concentrated, the pH adjusted to 8 and then diluted with water and extracted with dichloromethane. The water layer was further extracted with dichloromethane or refluxed with HCl. All subsamples of marc were subjected to refluxing with sodium chloride to determine radioactivity incorporated into water soluble polysaccharides, with EDTA to determine peptic polysaccharides, with sodium hydroxide to determine hemicellulose I or II and with sodium chlorate to determine lignin.

Total radioactivity was determined by combustion analysis and LSC. The nature of the residues was determined by fractionation and TLC using quinclorac, BH 514-1 (3-chloro-8-quinilone carboxylic acid) and their respective methylated samples as reference standards.

In the table below the extracted and identified radioactivity residue found at harvest in the different rotated crop matrixes is presented.

Table 36: Identification and characterization of radioactive residues in rotational crops (1st rotation, 120 days) following application of [3-^{14}C]-quinclorac to sorghum crop at a total rate of 1.0131 kg ai/ha

Metabolite fraction	Mustard green		Turnip				Barely					
			turnip top		root		grain		straw		forage	
	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg	% TRR	mg eq/kg
Dichloromethane I (neutral)	4.89	0.008	6.46	0.014	22.22	0.006	5.71	0.008	1.75	0.003	7.58	0.014
Dichloromethane II (acidic)	74.98	0.12	63.07	0.132	44.82	0.011	58.71	0.088	28.31	0.045	64.50	0.116
Dichloromethane III (hydrolysed)	-	-	-	-	2.80	< 0.001	5.33	0.008	6.55	0.01	1.77	0.003
Aqueous	6.01	0.01	8.19	0.017	13.1	0.003	13.29	0.020	27.79	0.044	10.52	0.019
Non-extracted residues (marc)	7.42	0.012	17.34	0.036	9.83	0.002	10.86	0.016	37.02	0.059	14.09	0.025
TRR*	100	0.16	100	0.21	100	0.025	100	0.18	100	0.16	100	0.15
Identification and characterization of TRR												
quinclorac	72.1	0.115	61.3	0.129	40.2	0.010	63.7	0.114	63.7	0.114	58.7	0.088
quinclorac methyl ester	3.82	0.006	4.17	0.009	1.76	< 0.001	< 0.3	< 0.001	< 2.9**	< 0.001	< 5.6**	< 0.008
Total identified	75.92	0.12	65.47	0.138	41.96	0.0011	64.0	0.115	66.6	0.115	64-3	0.097

*The TRR identified in the different fractions does not always sum up to the TRR in the combustion analysis.

** TLC was not performed on these samples

The parent quinclorac was a major residue in all matrices and the metabolite BH 514-Me (quinclorac methyl ester) a minor metabolite (3-4% TRR) in mustard green and turnips.

Field rotational crop study

Magnitude of quinclorac residues in rotational rape seed (canola) was investigated by Barney, WP (1993, BASF 1993/5157) in a field trial in Canada. Rape seed was planted in the same plot as barley which had been grown and treated the previous year with quinclorac in a single broadcast post emergence application at the rate of 0.2 kg ai/ha.

Rape seed samples (four replicates) were harvested at maturity and stored frozen until analysis within 5 months. Samples were analysed for quinclorac with method A8902 using GC/EDC detection. The method was validated to a LOQ of 0.05 mg/kg for oil seed and the method recovery was at fortification level 0.05 mg/kg was 96% (n=1) and at fortification level 0.5 mg/kg 82% (n=1).

Table 37 Residues from quinclorac in rotating seed from plots where barley was grown previous year and treated with 0.2 kg ai/ha

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage	matrix	PHI	Total quinclorac (mg/kg)	mean mg/kg	Reference
Canada Minto, Manitoba 1991 barley	0.2	1	Not reported	Not sampled	60	-	-	BASF 1993/5157
Canada Minto, Manitoba 1992 Rape seed	-	-	-	grain	-	< 0.05, < 0.05, < 0.05, < 0.05	< 0.05	BASF 1993/5157

ANALYTICAL METHODS

The meeting received analytical method description and validation data for quinclorac and its metabolite quinclorac methyl ester. Most matrices are validated with a LOQ of 0.05 mg/kg for both analytes, however in strawberry and oil seeds the analytes were validated also with a LOQ of 0.01 mg/kg. A summary of the analytical methods for plant and animal commodities is provided below.

Table 38 Overview of analytical methods used for the quantification of quinclorac residues in plant and animal matrices

Method (analytes)	Matrix	Extraction	Clean-up	Detection, LOQ
Method 268 Quinclorac	Animals (eggs, milk, muscle, kidney, fat, liver)	Acetone/sodium solution, acidify and partition with ethyl acetate, and derivatized with diazomethane.	filtration and C-18 SPE column	GLC-ECD SE 54 capillary column at 270-350°C, Quantification by external standards. Quinclorac-Me LOQ, 0.05 mg/kg
Method 268-1 amendment Quinclorac	Animals (eggs, milk, muscle, kidney, fat, liver)	Acetone/sodium solution, acidify and partition with dichloromethane, and derivatized with diazomethane.	filtration and amino SPE column	GLC-ECD SE 54 capillary column at 270-350°C, Quantification by external standards. Quinclorac-Me LOQ, 0.05 mg/kg
Method M829/A Quinclorac	strawberry and high water fruit crops	Acetic acid in acetonitrile in the presence of magnesium sulfate and sodium chloride		LC-MS/MS using a C18 analytical column. Quantification is made using internal standard The quinclorac ion transition 242→224 is used for quantification and the ion transition m/z 244-226 is used for confirmation. LOQ 0.01 mg/kg
Method A8902 Quinclorac	Rice (grain and straw rough rice, rice hulls, brown rice, rice bran, milled rice) Sorghum forage grain and stover.	Acetone /0.1 M NaOH solution acidify and partitioned with dichloromethane, and derivatized with diazomethane.	filtration and by solid phase extraction (silica gel column)	The methylated samples are analysed by GC-EDC at 300°C using a DB17 fused silica column at 200ºC and an electron capture detector (GC-ECD). Quantification by external standards. Quinclorac-Me LOQ 0.05 mg/kg
Method D9708 Quinclorac	Sorghum forage, grain and stover Validation data for	Acetone /0.1 M NaOH acidify and partitioned with dichloromethane, diluted with sodium	filtration and by using quaternary amine SPE column	HPLC-MS/MS using a Betasil C18 column Quantification by

Method (analytes)	Matrix	Extraction	Clean-up	Detection, LOQ
	sorghum stover/fodder was not presented	hydroxide and pH adjusted to 8-11		external standards. The ion transition m/z 240→196 is monitored. Quinclorac LOQ 0.05 mg/kg
Method D9708/1 Quinclorac	Wheat (forage, grain, straw, grain and processed commodities) Rape seed and oil	Plant material: Acetone /sodium solution, acidify and partition with dichloromethane Canola seed: hexane/sodium solution, partition with acetonitrile	filtration and C18 SPE column	HPLC-MS/MS using a Betasil C18. Quantification is performed using external standards. The ion transition 240→196 is used for quantification Quinclorac LOQ 0.05 mg/kg
Method D9806 Quinclorac-Me	Rape seed and oil	Seed: acetone/hexane and partitioned with acetonitrile/water and methanol. Oil: hexane and partitioned acetonitrile/water and methanol.	Filtration and C18 SPE columns	HPLC-MS/MS using a Betasil C18 column Quantification is performed using external standards. Quinclorac methyl ester. The ion transition m/Z 255-224 is used for quantification. LOQ 0.05 mg/kg
method D9708/01 and method D9706 Quinclorac and Quinclorac -Me	Cereal grain and oil seed	Quinclorac extracted as in method A8902. Quinclorac methyl ester was extracted by acetone and the residue diluted in hexane. Partitioned twice acetonitrile/water and methanol.	Filtration and C18 SPE columns	HPLC-MS/MS using a Betasil C18 column Quantification is performed using external standards. Quinclorac. The ion transmission m/Z 240-196 used for quantification Quinclorac methyl ester. The ion transition m/Z 255-224 is used for quantification LOQ 0.05 mg/kg
Method D9708/2 and Method D9806/2 Quinclorac and Quinclorac -Me	wheat grain and oil seed (canola)	The extraction procedure is the same as for method D9708, see above	Filtration and C18 SPE columns	HPLC-MS/MS using an Acquity UPLC HSS T3 column. Quantification is performed using external standards The quinclorac ion transition m/z 242→224 is used for quantification and the ion transition m/z 242→161 is used for

Method (analytes)	Matrix	Extraction	Clean-up	Detection, LOQ
				confirmation. The quinclorac methyl ester ion transition m/z 256→224 is used for quantification and the ion transition m/z 256→161 is used for confirmation LOQ 0.05 mg/kg for both analytes
Method R0036 Quinclorac and Quinclorac methyl ester	rape seed, rape oil	Plant material: *Quinclorac* acetone/sodium solution, acidify and partition with dichloromethane. *Quinclorac methyl ester* acetone. The centrifuged sample is saturated with sodium chloride and extracted with dichloromethane. Oil: *Quinclorac* hexane followed by acetonitrile/sodium hydroxide *Quinclorac methyl ester* hexane and acetonitrile/water and methanol. The centrifuged samples is saturated with sodium chloride, acidified and extracted with dichloromethane.	Not necessary using HPLC-MS/MS and the instruments high degree of specificity	HPLC-MS/MS using an Atlantis T3 column. The quinclorac ion transition m/z 242→224 is used for quantification and the ion transition m/z 242→161 is used for confirmation. The quinclorac methyl ester ion transition m/z 256→224 is used for quantification and the ion transition m/z 256→161 is used for confirmation LOQ 0.01 mg/kg for both analytes.

Animal commodities

For quantification of parent quinclorac in animal commodities method 268 was developed and validated by Mayer, F (1988, BASF 88/0542).

Method 268 (animal matrices)

The analytical method 268 was described and validated for parent quinclorac by Mayer, F (1988 a, BASF 88/0542) for cow and chicken tissues, milk and eggs. Homogenised samples (20g) were extracted with acetone/0.1 N NaOH (15:10, v/v) for 5 min followed by acidification with sulphuric acid. After centrifugation, the remaining solids were extracted again with acetone/0.1 N sulphuric acid (50:50 v/v). Both extracts were combined and the interferences were removed by clean-up on an Extrelut column, followed by $NaHCO_3$/ethyl acetate partition at pH =8. The extract was acidified to pH 2 and quinclorac was partitioned into ethyl acetate. After clean-up with C18 modified silica, quinclorac was derivatized (methylated) with diazomethane and determined by GC-ECD using a derivatized external standard. Confirmation was obtained by HPLC-UV or GC MS at m/z 224, 226, 255, 257. The reported LOQ was 0.05 mg/kg. Validation results are shown in Table 39

Method 268/1, amendment to method 268 (animal matrices)

In the amended method 268/1 by Mayer, F (1989 BASF/10911) the same procedure was followed except that quinclorac was partitioned into dichloromethane, cleaned using amino SPE and eluted with citrate buffer /dichloromethane.

Independent laboratory validation (ILV) studies for the method were not presented to the Meeting.

Table 39 Recovery data for determination of quinclorac in animal matrices

Cow	Fortification level	n	recovery mean	SD	CV	Analyte, reference
muscle	0.05	5	79.7	9.7	12.1	Quinclorac equivalents
	5	5	70.2	2.2	3.2	
Fat	0.05	5	68.7	5.8	8.4	(quantified as quinclorac-ME)
	5	5	66.7	3.4	5.1	
Liver	0.05	5	77.5	8.4	10.8	(BAS 514H)
	5	5	70.4	1.2	1.7	(1988, BASF 88/0542)
Kidney	0.05	5	70.9	7.8	11.0	method 268 original
	5	5	72.9	5.0	6.9	
Milk	0.05	5	76.9	4.6	6.0	
	5	5	69.6	5.1	7.4	
Chicken						
muscle	0.05	5	75.6	11.5	15.2	
	5	5	78.2	3.4	4.4	
skin + fat	0.05	5	75.1	15.7	20.9	
	5	5	77.1	2.3	3	
Liver	0.05	5	69.9	14.4	20.6	
	5	5	90.0	3.6	4.0	
Egg	0.05	5	70.0	2.9	4.1	
	5	5	68.8	2.7	4.0	
cow milk	0.05	5	90.2	1.9	2.1	Quinclorac (BAS F514H)
	5	5	82.6	1.4	1.7	(1989a, BASF 89/5001)
goat muscle	0.05	5	75.2	7.9	10.5	method 268/1
	5	5	85.0	2.1	2.5	
goat liver	0.05	5	81.4	7.5	9.3	
	5	5	63.6	5.6	8.8	

A radiovalidation of the method 268 was conducted by Mayer F (1988 b BASF/10179) with samples from muscle, skin with fat, liver, kidney and eggs from the hen metabolism study. The total radioactive residues were determined by combustion LSC and thereafter analysed in duplicate according to method 268. All fractions containing the parent compound were analysed by LSC. Concurrent recoveries verified on non-radiolabelled control samples ranged between 66–88%. Extraction efficiency in the different hen matrices varied from 91–98% TRR. Quinclorac as quantified by method 268 accounted for 60–81% TRR. This is slightly lower than the amounts found in the metabolism study, where 78–92% TRR could be assigned to parent. Losses mainly occurred during C18 clean-up due to irreversible adsorption to the column.

Table 40 Radiovalidation for hen matrices using method 268

Matrix	TRR mg/kg	Total extracted %TRR [a]	Parent %TRR method 268 (B)	Parent mg/kg method 268	Parent %TRR metabolism study (C)	Trueness ratio B:C	Concur recovery
Hen muscle 367; 372	4.29	91%, 93%	63%; 72%	2.72; 3.10	86-87%	0.78	84%
Hen skin with fat 367	6.41	98%, 98%	60%; 60%	3.85; 3.88;	86-88%	0.69	88%
Hen liver 367	9.28	91%; 95%	78%; 81%;	7.54; 7.20	91-92%	0.88	72%
Hen kidney 366-372	18.4	91%; 93%;	63%; 63%	11.7; 11.7	na	-	88%
Hen eggs	1.24	93%; 96%;	74%; 65%	0.92; 0.80;	78-83%	0.87	66%

367, day 2							

[a] Extraction using acetone/0.1 M NaOH and acetone; 0.1 M sulfuric acid (method 268)

A radiovalidation of the method 268 was conducted by Mayer, F (1989 BASF/5001) with samples from muscle, fat, liver, kidney and milk from the goat metabolism study. The total radioactive residues were determined by combustion LSC and thereafter analysed in duplicate according to method 268 and 268/1. All fractions containing the parent compound were analysed by LSC. Extraction efficiency in the different goat matrices varied from 72 to 104% TRR. Concurrent recoveries verified on non-radiolabelled control samples ranged between 54–77% for method 268. Quinclorac as quantified by method 268 accounted for 42–88% TRR, this is lower than the amounts found in the metabolism study, where 81–96% TRR could be assigned to parent. Losses mainly occur during C18 clean-up due to irreversible adsorption to the column. When the clean-up procedure was changed, as in method 268/1, concurrent recoveries improved to 66–96%. Quinclorac as quantified by method 268 accounted for 61–85% TRR, this is lower than the amounts found in the metabolism study, where 81–96% TRR could be assigned to parent.

Table 41 Radiovalidation for lactating goat matrices using method 268

Matrix	TRR mg/kg	Total extracted %TRR (A)	Parent %TRR method 268 (B)	Parent mg/kg method 268	Parent %TRR metabolism study (C)	Trueness ratio B:C	Concur recovery
Method 268,original method							
goat muscle	0.196	79%; 81%	48%; 57%	0.095; 0.112	na	na	77%
goat omental fat	0.191	73%; 72%	83%; 83%	0.159; 0.159	na	na	60%
goat subcu taneous fat	0.672	93%; 86%	70%; 67%	0.470 0.449	na	na	54%
goat liver	2.216	82%; 85%	42%; 47%	0.926; 1.05	81%	0.55	58%
goat kidney	11.54	102%; 104%	78%; 71%	9.03; 8.23	86%	0.87	66%
goat milk	0.117	73%; 76%	42%; 47%	0.048; 0.055	86%	0.52	77%
method 268/1 modification							
goat liver	2.307	93%; 94%	61%; 64%	1.40; 1.48	81%	0.77	71%; 79%
goat muscle	0.230	96%; 94%	77%; 80%	0.178; 0.183	na	na	66%; 74%
goat milk	0.090	96%; 96%	85%; 82%	0.076; 0.073	86%	0.97	92%; 96%

Plant commodities

Strawberry

The analytical (enforcement) (method M829/A was developed by White, G (2015, J20044) for the determination of quinclorac in strawberry representing a high water content crop. Residues of quinclorac are extracted from plant matrices by sonication with 1% acetic acid in acetonitrile in the presence of magnesium sulfate and sodium chloride. Following centrifugation, samples are diluted with 0.1% formic acid and analysed by LC-MS/MS. The determination of the residues is calculated using matrix matched standards employing triphenyl phosphate (TPP) as the internal standard. The quinclorac ion transition 242→224 is used for quantification and the ion transition m/z 244-226 is used for confirmation. LOQ is 0.01 mg/kg.

The applicability of the method was confirmed in an independent laboratory by Moinuddin, A (2015, JRF/228-2-13-10872). In both laboratories parent quinclorac were analysed with validated LOQ of 0.01 mg/kg in strawberry see Table 46).

Rice

The analytical method A8902 was validated for parent quinclorac by Single, YM (1989 BASF 5007) for residues in rice grain and straw with an LOQ of 0.05 mg/kg. The residues are extracted from 5–10 g plant materials. Samples are soaked in 0.1 N sodium hydroxide for 1 hr prior to extraction with acetone (acetone/0.1 M NaOH, 10:15, v/v). After centrifugation in the presence of Celite, the extract was acidified with sulfuric acid and the acetone was removed by evaporation at 50 °C. The extract was adjusted to pH 8 by $NaCO_3$ and partitioned with dichloromethane to remove matrix impurities. The aqueous phase was acidified and residues were partitioned into dichloromethane. After filtration and cleaning by SPE (silica gel column) quinclorac residues were derivatized (methylated) with diazomethane and determined by GC-ECD. Quantification is performed using a derivatized external standard. Residues are expressed as quinclorac.

Independent laboratory validation (ILV) studies for the method were not presented to the Meeting.

A radiovalidation of the method A8902 was conducted by Single Y (1989 BASF 5006) with samples from rice grain, straw and forage from the rice metabolism study. The total radioactive residues were determined by combustion LSC and thereafter analysed in duplicate according to method A8902. All fractions containing the parent compound were analysed by LSC. Extraction efficiency in the different rice matrices were 88% for the grain, 90% for the straw and 84% for the forage. Average concurrent recoveries verified on non-radiolabelled control samples for rice grain were 87% for method A8902. Quinclorac as quantified by method A8902 accounted for 69–77% TRR, this is lower than the amounts found in the metabolism study, where 85–94% TRR could be assigned to parent.

Table 42 Radiovalidation for rice using method A8902

Matrix	TRR mg/kg	Total extracted %TRR [a]	Parent %TRR method A8902 (B)	Parent mg/kg method A8902	Parent %TRR metabolism study (C)	Trueness ratio B:C	Concur recovery
rice grain (growth chamber)	1.66	88	77	1.28	94	0.82	87
rice straw (growth chamber)	13.5	90	86	11.6	86	1.00	-
rice forage (field)	0.68	84	69	0.40	85	0.81	-

[a] Extraction with 0.1 N NaOH in acetone as for method A8902

Wheat

The analytical method D9708/1 was validated for parent quinclorac in wheat (forage, grain, straw, flour and bran) with an LOQ of 0.05 mg/kg by Guirguis M, and Riley M (1998 BASF/5095**).** The residues were extracted from 5–10 g plant material. Samples were soaked in 0.1 N sodium hydroxide for 1 hr prior to extraction with acetone (acetone/0.1 M NaOH, 10:15, v/v). After centrifugation an aliquot of the extract was acidified with HCl to pH < 2 and evaporated at 50 °C to remove the acetone. The residues in the extract were partitioned into dichloromethane. The dichloromethane was evaporated to dryness and redissolved in 0.0025 M NaOH (pH 9–11). After cleaning using a quaternary amine SPE column, the solution was analysed for quinclorac by HPLC-MS/MS using ion transition 240→196 for quantification and using external standards. Validation data for the method is presented in Table 46

The applicability of method D9708/2 for determination of quinclorac in wheat grain was confirmed in an independent laboratory by Li F and Patel D (2013 a, BASF/7000579). Parent quinclorac was analysed with validated LOQ of 0.05 mg/kg Table 46.

Sorghum

The analytical method D9708 was validated for the determination of parent quinclorac in sorghum commodities by Haughey D, *et.al.* (1998, BASF/5081). The residue was extracted from ≥ 0.9 kg plant material. Further description as for wheat D9708/1.

The analytical method D9708 was validated for the determination of parent quinclorac in forage, grain and fodder by Versoi, P. et al (1996/5136). The residue was extracted from >2 kg plant material. Further description is as for rice A9002.

Rape seed

The analytical method D9806 was validated for rape seed by Guirguis M and Riley M (1998 BASF/5184) for the determination of quinclorac methyl in rape seed and oil (canola). Seed samples (10 g) were extracted with acetone. An aliquot of the extract is evaporated to dryness and redissolved in hexane. Oil samples (2g) are dissolved in hexane. Hexane solutions from seeds or oil are partitioned twice with 95% acetonitrile/water (2:1, v/v)/5% methanol. The samples are cleaned-up using C18 SPE columns. The eluates are evaporated to dryness and redissolved in HPLC mobile phase. The samples are analysed for quinclorac-methyl by HPLC-MS/MS. The ion transition m/z 255→224 is used for quantification. Quantification is performed using external standards.

The analytical method D9708/1 for the determination of quinclorac and analytical method D9806 for determination of quinclorac methyl ester were validated for oilseed rape seed by Guirguis M, (1998/ BASF 5174).

The applicability of the method D9708/2 for determination of parent quinclorac and method D9806/2 for determination quinclorac methyl ester was confirmed in an independent laboratory for wheat grain and rape seed (canola) by Li F, and Patel D 2013a BASF/7000579). Quinclorac and quinclorac methyl ester were analysed with a validated LOQ of 0.05 mg/kg.

Recovery data are presented in table below.

Table 43 Procedural recovery for quinclorac with method D9708/2

Matrix	Fortification level (mg/kg)	n	recovering	average rec	SD	% RSP
wheat grain	Primary quantification (mz 242-mz 224) using LC-MS/MS					
	0.05	5	85, 86, 89, 92, 94	87	3.2	3.6
	5.0	5	87, 887, 79,79 86	84	4.4	5.3
	Confirmatory quantification (mz 256-m/z 161)					
	0.05	5	85, 82, 86, 94, 84	86	4.4	5.1
	5.0	5	87, 86, 79, 77, 85	83	4.6	4.6
canola seed	Primary quantification (mz 242-mz 224) using LC-MS/MS					
	0.05	5	85, 105,84,72,86	86	11.8	13.6
	5.0	5	86,83,90,99,105	93	9.3	10.0
	Confirmatory quantification (mz 256-m/z 161)					
	0.05	5	87, 107, 78, 71, 82	85	13.8	16.2
	5.0	5	86, 83, 86,99,102	91	8.6	9.4

Table 44 Procedural recovery for quinclorac methyl ester (BH 514-Me)

Matrix	Fortification level (mg/kg)	n	recovering	average rec	SD	% RSP
canola seed	Primary quantification (mz 242-mz 224) using LC-MS/MS					
	0.05	5	76, 95, 109, 98, 84,	92	12.8	13.9
	5.0	5	96, 85, 88, 92, 90,	90	4.1	4.5
	Confirmatory quantification (mz 256-m/z 161) using LC-MS/MS					
	0.05	5	67, 84, 100, 89, 73	83	13.1	15.8
	5.0	5	93, 83, 86, 90, 88	88	3.9	4.4

A radiovalidation of the method D9708/1 (quinclorac) was conducted by Parker 1998a (BASF 1998/5180). Analytical method D9708/1 was used to quantify quinclorac in the rape seed from the rape seed metabolism study and 45.3% TRR (0.218 mg/kg) accounted for parent quinclorac. Compared to the metabolism study, where 37.1% TRR (0.176 mg/kg) accounted for parent quinclorac after extraction with acetone/buffer pH 7, the analytical method results in higher residue levels for the parent compound. This can be explained by the partial conversion of quinclorac methyl back to parent as a result of the alkaline extraction conditions (acetone/0.1 M NaOH) used in the analytical method. The conversion percentage was determined by fortifying control samples with 0.5 mg/kg quinclorac methyl and analysing the rapeseed by method D9708/01 (for parent quinclorac). The conversion averaged 25.2% for four samples with a range of 15.8–32.6%. Method D9708/1 is therefore not suitable for determination of parent quinclorac.

A radiovalidation of the method D9806 (quinclorac methyl) was conducted by Parker 1998a (BASF 1998/5180). Analytical method D9806 was used to quantify quinclorac methyl in the rape seed from the rape seed metabolism study and 30.3% TRR (0.144 mg/kg) accounted for quinclorac methyl. Compared to the metabolism study where 37.1% TRR (0.176 g/kg) accounted for quinclorac methyl, the analytical method results are within acceptable levels.

The analytical (enforcement) method R0036 was validated by Malinsky, D, S (2013 BASF 7002468) for the determination of quinclorac and quinclorac methyl ester residues in rape seed and oil. Validation data for the method is presented in Table 45.

Parent quinclorac residues in/on plant samples (5 g each) are extracted using acetone/0.1 N NaOH (3:1, v/v). After centrifugation, residues in an aliquot of sample extract are cleaned up by liquid-liquid partitioning in which residues are diluted with water and saturated NaCl solution, concentrated to remove the acetone, and partitioned against dichloromethane, which is discarded. The residues in the aqueous phase are then acidified (pH ~2–3) with concentrated formic acid, partitioned into dichloromethane, and evaporated to dryness. The residues are re-dissolved in a final volume of acetonitrile:water (10:90, v/v), filtered, and analysed by HPLC-MS/MS.

From oil samples (5 g each), parent quinclorac residues are extracted with a mixture of hexane, acetonitrile:0.1 N NaOH (1:1, v/v), and methanol. After centrifugation, residues in the aqueous acetonitrile layer are diluted to volume with acetonitrile:0.1 M NaOH (1:1, v/v). An aliquot of the extract is concentrated to remove the acetonitrile, and residues in the aqueous remainder are then subjected to extensive liquid-liquid partitioning, finally into dichloromethane, the combined extracts of which are evaporated to dryness. The residues are re-dissolved in acetonitrile:water (10:90, v/v), filtered, and then analysed by HPLC-MS/MS.

Residues of quinclorac methyl ester in/on canola seed samples (5 g each) are extracted with acetone. An aliquot of extract is evaporated to dryness, and the residues are redissolved, and subjected to liquid-liquid partitioning, in saturated NaCl solution and dichloromethane. The residues in an aliquot of the dichloromethane layer are evaporated to dryness, re-dissolved in methanol:water (1:1, v/v), filtered, and then analysed by HPLC-MS/MS.

From oil samples (5 g each), quinclorac methyl ester residues are extracted with a mixture of hexane, acetonitrile:water (2:1, v/v), and methanol. The residues in the aqueous acetonitrile layer are diluted with acetonitrile:water (2:1, v/v), an aliquot is taken, further diluted with methanol-water (1:1, v/v), filtered, and analysed by HPLC-MS/MS.

Quantification is performed using external standards. Quinclorac is quantified using m/z 242→224 for quantification and m/z 242→161 for confirmation. Quinclorac methyl is quantified using m/z 256→224 for quantification and 256→161 for confirmation. LOQ is 0.01 mg/kg for both analytes.

Acceptable linearity was observed within the 0.01–0.25 ng/mL standard range and the two mass transitions for each analyte ($r = \geq 0.9976$). No interfering peaks were found at the retention times for these analytes. Matrix effects on the detector response were less than 20%); therefore, the validation samples were analysed only using solvent-based calibration standard solutions. Further validation results are shown in Table 45.

The applicability of the method was confirmed in an independent laboratory by Schmitt J.L (2013 a, BASF/7002603). In both laboratories parent quinclorac and quinclorac methyl ester were analysed with validated LOQ of 0.01 mg/kg. Validation results are shown in table below.

Table 45 Recovery data for determining quinclorac and quinclorac methyl ester for Method R0036

Matrix	Analyte	No. of tests	Fortification level [mg/kg]	Transition 242 > 224			Transition 242 > 161		
				mean [%]	SD [+/-]	CV [%]	mean [%]	SD [+/-]	CV [%]
Lettuce leaves	Quinclorac	5	0.01	94	8	8	97	8	8
		5	1.0	100	2	2	101	5	5
		10	Overall	97	6	7	99	7	7
Corn grain	Quinclorac	5	0.01	90	4	5	92	4	5
		5	1.0	105	4	4	106	2	2
		10	Overall	98	9	9	99	8	8
Bean, dried seed	Quinclorac	5	0.01	99	4	4	103	1	1
		5	1.0	91	9	10	88	7	8
		10	Overall	95	8	8	96	9	9
Grape, fruit	Quinclorac	5	0.01	105	6	6	110	4	3
		5	1.0	109	4	3	109	7	7
		10	Overall	107	5	5	109	6	5
Canola Seed	Quinclorac	5	0.01	104	2	2	108	2	2
		5	1.0	107	6	6	108	5	5
		10	Overall	106	5	4	108	4	4
Canola Oil	Quinclorac	5	0.01	104	8	8	110	9	8
		5	1.0	99	6	7	100	4	4
		10	Overall	101	7	7	105	8	8
Canola Seed	Quinclorac methyl ester	5	0.01	85	15	17	73	11	15
		5	1.0	95	3	3	91	3	3
		10	Overall	90	11	13	82	12	15
Canola Oil	Quinclorac methyl ester	7	0.01	90	5	6	82	3	4
		7	1.0	86	2	2	86	4	4
		14	Overall	88	4	4	84	4	5

A radiovalidation study showed that extraction with acetone/0.1 M NaOH converts quinclorac-methyl partly into parent compound. For this reason, the parent is overestimated in samples containing quinclorac-methyl ester. Methods D9708/1 (quinclorac) and R0036 (quinclorac) use acetone/0.1 M NaOH and are therefore not suitable for the determination of parent compound in oilseed rape seed and possibly other pulses and oilseeds, where the quinclorac methyl ester can be expected to be present.

Table 46 Overview of recovery data for determination of quinclorac in plant matrices with presented methods

Matrix	Fortification level	n	recovery mean	SD	CV	Analyte, reference, MRM transition
rice grain	0.05	9	93	17	19	Quinclorac (1989 BASF 5007), method A8902
	1.0	6	85	11	13	
	5.0	5	84	9.5	11	
	10.0	1	91	-	-	
rice straw	0.05	9	93	14	15	
	1.0	5	93	18	20	
	5.0	2	101	28	27	
	10.0	2	92	4.2	4.6	
	20.0	3	97	18	18	
rough rice	0.05	2	88	7.2	8.2	Quinclorac (1989a BASF 5004)
	0.5	1	80	-	-	
rice hulls	0.05	2	93	3.7	4.9	
	0.5	1	85	-	-	
	1.0	1	87	-	-	
brown rice	0.05	2	93	8.8	9.4	
	0.5	1	85	-	-	
	1.0	1	87	-	-	

Matrix	Fortification level	n	recovery mean	SD	CV	Analyte, reference, MRM transition
rice bran	0.05	4	76	7.1	9.4	
	0.5	2	83	7.8	9.4	
	1.0	1	64	-	-	
	2.0	1	82	-	-	
milled rice	0.05	2	88	12	14	
	0.5	1	89	-	-	
	1.0	1	90	-	-	
rice straw	0.05	3	77	10	13	
	1.0	1	88	-	-	
	5.0	2	72	11	15	
wheat straw	0.05	4	83	20	24	Quinclorac (1998a BASF 5008
	0.5	4	86	7.2	8.4	
	5.0	4	87	22	26	
wheat grain	0.05	6	89	9.9	11	
	0.5	6	85	25	29	
	5.0	6	99	7.8	7.9	
wheat flour	0.05	4	89	9.0	10	
	0.5	4	95	4.3	4.5	
	5.0	4	92	3.9	4.3	
wheat bran	0.05	4	75	14	19	
	0.5	4	83	21	25	
	5.0	4	86	15	17	
wheat forage	0.05	4	93	26	28	
	0.5	4	100	14	15	
	5.0	4	95	5.0	5.3	
Rape seed	0.05	4	81	19	23	
	0.5	4	85	11	14	
	5.0	4	84	15	18	
Rape oil	0.05	4	84	10	12	
	0.5	4	82	13	16	
	5.0	4	82	7.6	9.3	
Rape seed	0.05	3	76.7	9.0	11.8	Quinclorac (1998 BASF 5174)
	0.5	10	73.7	9.9	13.4	
Strawberry fruit	0.01	5	92.8	2.56	2.76	Quinclorac (2015, J20044)
	0.10	5	92.2	3.8	4.13	
Sorghum forage	0.05	5	74.4	12.0	16.2	Quinclorac (1996/5136)
	1.0	5	83.8	13.7	16.3	
Sorghum grain	0.05	5	79.6	9.9	12.5	
	1.0	5	82.8	6.7	8.1	
Sorghum fodder	0.05	4	80.0	8.5	10.6	
	1.0	3	90.7	5.0	5.6	
Sorghum forage	0.05	1	65	-	-	Quinclorac (1998/5081)
	1.0	2	94	8.5	9.0	
Sorghum grain	0.05	1	87	-	-	
	1.0	2	101	4.2	4.2	
Sorghum fodder	0.05	3	93	20.0	21.5	
Rape seed (canola)			Transition 242 > 224			Transition 242 > 161			Quinclorac (2013/7002468
			recovery mean	SD	CV	recovery mean	**SD**	**CV**	
seed	0.01	5	104	2	2	108	2	2	m/z 242-224 quantification
	1.0	5	107	6	6	108	5	5	
oil	0.01	5	104	8	8	110	9	8	m/z 242-161 confirmation
	1.0	5	99	6	7	100	4	4	

Matrix	Fortification level	n	Recovery mean	SD	CV	Analyte, reference, MRM transition
Rape seed	0.05	3	87.7	7.8	8.9	Quinclorac Methyl Ester
	0.5	6	94.5	16.2	17.1	

Matrix	Fortification level	n	Recovery mean			SD		CV	Analyte, reference, MRM transition
									(1998 BASF 5174)
Rape seed	0.05	4	105			4.8		4.6	Quinclorac Methyl Ester (1998/5184)
	0.5	4	100			1.5		1.5	
	5.0	4	95			8.0		8.5	
Rape oil	0.05	4	95			16		16	
	0.5	4	85			2.5		2.9	
	5.0	4	75			11		15	
			Quantification			Confirmation			
			recovery	mean	SD	recovery	mean	SD	
Rape seed	0.01 1.0	5 5	85 95	15 3	17 3	73 91	11 3	15 3	Quinclorac Methyl Ester ((2013/7002468) m/z 256-224 quantification m/z 256-161 confirmation
Rape oil	0.01 1.0	7 7	90 86	5 2	6 2	82 86	3 4	4 4	

Soil

The method A8903 was validated by Mayer, F et al (1989, BASF 1989/5017) for analysis of quinclorac and its metabolite BH 514-1 (3-chloro-8-quinolinecarboxylicacid) in soil. Residues of quinclorac are extracted from soil (25 g) with sodium hydroxide followed by acetone/aqueous solution and then acidified with concentrated sulphuric acid and extracted with dichloromethane.

The samples are analysed by high performance liquid chromatography with ultra-violet detected (HPLC-UV) at 230 nm, using Nucleosil 100-5-C18 column (50 mm × 4.6 mm −pre-column and 250 mm × 4.6 mm main column) and a waters Guard-Pak Pre-column with gradient elution using mobile phases of acetonitrile/water/acetic acid. Quantification is performed using external standards. Limit of quantification was 0.05 mg/kg for both analytes.

Recovery data generated from samples fortified at the LOQ and from samples fortified at 10 × LOQ are presented in the table below.

Table 47 Recovery data for quinclorac and BH 514-1 (3-chloro-8-quinolinecarboxylicacid) in soil

Test	Analyte	No of tests	mean (%)	SD (±)	CV (%)
87101	Quinclorac	5	85	6	7
	BH 514-1	5	72	10	14
87127	Quinclorac	12	85	11	13
	BH 514-1	12	74	12	16
87125	Quinclorac	6	81	6	7
	BH 514-1	6	70	6	9
87098	Quinclorac	10	76	7	9
	BH 514-1	8	59	4	7

For the analysis of quinclorac and its metabolites BH 514-2-OH (2-hydroxyquinclorac) and (BH 514-ME) (quinclorac methyl ester) in soil the method D9513 was validated by Jordan J (1996, BASF 1996/5149). The extraction of quinclorac and BH 514-2-OH from soil samples (10g) are first extracted with sodium hydroxide acidified and partitioned with 8:2 methylene chloride/ethyl acetate. The metabolite BH 514-ME is converted to parent quinclorac and is analysed as parent equivalents in the method. For the determination of BH 514-ME soil samples are extracted in a mixture of methylene chloride, ethyl acetate and methanol.

The final quantitative determination of quinclorac, BH 514-2-OH and BH 514-ME is made by LC/MS/MS using multiple reaction monitoring. The LOQ for each metabolite is defined as the lowest fortification that was successfully run through the method. For this method it is 10 ppb. The average

recoveries for BAS 514 was 85.3% +/- 3.6 (n=6) for the shake extraction method and 95.3% +/- 7.7% for the reflux extraction. The average recoveries for BH 514-2-OH was 81.7% +/- 4.5% (n=6) for the shake extraction and 83.6% +/- 8.4% (n=13) for the reflux extraction. The average recovery for BH 514-ME is 89.3% +/- 3.3% (n=13).

Stability of residues in stored analytical samples

Plant matrices

Storage stability of quinclorac was investigated in rice (grain and straw) and sorghum (forage, hay, grain, silage and fodder) matrixes up to 38 months by Burkey, J (1994, BASF/5015) in wheat up to 26 months by Burkey, J (1996, BASF/5110) and in cranberry up to 14 months by Barney, WP, Homa K (2010, BASF /7018348).

Homogenized samples of rice, sorghum and wheat were fortified individually at levels of 1 mg/kg for quinclorac and stored frozen. Bulk control matrix was placed into storage simultaneously. At each sampling interval, two fortified samples and control samples were removed from the freezer. Subsequently, two control samples of each sampling material were freshly fortified with quinclorac 1 mg/kg to determine the procedural recovery.

For cranberry triplicate untreated field samples were individually fortified with quinclorac at 0.5 mg/kg (10 × method LOQ). At two time intervals three fortified and one control samples freshly fortified with 0.5 mg/kg were prepared to test procedural recovery.

The analytical method A8902 was used to determine quinclorac total in all matrixes. The samples (10g) were soaked in a 0.1N sodium hydroxide solution and extracted with acetone. Samples were then acidified, extracted with dichloromethane and derivatized with diazomethane. Quantification of samples was done using a calibration curve for quinclorac. The LOQ was 0.05 mg/kg.

The storage stability of quinclorac and the metabolite BH514-Me (quinclorac methyl ester) in rape seed (seed, meal and oil) up to 671 days was investigated by Saha, M (2013, BASF/7000581).

Samples from a field trial of homogenized seed, meal and oil were individually fortified with 1 mg/kg quinclorac and quinclorac methyl ester respectively and stored frozen. At each sampling interval two fortified samples and three control samples were removed from the freezer. Two of the control samples were fortified with 1.0 mg/kg each analyte. The modified versions of analytical methods D9708/1 and D9806 were used to determine quinclorac and quinclorac methyl ester.

Residues of parent quinclorac in/on seed and meal samples (10 g each) were extracted were soaked in a 0.1N sodium hydroxide solution and extracted with acetone. Samples were then acidified, extracted with dichloromethane.

Residues of quinclorac methyl ester in/on seed and meal samples (10 g each) were extracted with acetone partitioned with dichloromethane/methanol and water. Quantification was performed using external standards.

The residues were analysed by LC-MS/MS. The MS/MS detection in the positive ionization mode was used to monitor ion transition from m/z 242-160.8 for quinclorac and m/z 256 to 224 for quinclorac methyl ester. The LOQ was 0.05 mg/kg

In the following tables the recovered residues in stored samples are summarized

Table 48 Storage stability of quinclorac in plant commodities fortified at level of 1 mg/kg

Matrix	Storage period months	Procedural recovery mg/kg**	Residues remaining mg/kg**
Rice grain	0	0.87	0.87
	8	0.79	0.76
	19	0.93	0.79
	38	0.92	0.75
Rice straw	0	0.86	0.86

Matrix	Storage period months	Procedural recovery mg/kg**	Residues remaining mg/kg**
	8	0.91	0.77
	19	1.07	0.98
	38	1.01	0.90
Sorghum forage	0	0.98	0.98
	25	0.75	0.91
	38	0.84	0.85
Sorghum hay	0	1.09	1.09
	25	0.75	0.89
	38	0.92	0.90
Sorghum grain	0	0.91	0.91
	25	0.86	0.94
	38	0.97	0.97
Sorghum silage	0	1.04	1.04
	25	0.95	0.79
	38	0.90	0.84
Sorghum fodder	0	1.01	1.01
	25	0.90	0.80
	38	0.86	0.84
Wheat grain	0		-
	6	0.83	0.82
	13	74	0.86
	26	85	0.9
cranberry fruit	8	73	75
	14	90	93

* Values are the average from duplicate or triplicate analyses

** days

*** only one replicate

Table 49 Storage stability of quinclorac and quinclorac methyl ester in rape seed commodities fortified at level of 0.5 mg/kg

Matrix	Storage period days	Procedural recovery %	Residues remaining %
Quinclorac			
Seed	0	87	86
	31	92	88
	94	76	86
	185	95	92
	377	77*	78
	397	76	96
	669	87	77
Meal	0	84	85
	31	96	94
	94	73	75
	185	84	89
	377	107	92
	398	71	81
	669	70	92
Oil	0	98	93
	34		84
	95	76	69
	186	67	50
	390	69	81
	671	97	98
Quinclorac methyl ester			
Seed	0	89	95
	31	84	73
	94	82	65
	185	86	73
	384	82	74

Matrix	Storage period days	Procedural recovery %	Residues remaining %
	668	72	77
Meal	0	100	94
	31	96	86
	94	95	79
	185	94	86
	384	96	93
	668	89	81
Oil	0		80
	31	74	78
	94	73	71
	185	82	82
	384	89	76
	668	76	75

* Values are the average from duplicate analyses

Animal matrices

For animal matrices no procedural recovery studies (with fortified samples) for storage stability were provided. The maximum storage time for hen was eggs were 90 days and tissue 74 days and for lactating goat milk 31 days, subcutaneous fat 58 days, peritoneal fat 56 days and muscle 51 days.

USE PATTERN

Quinclorac is registered for uses in berries and other small fruits stalk and stem vegetables, cereal grains and rape seed in a number of countries. Information on GAP with supporting labels from Canada and USA was provided to the Meeting. Quinclorac is a systemic herbicide with uptake through roots and foliage and used to control annual grass and broadleaf weeds. Its mode of action is overstimulation of growth resulting in the rupture of the cell membranes.

Table 50 Registered uses quinclorac from labels provided.

Crop	Country	Application details					Comments
		Method	Rate; kg ai/ha min.-max. (max. kg ai/ha /season)	Crop growth stage at last treatment	No (interval in days)	PHI	Restrictions
Berries and other small fruits							
Cranberry	USA* Quinstar 4L	ground spray post emergent	0.24-0.48 (0.48)		1-2 (30)	60	Do not allow livestock to graze in treated areas
Stalk and stem vegetables							
Rhubarb	USA* Quinstar 4L	ground spray	0.35-0.7 (0.7)		1-2 (30)	30	Do not allow livestock to graze in treated areas
Cereal grains							
Rice	USA* Quinstar 4L	aerial or ground spray Soil: to soil surface pre-planting or pre-emergent (dryland rice) Foliar: after 2-leaf stage (but before heading) on	0.29-0.54 (0.54)	Do not apply to rice that is heading Rice must be in at least 2-leaf stage.	1	40	Do not plant any crop other than rice for a period of 309 days following application State-specific restrictions in Arkansas. Do not use in California or

Crop	Country	Application details					Comments
		Method	Rate; kg ai/ha min.-max. (max. kg ai/ha /season)	Crop growth stage at last treatment	No (interval in days)	PHI	Restrictions
		dryland and water seeded/paddy					Florida. Can be used in paddy rice post emergently as long as the water depth is reduced to expose the grass and/or broadleaf weeds.
Wheat (spring and durum)	Canada** Accord DF	ground spray post-emergent	0.135-0.165 (0.165)	1-5 leaf	1	77	Do not graze the treated wheat or barley or cut for hay within 77 days of application
Spring barely	Canada ** Accord DF		0.135	1-4 leaf (prior to tillering)	1	80	
Wheat	USA* Facet L	ground spray, air application in certain states pre-plant	(0.29)	pre-plant	1	-	
Wheat	USA* Quinstar 4L	ground spray, air application in certain states pre-plant application	(0.29)	pre-plant	1	-	Do not feed forages, hay, silage or straw to livestock. Do not apply in ID, MT, NV, OR, UT, WA or WY
Sorghum	USA* Quinstar 4L	aerial or ground spray pre-plant	0.29	pre-plant	1	-	Quinclorac can be applied both pre and post emergently as long as the seasonal maximum amount of 0.78 kg ai/ha is not exceeded.
		post-emergent	0.56	Up to 30 cm tall stage	1		
Sorghum	USA* Facet L	aerial or ground spray pre-plant	0.29	pre-plant	1	-	Quinclorac can be used both pre and post emergently as long as the seasonal maximum amount is not exceeded.
		post-emergent	0.3-0.42	Up to 30 cm tall	1		
Oilseed rape							
Rape seed	Canada** Accord DF	ground spray post-emergent	0.135	2-6 leaf stage	1	60	Only grain and meal can be fed to livestock. Do not graze or feed other portions of the treated rape seed to livestock

*SL (liquid flowable)
** DF (dry flowable)

RESIDUES RESULTING FROM SUPERVISED TRIALS ON CROPS

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

Group	Crop commodity	Portion of commodity to which MRL apply	Countries	Table No
FB, Berries and other small fruits	Cranberry	Whole commodity after removal of caps and stems	USA	51
VS, Stalk and stem vegetables	Rhubarb	Whole commodity after removal of obviously decomposed or withered leaves	USA	52
GC, Cereal grain	Rice	Whole commodity	USA	53-55
	Wheat	Whole commodity	Canada, USA	56-58
	Sorghum	Whole commodity	USA	59-60
SO, Rapeseed	Canola	Whole commodity	Canada, USA	61

Conditions of the supervised residue trials were generally well reported in detailed field reports. Field reports provided data on the sprayers used and their calibration, plot size, residue sample size and sampling date. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOQ. Residue levels are reported as measured, when residues were not detected they are shown as below the LOQ (e.g. < 0.01 mg/kg). Residue data are recorded unadjusted for % recovery.

Laboratory reports included method validation including batch recoveries with spiking at residue levels similar to those occurring in samples from supervised trials. Data of analysis or duration of residue samples storage were also provided. Residues values from trials conducted according to a maximum registered GAP with supporting trials have been used for the estimation of maximum residue levels. The results included in the evaluation of the MRL, STMR and HR is underlined.

Cranberry

To determine magnitude of residue of quinclorac in cranberry five supervised field trials were conducted in USA (Massachusetts Wisconsin and Oregon). Quinclorac was applied as two post-emergence ground broadcast applications each at 0.28 kg ai/ha using a SL formulation. All applications contained crop oil concentrate as spray adjuvant.

Duplicate cranberry fruit samples were collected and stored frozen (< -27 °C) until homogenization. Frozen samples were processed in presence of dry ice. Upon grinding, all samples were subsampled. Samples were analysed for quinclorac using GC/EDC detection. The LOQ was of 0.05 mg/kg and average recovery, 86 ± 14% (n=14).

The method validation recoveries of quinclorac at 0.05, 0.5, 0 5 mg/kg was 86 ± 14% (n=12). Concurrent recoveries ranged from 72% to 104% (average 83 ± 13 (n=8). The limit of storage stability for quinclorac in rhubarb petioles were 385 days. The maximum storage time for samples (from sampling to extraction) was 334 days. The storage period is covered by the storage stability studies (385 days).

Results from residues in cranberry fruit are presented in the table below.

Table 51 Residues of quinclorac residue in cranberry fruit following two post-emergence foliar broadcast applications with an SL formulation.

Location	Application			Residues			Trial
Year, (variety)	Total Rate, (kg ai/ha)	Growth stage	PHI (days)	Matrix	quinclorac (mg/kg)	mean (mg/kg)	Trial comment
USA Plymouth County, MA, 2008 (Stevens) Stevens 1	2 x 0.27	Bloom July 5, Fruit set July 31	59	Mature cranberries	0.50, 0.60	0.55	08000.08-MA01 2010/7018348
USA Wareham, MA 2008 (Early Blacks) Early blacks 1	2 × 0.28	Bloom July 5, Fruit set July 31	59	Mature cranberries	0.16, 0.20	0.18	08000.08-MA03 2010/7018348
USA Warrens, WI 2008 (Stevens) 5	2 × 0.28	Bloom, July 7 Fruiting August 4	57	Mature cranberries	0.17, 0.16	0.17	08000.08-WI01 2010/7018348
USA Warrens, WI 2008 (Ben Lear) 5	2 × 0.28	Bloom, July 7 Fruiting August 4	57	Mature cranberries	0.16, 0.15	0.16	08000.08-WI02 2010/7018348
USA Langlois, OR 2008 (Pilgrims) 12	2 × 0.29	End of bloom, July 1 Green fruit August 6	62	Mature cranberries	0.66, 0.68	0.67	08000.08-OR10 2010/7018348

Rhubarb

To determine magnitude of residue of quinclorac in rhubarb four field trials were conducted in USA (Michigan and Oregon). Quinclorac was applied as two post-emergence ground broadcast applications each at 0.42 kg ai/ha and a ~ 30 days interval. All applications contained crop oil concentrate as spray adjuvant**.**

Duplicate samples of rhubarb petioles were collected and stored frozen (< -15°C) until homogenization. After processing the samples were returned to frozen storage until analysis within 357 days. Samples were analysed for quinclorac according to method A8902 using GC/EDC detection. Method validation recoveries of quinclorac at 0.05, 0.5, 0 5 mg/kg were in 88 ± 12% (n=9). Concurrent recoveries ranged from 80% to 117% (average 98 ± 9 (n 13). The maximum storage time of samples (from sampling to extraction) was 357 days. The storage period is covered by the storage stability studies (385 days).

Results from residues in rhubarb fruit are presented in the table below.

Table 52 Residues of quinclorac in rhubarb following two post-emergence broadcast applications with a SL formulation

Location	Application			Residues			Trial
Trial Identification Year, variety	Total Rate, kg ai/ha	Growth stage	PHI (days)	Matrix	quinclorac (mg/kg)	mean (mg/kg)	report comment
USA Holt, MI 2009 (German wine)	0.42+0.43	Vegetative April 22 Blooming May 26	29	Rhubarb	0.18, 0.23	0.21	10135.09-M108 2010/7018328
USA Hillsboro, OR 2009 (Crimson red)	0.43+0.44	Late dormancy March 18 Vegetative April 15	33	Rhubarb	0.20, 0.15	0.18	10135.09-OR10 2010/7018328
USA Canby, OR 2009 (Red Crimson)	0.43+0.40	Coming out of dormancy March 14 Vegetative April 15	32	Rhubarb	0.05, 0.05, 0.10, 0.13, 0.14, 0.13, 0.14	0.11	10135.09-OR11 2010/7018328
USA Canby, OR 2009 (Red Crimson)	0.46 + 0.43	Spring growth beginning March 19 Vegetative April 17	33	Rhubarb	0.08, 0.06	0.07	10135.09-OR112 2010/7018328

Rice

Results from supervised trials from USA on rice were provided to the Meeting.

To compare aerial and ground application a total of nine field trials were performed during growing season 1988 in USA (California, Texas, Arkansas, Louisiana and Mississippi) using a WP formulation. In all trials except two conducted in California, quinclorac was applied to a non-flooded rice field.

Single rice grain samples were homogenized and straw samples were pre-cut, ground and stored at -5 °C until analysis within 4–5 months. Samples were analysed for quinclorac by method A8902 using GC/ECD detection. The LOQ was 0.05 mg/kg and the average recovery were 88±14% (n=21) for grain and 94±15% (n=21) for the straw.

Table 53 Residues of quinclorac in rice grain and straw following aerial and ground broadcast application with a WP formulation

Location	Application						Residues				Trial no.
Year (variety)	kg ai/hl	water L/ha	kg ai/ha	treatment	no	BBCH	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference comment
USA (CA) 1989, (M202)	0.581	96	0.560	aerial	1	41-43 (booting)	grain	77	1.5	-	88045 BASF 1989/5007
							straw	77	2.6	-	
USA (CA) 1989, (M202)	0.565	99	0.560	ground	1	nr	grain	77	1.9	-	88045 BASF 1989/5007 Adjuvant
							straw	77	3.2	-	
USA (CA)	0.594	132	0.784	ground	1	n.r.	grain	77	4.3	-	88045 BASF
							straw	77	11.1	-	

Location	Application						Residues				Trial no.
Year (variety)	kg ai/hl	water L/ha	kg ai/ha	treatment	no	BBCH	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference comment
1989, (M202)											1989/5007 Adjuvant
USA (CA) 1989, (KRM2)	0.581	96	0.560	aerial	1	n.r.	grain	77	1.6	-	88046 BASF 1989/5007
							straw	77	4.0	-	
USA (CA) 1989, (KRM2)	0.301	224	0.672	ground	1	n.r.	grain	77	2.2	-	88046 BASF 1989/5007 adjuvant
							straw	77	4.0 6.7	5.4	
USA (TX) 1989 (Gulf Mont)	1.197	47	0.560	aerial	1	n.r.	grain	77	< 0.05	-	88047 BASF 1989/5007
							straw	77	0.120	-	
USA (TX) 1989 (Gulf Mont)	0.454	123	0.560	ground	1	n.r.	grain	77	0.06, 0.07	0.065	88047 BASF 1989/5007 adjuvant
							straw	77	0.10, 0.47	0.285	
USA (TX) 1989 (Lemont)	1.197	47	0.560	aerial	1	n.r.	grain	76 174	0.12 < 0.05	- -	88048 BASF 1989/5007
							straw	76 174	0.18 < 0.05	- -	
USA (TX) 1989 Lemont	0.599	94	0.560	ground	1	n.r.	grain	76 174	0.08, 0.09 < 0.05	0.085 -	88048 BASF 1989/5007 adjuvant
							straw	76 174	0.18, 0.23 < 0.05	0.20 -	
USA (AR) 1989 (Mars)	0.599	94	0.560	aerial	1	n.r.	grain	76	< 0.05	-	88049 BASF 1989/5007
							straw	76	0.14	-	
USA (AR) 1989 (Mars)	0.299	187	0.560	ground	1	n.r.	grain	76	0.09, 0.10	0.095	88049 BASF 1989/5007 adjuvant
							straw	76	0.39, 0.46	0.425	
USA (AR) 1989 (Lemon)	0.599	94	0.560	aerial	1	n.r.	grain	80	0.12	-	88050 BASF 1989/5007
							straw	80	0.23	-	
USA (AR) 1989 (Lemont)	0.599	94	0.560	ground	1	n.r.	grain	80	0.22	-	88050 BASF 1989/5007 adjuvant
							straw	80	0.23, 0.24	0.235	
USA (LA) 1989 (Lemon)	0.599	94	0.560	aerial	1	n.r.	grain	98	< 0.05	-	88051 BASF 1989/5007
							straw	98	0.08	-	

Location	Application						Residues				Trial no.
Year (variety)	kg ai/hl	water L/ha	kg ai/ha	treatment	no	BBCH	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference comment
USA (LA), Newelton 1989 (Lemont)	0.599	94	0.560	ground	1	n.r.	grain	98	< 0.05, 0.08	0.065	88051 BASF 1989/5007 adjuvant
							straw	98	0.05, 0.11	0.08	
USA (LA), Midland 1989 (Lemont)	1.197	47	0.560	aerial	1	n.r.	grain	76	0.08	-	88052 BASF 1989/5007
							straw	76	0.03	-	
USA (LA), Midland 1989 (Lemont)	0.440	127	0.560	ground	1	n.r.	grain	76	< 0.05, 0.15	0.1	88052 BASF 1989/5007 adjuvant
							straw	76	0.09, 0.54	0.31	
USA (MS), 1989 (Lemont)	1.197	47	0.560	aerial	1	n.r.	grain	78	< 0.05		88053 BASF 1989/5007
							straw	78	< 0.05		
USA (MS), 1989 (Lemont)	0.599	94	0.560	ground	1	n.r.	grain	78	0.06, 0.16	0.11	88053 BASF 1989/5007 adjuvant
							straw	78	< 0.05, 0.11	0.08	

n.r. = not reported

PHI = Pre-harvest interval

To determine magnitude of residues of quinclorac in rice, field trials were performed during growing season 1996 in USA (Texas, Arkansas, Louisiana, Mississippi, Missouri, and Texas) using a DF formulation. In all trials quinclorac was applied as a single post-emergence ground spray to flooded (paddy field) rice fields. All applications contained crop oil concentrate as spray adjuvant.

Duplicate samples of rice grain and straw were sampled and kept at < -10 °C until they were homogenized at room temperature (grain) and in dry ice (straw) and then returned to frozen storage until analysis within 5 months. The storage period is covered by the storage stability studies (38 months). Samples were analysed for quinclorac by method A8902 using GC/EDC detection. The LOQ was 0.05 mg/kg and the average recoveries were 82±13% (n=26) for grain and 84±14% (n=24) for the straw.

Results from residues in rice grain are presented in Table 54 and from straw in Table 55.

Table 54 Residues of quinclorac in rice grain following broadcast ground application with a DF formulation

Location	Application					Residues				Trial
Year (variety)	kg ai/hl	water L/ha	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference
USA (MS), Washington county 1996 (Lemont)	0.599	94	0.560	1	Booting	grain	34	0.37, 0.44	0.40	96152 BASF/97/5051
						grain	37	0.35, 0.39	0.37	
						grain	40	0.40, 0.37	0.38	
						grain	43	0.35, 0.34	0.35	
						grain	46	0.43, 0.31	0.37	

Location	Application					Residues				Trial
Year (variety)	kg ai/hl	water L/ha	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference
USA (MS) Bolivar county, 1996 (Lemont)	0.570	94	0.549	1	Booting	grain	40	1.7, 1.9	1.8	96154 BASF/97/5051
USA (AR) Crittenden county 1996 (Bengal)	0.593	95	0.560	1	heading	grain	34	4,05, 3.20	3.63	96155 BASF/97/5051
						grain	37	4.24, 4.45	4.35	
						grain	40	3.74, 3.84	3.79	
						grain	43	2.97, 3.58	3.28	
						grain	46	3.67, 4.27	3.97	
USA (AR) Crittenden county 1996 (Bengal)	0.604	96	0.582	1	heading	grain	40	0.325, 0.366	0.346	96156 BASF/97/5051
USA (AR) St Francis county 1996 (Kaybonnet)	0.605	95	0.571	1	Early booting	grain	40	0.480, 0.631	0.556	96157 BASF/97/5051
USA (LA) St Laundry parish 1996 (Cypress)	0.576	97	0.560	1	Early booting	grain	40	0.710, 0.822	0.766	96158 BASF/97/5051
USA (LA) Evangeline parish 1996 Cypress	0.565	99	0.560	1	Early booting	grain	40	0.551, 0.429	0.490	96159 BASF/97/5051
USA (LA) Jeff Davis Parish 1996 (Cypress)	0.571	100	0.571	1	Early booting	grain	41	0.271, 0.252	0.262	96160 BASF/97/5051
USA (LA) St Laundry county 1996 (Bengal)	0.593	94	0.560	1	Early booting	grain	40	0.912, 0.662	0.787	96161 BASF/97/5051
USA (LA) St Laundry county 1996 (Maybell)	0.599	95	0.571	1	Early booting	grain	40	1,07, 1.07	1.07	96162 BASF/97/5051
USA (M0) Permiscot 1996 (Lemont)	0.549	102	0.560	1	Booting	grain	40	0.137, 0.083	0.110	96163 BASF/97/5051
USA (M0) Stoddard county 1996 Cypress	0.604	96	0.582	1	Heading	grain	40	1.96, 1.52	1.74	96164 BASF/97/5051
USA (TX) Walter county 1996 (Cypress)	0.571	102	0.582	1	Full boot stage	grain	40	0.675, 0.743	0.709	96166 BASF/97/5051

PHI = Pre-harvest interval

Trial 96165 is missing

To determine the influence of the formulation on the residues in rice grain five supervised trials were conducted during the growing season 2009 in USA (Arkansas and Louisiana). Each trial consisted of side-by-side tests comparing the dry flowable (DF) and the soluble liquid (SL). The rice was irrigated according to typical commercial practices for paddy-grown rice

Duplicate samples were sampled and maintained frozen until analysis within 7.7 months. Samples were analysed for quinclorac method D9708/1 using LC- MS/MS. The LOQ was 0.05 mg/kg and the average recovery was 94% (n=2).

Table 55 Residues of parent quinclorac in rice grain following ground foliar application with a DF and a SL formulation

Location	Application					Residues				Trial
Year (variety)	formulation	water L/ha	kg ai/ha	no	BBCH	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference
USA (LA) Rapides 2009 (Cheniere)	DF	214 217	0.277 0.277	2	88-89	grain	110	< 0.05, < 0.05	< 0.05	RO90420 BASF/2013/7000580
USA (AR) Crittenden 2009 (Wells)	DF	189 190	0.280 0.289	2	88-89	grain	96	0.09, 0.08	0.085	RO90421 BASF/2013/7000580
USA (LA) Rapides 2009 (Cheniere)	SL	217 219	0.281 0.281	2	88-89	grain	110	< 0.05, < 0.05	< 0.05	RO90420 BASF/2013/7000580
USA (AR) Crittenden 2009 (Wells)	SL	189 190	0.279 0.281	2	88-89	grain	96	0.12, 0.11	0.115	RO90421 BASF/2013/7000580

PHI = Pre-harvest interval

Wheat

Results from supervised trials from Canada and USA on wheat were provided to the Meeting.

To determine magnitude of residues of quinclorac in spring wheat field trials were performed during growing season 1998 in Canada (Alberta, Manitoba, Saskatchewan). At each trial four different treatments were applied each including quinclorac. One treatment was only quinclorac and the other three were with quinclorac plus one or more tank mix partner. In all trials quinclorac was applied as a single broadcast post-emergence spray 75 days prior to harvest. Forage was sampled 9 to 16 days after treatment

Duplicate samples of wheat forage, grain and straw were sampled and stored frozen (<-15 °C) until they were homogenized and until analysis within 7 months. The storage period is covered by the storage stability studies (26 months). Samples were analysed for quinclorac by method A8902 using GC/ECD detection. The LOQ was 0.05 mg/kg and the average recovery were 85±14% (n=8) for forage, 80±9% (n=6) for grain and 103±1 7% (n=7) for the straw.

Results from residues in wheat grain are presented in Table 56 and from forage and straw in Tables 64-5.

Table 56 Residues of quinclorac) in spring wheat grain following broadcast foliar application with a DF formulation

Localisation	Treatment			Residues				Trial
Year (variety)	Treatment kg ai/ha	no	BBCH	matrix	PHI	quinclorac	mean	Reference

Localisation	Treatment			Residues				Trial
Year (variety)	Treatment kg ai/ha	no	BBCH	matrix	PHI	quinclorac	mean	Reference
Canada Saskatchewan 1995 (Katepwa)	quinclorac 0.123	1	22-29	grain	75	0.136, 0.252	0.194	95106 BASF/96/5103
Canada Saskatchewan 1995 (Katepwa)	quinclorac; 0.125, imazethabenz; 2,4-D	1	22-29	grain	75	0.10, 0.15	0.125	95106 BASF/96/5103
Canada Saskatchewan 1995 (Katepwa)	quinclorac; 0.125, imazethabenz; Tribenuron/thifensulfuron;	1	22-29	grain	75	0.14, 0.17	0.155	95106 BASF/96/5103
Canada Saskachewan 1995 (Katepwa)	quinclorac 0.125 Bromonynil/MCPA	1	22-29	grain	75	0.18, 0.19	0.185	95106 BASF/96/5103
Canada Nisku, Alberta 1995 (Katepwa)	quinclorac 0.122	1	22-29	grain	75	0.088, 0.096	0.092	95107 BASF/96/5103
Canada Nisku, Alberta 1995 (Katepwa)	quinclorac; 0.125, imazethabenz; 2,4-D	1	22-29	grain	75	0.077 0.049	0.063	95107 BASF/96/5103
Canada Nisku, Alberta 1995 (Katepwa)	quinclorac; 0.125, imazethabenz; Tribenuron/thifensulfuron	1	22-29	grain	75	0.120 0.107	0.114	95107 BASF/96/5103
Canada Nisku, Alberta 1995 (Katepwa)	quinclorac 0.125 Bromonynil/MCPA	1	22-29	grain	75	0.161 0.143	0.152	95107 BASF/96/5103

PHI = Pre-harvest interval

To determine magnitude of residues of quinclorac in spring wheat field trials were performed during growing season 1998 in USA (Minnesota, Montana, North Dakota, Oregon, South Dakota and Washington) using a DF formulation. In all trials quinclorac was applied as a single broadcast post-emergence spray 70–74 days prior to harvest. All applications contained crop oil concentrate as spray adjuvant.

Samples of wheat forage (duplicate), grain (single) and straw (triplicate) were sampled and stored frozen (< -10 °C) until they were homogenized and until analysis within 27 months. Samples were analysed for quinclorac by method A8902 using ECD detection. The LOQ was 0.05 mg/kg and the average recoveries were 78±12% (n=15) for forage, 83±11% (n=12) for grain and 75±7% (n=12) for the straw.

Results from residues in wheat grain are presented in Table 57 and from forage and straw in Tables 64-5.

Table 57 Residues of quinclorac in spring wheat grain following broadcast foliar application with a DF formulation

Location	Application			Residues			Reference
Year (variety)	kg ai/ha	no	Growth stage BBCH	matrix	PHI	quinclorac (mg/kg)	Reference
USA (MN) 1998 Pioneer	0.56	1	20-29 (tillering)	grain	71	0.22	90056 BASF/1998/5104
USA (MN) 1998 Stoa	0.56	1	20-29 (tillering)	grain	70	0.14	90057 BASF/1998/5104
USA Grand Forks (ND) 1998 Marshall	0.56	1	20-29 (tillering)	grain	70	0.26	90058 BASF/1998/5104
USA Steele (ND) 1998 Marshall	0.56	1	20-29 (tillering)	grain	70	0.17	90059 BASF/1998/5104
USA Grand Forks (ND) 1998 Marshall	0.56	1	20-29 (tillering)	grain	73	0.13	90060 BASF/1998/5104
USA* Minehaha (SD) 1998 Guard	0.56	1	20-29 (Tillering)	grain	70	0.49	90061 BASF/1998/5104
USA* Minehaha (SD) 1998 Guard	0.56	1	20-29 (tillering)	grain	71	0.76	90062 BASF/1998/5104
USA (MT) 1998 926	0.56	1	20-29 (tillering)	grain	82	0.80	90063 BASF/1998/5104
USA (MT) 1998 Nevanna	0.56	1	20-29 (tillering)	grain	72	0.53	90064 BASF/1998/5104
USA (ID) 1998 Pondera	0.56	1	20-29 (tillering)	grain	73	0.45	90065 BASF/1998/5104
USA (WA) 1998 Yecora Rojo	0.56	1	51 (beginning of heading)	grain	71	2.86	90066 BASF/1998/5104
USA (OR) 1998 Ovens	0.56	1	20-29 (tillering)	grain	74	0.73	90067 BASF/1998/5104

PHI = pre harvest interval

*Different planting dates, independent from each other

scaling factor = 0.22 (0.125/0.56 = 0.22)

BBCH 51= Inflorescence emergence

To determine magnitude of residues of quinclorac in spring wheat field trials were performed during growing season 1998 in Canada (Alberta, Manitoba, Saskatchewan) using a DF formulation. In all trials quinclorac was applied as a single broadcast post-emergence spray 90-76 days prior to harvest for grain and straw and . All applications contained crop oil concentrate as spray adjuvant.

Samples (four replicates) of wheat forage (duplicate), grain (single) and straw (triplicate) were sampled and stored frozen (< -5 °C) until they were homogenized and analysed within 8 months. Samples were analysed for quinclorac by method A8902 using GC/ECD detection. . The LOQ was 0.05 mg/kg and the average recoveries were 89±15% (n=17) for forage, 88±18% (n=24) for grain and 83±9% (n=18) for the straw.

Results from residues in wheat grain are presented in Table 58 and from forage and straw in Table 63

Table 58 Residues of total quinclorac in spring wheat grain following broadcast foliar application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage BBCH	matrix	PHI	Total quinclorac (mg/kg)	mean mg/kg	Reference
Canada Minto, Manitoba 1994 Katepwa	0.126	1	23 (three tillers)	grain	90	4x < 0.05	< 0.05	94108 BASF/1995-7004167
Canada Aberdeen, Saskatchewan 1994 Katepwa	0.126	1	23 (three tillers)	grain	77	0.14, 0.16, 0.16, 0.17	0.16	94109 BASF/1995-7004167
Canada Portage, Manitoba 1994 Katepwa	0.126	1	23 (three tillers)	grain	76	3 x < 0.05, 0.5	0.05	94110 BASF/1995-7004167
Canada Swift current Saskatchewan 1994 Katepwa	0.126	1	23 (three tillers)	grain	76	0.10, 0.07, 0.07, 0.12	0.09	94111 BASF/1995-7004167

Zadoks 23-25; tillering with 3-5 tillers present

Sorghum

Results from supervised trials from USA on sorghum were provided to the Meeting.

To determine magnitude of residues of quinclorac in sorghum field trials were performed during growing season 1995 in USA (Kansas, Nebraska, Oklahoma and Texas) using a DF formulation. In all trials quinclorac was applied as a single broadcast post-emergence spray. All applications contained crop oil concentrate as spray adjuvant.

Duplicate samples of sorghum grain and straw were sampled and kept at < -10 °C until they were homogenized in room temperature (grain) and in dry ice (straw) and then returned to frozen storage until analysis within 12 months. The storage period is covered by the storage stability studies (38 months). Samples were analysed for quinclorac by method A8902 using GC/ECD detection. The LOQ was 0.05 mg/kg and the average recoveries were for trials 94200-94203; 79±17% (n=10) for forage, 81±10.1% (n=10) for grain and 85±11% (n=7) for the fodder and for trials 9766-97270; 84±21% (n=3) for forage, 96±9.4% (n=3) for grain and 93±21.5% (n=3) for the fodder.

Results from residues in sorghum grain are presented in Table 59 and from forage and straw in Table 66.

Table 59 Residues of quinclorac in sorghum grain following broadcast application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac (mg/kg)	mean (mg/kg)	Reference
USA (KS) 1995 (Hoegemeyer S-688)	0.29	1	6-leaf stage	grain	98	0.06, 0.06	0.06	94200 BASF/1996/5136
				grain	103	0.10, 0.08	0.09	
				grain	108	0.07, 0.06	0.065	
				grain	118	0.07, 0.07	0.07	
USA (NE) 1995 (NK 1210)	0.29	1	6-leaf stage	grain	89	< 0.05, < 0.05	< 0.05	94201 BASF/1996/5136
USA (OK) 1995 (Cargill 630)	0.29	1	5-7 leaves, mainly 6	grain	81	0.278, 0.242	0.26	94202 BASF/1996/5136
USA (KS) 1995 (DK 705)	0.29	1	6-leaf stage	grain	93	0.231, 0.234	0.233	94203 BASF/1996/5136
USA (NE) York county 1997 (NK 11210)	0.28	1	6-leaf stage	grain	86	< 0.05, < 0.05	< 0.05	97266 BASF/1998/5081
USA (NE) Hall county 1997 (NK 11210)	0.28	1	6-leaf stage	grain	87	< 0.05, < 0.05	< 0.05	97267 BASF/1998/5081
USA (CO) 1997 (Cargill 577)	0.29	1	6-leaf stage	grain	91	0.08, 0.08	0.08	97268 BASF/1998/5081
USA (NE) 1997 (Pioneer 8699)	0.28	1	6-leaf stage	grain	95	0.31, 0.28	0.30	97269 BASF/1998/5081
USA (NE) 1997 (F270E)	0.28	1	6-leaf stage	grain	93	0.49, 0.51	0.50	97270 BASF/1998/5081

To determine the influence of the formulation on the residues in sorghum grain five supervised trials were conducted during the growing season 2009 in USA (Arkansas and Louisiana). Each trial consisted of side-by-side tests comparing the dry flowable (DF) and the soluble liquid (SL). The rice was irrigated according to typical commercial practices for paddy-grown rice

Duplicate samples were sampled and maintained frozen until analysis within 7.7 months. Samples were analysed for quinclorac using method D9708/1 using LC- MS/MS. LOQ was 0.05 mg/kg and the average recovery was 94% (n=2).

Table 60 Residues of quinclorac in sorghum grain following ground foliar application with a DF and a SL formulation

Location	Application	Residues	Trial

Year	formulation	water L/ha	kg ai/ha	no	BBCH	matrix	PHI	quinclorac (mg/kg)	Reference
USA (LA) Rapid Parish 2009	DF	205	0.413	1	4-5 leaf	grain	97	< 0.05	RO90424 BASF/2013/7000580
USA (ND) Cass 2009	DF	210	0.429	1	BBCH 15	grain	113	< 0.05	RO90425 BASF/2013/7000580
USA (LA) Rapid Parish 2009	SL	205	0.459	1	4-5 leaf	grain	97	< 0.05	RO90424 BASF/2013/7000580
USA (ND) Cass 2009	SL	211	0.477	1	BBCH 15	grain	113	< 0.05	RO90425 BASF/2013/7000580

PHI = Pre-harvest interval

Rape seed

To determine magnitude of residue of quinclorac in rape seed seventeen supervised field trials were conducted in Canada (16) and USA (1). Quinclorac was applied as a single post-emergence broadcast application.

Duplicate rape seed samples were collected and stored frozen (< -10 °C) until homogenization. After homogenization samples were returned to frozen storage until analysis within 6 months for quinclorac and 12 months for quinclorac methyl ester. The storage period is covered by the storage stability studies (22 months) for both analytes. Samples were analysed for quinclorac according to method D9708/1 with LOQ of 0.05 mg/kg and average recovery of 75±13% (n=13) and for quinclorac methyl ester according to method D9806 with LOQ of 0.05 mg/kg and average recovery of 92±15% (n=9).

Results from residues in rapeseed (canola) grain are presented in table below.

Table 61 Residues in rape seed following ground broadcast application with quinclorac (DF formulation)

Location		Application			Residues				Trial
Year (variety)	Total Rate,	no	Growth stage	Matrix	PHI (days)	Quinclorac residues (mg/kg)	Methyl ester residues (mg/kg)	Mean total residues (mg/kg)	Comment
Canada Hines Creek, Alberta, 1997 Reward	(kg ai/ha)	1	6 -leaf stage	seed	60	< 0.05, < 0.05	< 0.05, < 0.05	< 0.10	RCN 97334 1998/5094
Canada Fairview, Alberta, 1997 Reward	0.1	1	6 -leaf stage	seed	53 60 67 74	< 0.05 < 0.05 < 0.05 < 0.05	< 0.05 < 0.05 < 0.05 < 0.05	< 0.10 < 0.10 < 0.10 < 0.10	RCN 97335 1998/5174
Canada, Lacombe, Alberta, 1997	0.1	1	7 leaves and bolting	seed	60	0.10, 0.09	0.19 0.17	0.28	RCN 97336 1998/5094

Location		Application			Residues				Trial
Year (variety)	Total Rate,	no	Growth stage	Matrix	PHI (days)	Quinclorac residues (mg/kg)	Methyl ester residues (mg/kg)	Mean total residues (mg/kg)	Comment
Quantum									
Canada Stettler, Alberta 1997 Quantum	0.1	1	7-8 leaves and bolting	seed	60	0.18, 0.22	0.09, 0.08	0.29	RCN 97337 1998/5094
Canada Red Deer, Alberta 1997 Hyson 110	0.1	1	5-leaf stage	seed	60	< 0.05, < 0.05	0.12, 0.13	0.18	RCN 97338 1998/5094
Canada, Aberdeen, Saskatchewan 1997 Quantum	0.1	1	3-8 leaves	seed	60	0.14, 0.12	0.06, < 0.05	0.20	RCN 97339 1998/5094
Canada, Rosthern, Saskatchewan 1997 Quantum	0.1	1	3 leaves	seed	60	0.30, 0.18	0.09, 0.09	0.37	RCN 97340 1998/5094
Canada, Wakaw, Saskatchewan 1997 Ebony	0.1	1	43-82 cm tall, 5-10 leaves	seed	60	< 0.05, < 0.05	< 0.05, < 0.05	< 0.10	RCN 97341 1998/5094
Canada, Melfort, Saskatchewa 1997 Quantum	0.1	1	5-10 leaves	seed	60	0.09, 0.08	0.08 0.06	0.16	RCN 97342 1998/5094
Canada, Duck Lake, Saskatchewa 1997 Garrison	0.1	1	6-8 leaves and flowering	seed	60	0.21, 0.25	0.12, 0.10	0.34	RCN 97343 1998/5094
Hague, Saskatchewan Canada, 1997 Garrison	0.1	1	5-7 leaves and flowering	seed	60	0.63, 0.57	0.14, 0.11	0.73	RCN 97344 1998/5094
Canada, Saskatoon, Saskatchewan 1997 Garrison	0.1	1	4-6 leaves	seed	60	0.85 0.86	0.15 0.12	0.99	RCN 97345 1998/5094
Canada, Boussevain, Manitoba 1997 46A05	0.1	1	11 leaves	seed	60	0.24, 0.21	0.23, 0.07	0.38	RCN 97346 1998/5094
Canada Minto, Manitoba 1997 A5471	0.1	1	11 leaves	seed	60	0.15, 0.17	< 0.05 < 0.05	0.21	RCN 97347 1998/5094

Location		Application			Residues				Trial
Year (variety)	Total Rate,	no	Growth stage	Matrix	PHI (days)	Quinclorac residues (mg/kg)	Methyl ester residues (mg/kg)	Mean total residues (mg/kg)	Comment
Canada, Portage La Prairie, Manitoba 1997 46A72	0.1	1	22 leaves and flowering	seed	60	< 0.05, 0.05	0.10 0.10	0.15	RCN 97348 1998/5094
Canada Bagot, Manitoba 1997 Quantum	0.1	1	8-10 leaves, mid flowering	seed	60	0.21, 0.21	0.23, 0.13	0.39	RCN 97349 1998/5094
USA New Rockford (ND,) 1997 Hyola 308	0.1	1	22 leaves, early bloom	seed	53 60 67 74	0.07, < 0.05 < 0.05, 0.06 0.06, 0.05 < 0.05, < 0.05	< 0.05 < 0.05 < 0.05, < 0.05 < 0.05, < 0.05 < 0.05, < 0.05	0.11 0.11 0.11 < 0.10	RCN 97350 1998/5094

RESIDUES IN ANIMAL COMMODITES

Straw, forage, fodder of cereal grains

Table 62 Residues of quinclorac in rice straw following a broadcast ground application with a DF formulation

Year (variety)	kg ai/hl	water L/ha	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac	mean	Reference
USA (MS), 1996 (Lemont)	0.599	94	0.560	1	Booting	straw	34	0.419, 0.258	0.339	96152 BASF/97/5051
						straw	37	0.328, 0.233	0.281	
						straw	40	0.443, 0.275	0.359	
						straw	43	0.357, 0.170	0.259	
						straw	46	0.379, 0.216	0.298	
USA (MS), 1996 (Lemont)	0.570	94	0.549	1	Booting	straw	40	1,74, 1.84	1,79	96154 BASF/97/5051
USA (AR) 1996 (Bengal)	0.593	95	0.560	1	heading	straw	34	1.49, 1.64	1.57	96155 BASF/97/5051
						straw	37	2.37, 1.42	1.90	
						straw	40	1.15, 1.29	1.22	
						straw	43	2.30, 1.74	1.89	
						straw	46	1.25, 1.33	1.29	
USA (AR) 1996 (Bengal)	0.604	96	0.582	1	heading	straw	40	0.107, 0.133	0.120	96156 BASF/97/5051
USA (AR) 1996 (Kaybonnet)	0.605	95	0.571	1	Early booting	straw	40	1.05, 0.865	0.958	96157 BASF/97/5051

Year (variety)	kg ai/hl	water L/ha	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac	mean	Reference
USA (LA) 1996 (Cypress)	0.576	97	0.560	1	Early booting	straw	40	1.23, 1.08	1.16	96158 BASF/97/5051
USA (LA) 1996 (Cypress)	0.565	99	0.560	1	Early booting	straw	40	0.769, 0.622	0.696	96159 BASF/97/5051
USA (LA) 1996 (Cypress)	0.571	100	0.571	1	Early booting	straw	41	1.15, 1.22	1.19	96160 BASF/97/5051
USA (LA) 1996 (Bengal)	0.593	94	0.560	1	Early booting	straw	40	1.56, 0.659	0.11	96161 BASF/97/5051
USA (LA) 1996 (Maybell)	0.599	95	0.571	1	5 cm pancile in the sheat	straw	40	1.35, 1.20	1.28	96162 BASF/97/5051
USA (M0) 1996 (Lemont)	0.549	102	0.560	1	7,6 cm panicle in the sheat	straw	40	0.473, 0.31	0.392	96163 BASF/97/5051
USA (M0) 1996 (Cypress)	0.604	96	0.582	1	heading	straw	40	1.94, 3.54	2.74	96164 BASF/97/5051
USA (TX) 1996 (Cypress)	0.571	102	0.582	1	Full boot stage	straw	40	0.757, 0.927	0.84	96166 BASF/97/5051

PHI = Pre-harvest interval

Table 63 Residues of quinclorac in spring wheat forage and straw following broadcast foliar application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac	mean mg/kg	Reference
Canada Minto, Manitoba 1994 Katepwa	0.126	1	23 (three tillers)	forage	21	4x < 0.05	< 0.05	94108 BASF/1995-7004167
				straw	90	4x < 0.05	< 0.05	
Canada Aberdeen, Saskatchewan 1994 Katepwa	0.126	1	23 (three tillers)	forage	24	0.62, 0.51, 0.56, 0.49	0.545	94109 BASF/1995-7004167
				straw	77	0.06, 0.05, 2x< 0.05	0.063	
Canada Portage, Manitoba 1994 Katepwa	0.126	1	22 (two tillers)	forage	15	0.10, 0.13, 0.09, 0.11	0.108	94110 BASF/1995-7004167
				straw	76	4x < 0.05	< 0.05	
Canada Swift current Saskatchewan 1994 Katepwa	0.126	1	24 (four tillers)	forage	23	0.22, 0.19, 0.17, 0.13	0.179	94111 BASF/1995-7004167
				straw	76	4x < 0.05	< 0.05	
Canada Alberta	not done	-	-	no data	no data	no data	no data	94112 BASF/1995-

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac	mean mg/kg	Reference
1994 Katepwa								7004167

Table 64: Residues of quinclorac in spring wheat forage and straw following broadcast foliar application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	Treatment kg ai/ha	no	Growth stage BBCH	matrix	PHI	quinclorac	mean	Reference
Canada Manitoba 1995 Katepwa	quinclorac 0.125	1	21-22 (max two tillers)	forage only	16	0.06, 0.07	0.065	95105 BASF/96/5103
Canada Manitoba 1995 Katepwa	quinclorac; 0.125, imazamethabenz; 2,4-D	1	21-22 (max two tillers)	forage	16	0.06, 0.05	0.06	95105 BASF/96/5103
Canada Manitoba 1995 Katepwa	quinclorac; 0.125, imazamethabenz; Tribenuron/thifensulfuron;	1	21-22 (max two tillers)	forage	16	0.08, 0.07	0.075	95105 BASF/96/5103
Canada Manitoba 1995 Katepwa	quinclorac 0.125 Bromoxynil/MCPA	1	21-22 (max two tillers)	forage	16	0.06, 0.08	0.07	95105 BASF/96/5103
Canada Saskatchewan 1995 Katepwa	quinclorac 0.123	1	Zadock 23-30 20-25 cm high with 4-6 tillers	forage	9	1.8, 1.5	1.7	95106 BASF/96/5103
				straw	75	0.20, 0.17	0.19	
Canada Saskatchewan 1995 Katepwa	quinclorac; 0.125, imazamethabenz; 2,4-D	1	21-22 (max two tillers)	forage	9	1.0, 1.1	1.05	
				straw	75	0.2, 0.17	0.19	
Canada Saskatcoon 1995 Katepwa	quinclorac; 0.125, imazamethabenz; Tribenuron/thifensulfuron;	1	21-22 (max two tillers)	forage	9	1.1, 1.1	1.1	95106 BASF/96/5103
				straw	75	0.14, 0.16	0.15	
Canada Saskatchewan 1995 Katepwa	quinclorac 0.125 Bromoxynil/MCPA	1	21-22 (max two tillers)	forage	9	1.5, 1.6	1.55	95106 BASF/96/5103
				straw	75	0.1, 0.12	0.11	
Canada Nisku, Alberta 1995 Katepwa	quinclorac 0.122	1	21-22 (max two tillers)	forage	9	0.23, 0.23	0.23	95107 BASF/96/5103
				straw	75	< 0.05, < 0.05	≤ 0.05	
Canada Alberta 1995 Katepwa	quinclorac; 0.125, imazamethabenz; 2,4-D	1	21-22 (max two tillers)	forage	9	0.13, 0.14	0.135	95107 BASF/96/5103
				straw	75	< 0.05, < 0.05	< 0.05	
Canada Alberta 1995 Katepwa	quinclorac; 0.125, imazamethabenz; Tribenuron/thifensulfuron	1	21-22 (max two tillers)	forage	9	0.18, 0.19	0.175	95107 BASF/96/5103
				straw	75	< 0.05, < 0.05	< 0.05	
Canada	quinclorac 0.125	1	21-22	forage	9	0.3, 0.29	0.295	95107

Location	Application			Residues				Trial
Year (variety)	Treatment kg ai/ha	no	Growth stage BBCH	matrix	PHI	quinclorac	mean	Reference
Alberta 1995 Katepwa	Bromoxynil/MCPA		(max two tillers)	straw	75	< 0.05, < 0.05	< 0.05	BASF/96/5103

Table 65 Residues of quinclorac in spring wheat forage and straw following broadcast foliar application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage BBCH	matrix	PHI	quinclorac	Scaled quinclorac residues at 0.125 kg ai/ha	Reference
(USA MN) 1998 Pioneer	0.56	1	20-29 (tillering)	forage	22	0.27	0.059	90056 BASF/1998/5104
				straw	71	0.10[a]	0.022	
USA (MN) 1998 Stoa	0.56	1	20-29 (tillering)	forage	15	0.67	0.147	90057 BASF/1998/5104
				straw	70	0.05[a]	0.011	
USA Grand Forks (ND) 1998 Marshall	0.56	1	20-29 (tillering)	forage	22	0.47[b]	0.103	90058 BASF/1998/5104
				straw	70	0.04[a]	0.0088	
USA Steele (ND) 1998 Marshall	0.56	1	20-29 (tillering)	forage	15	0.27	0.059	90059 BASF/1998/5104
				straw	70	0.10	0.022	
USA Grand Forks (ND) 1998 Marshall	0.56	1	20-29 (tillering)	forage	15	0.60	0.132	90060 BASF/1998/5104
				straw	73	0.10	0.022	
USA* Minehaha (SD) 1998 Guard	0.56	1	20-29 (tillering)	forage	15	0.94	0.207	90061 BASF/1998/5104
				straw	70	0.32	0.070	
USA* Minehaha (SD) 1998 Guard	0.56	1	20-29 (tillering)	forage	15	1.55[a]	0.34	90062 BASF/1998/5104
				straw	71	0.74	0,163	
USA (MT) 1998 926	0.56	1	20-29 (tillering)	forage	15	1.1 [a]	0.24	90063 BASF/1998/5104
				straw	82	0.47	0.103	
USA (MT) 1998 Nevanna	0.56	1	20-29 (tillering)	forage	15	3.62[b]	0.796	90064 BASF/1998/5104
				straw	72	0.55[b]	0.121	
USA (ID) 1998 Pondera	0.56	1	20-29 (tillering)	forage	15	1.08[a]	0.234	90065 BASF/1998/5104
				straw	73	0.14	0.031	
USA (WA) 1998 Yecora Rojo	0.56	1	51 (beginning of heading)	forage	15	0.84	0.185	90066 BASF/1998/5104
				straw	71	0.50[b]	0.11	

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage BBCH	matrix	PHI	quinclorac	Scaled quinclorac residues at 0.125 kg ai/ha	Reference
USA (OR) 1990 Ovens	0.56	1	20-29 (tillering)	forage	15	0.85[b]	0.187	90067 BASF/1998/5104
				straw	74	0.57[b]	0.125	

PHI = pre harvest interval

[a] Value is the average of three analysis

[b] Value is the average of two analysis

n.r. = not reported

scaling factor = 0.22 (0.125/0.56 = 0.22)

Table 66 Residues of quinclorac in sorghum forage and stover following broadcast foliar application with a DF formulation

Location	Application			Residues				Trial
Year (variety)	kg ai/ha	no	Growth stage	matrix	PHI	quinclorac	mean	Reference
USA (NE) Hall county 1997 (NK 11210)	0.28	1	6-leaf stage	forage	64	< 0.05, < 0.05	< 0.05	97267 BASF/1998/5081
				stover	87	< 0.05, < 0.05	< 0.05	
USA (CO) 1997 (Cargill 577)	0.29	1	6-leaf stage	forage	50	0.06, 0.06	0.06	97268 BASF/1998/5081
				stover	91	< 0.05, < 0.05	< 0.05	
USA (NE) 1997 (Pioneer 8699)	0.28	1	6-leaf stage	forage	54	0.15, 0.12	0.14	97269 BASF/1998/5081
				stover	95	< 0.05, < 0.05	< 0.05	
USA (NE) 1997 (F270E)	0.28	1	6-leaf stage	forage	62	0.20, 0.17	0.19	97270 BASF/1998/5081
				stover	93	< 0.05, < 0.05	< 0.05	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

Storage stability of quinclorac in sorghum starch was investigated up to 20 months by Brukey, J and Stewart J (1997/5046).

Control sorghum starch samples from study 1994/5104 study were fortified with 1.0 mg/kg quinclorac. The fortified samples were stored frozen (<-5 ºC) for a period of 20 months. Duplicate samples were analysed for total quinclorac using Method A8902 at 1 day and then 7, 17 and 20 months after the initial fortification.

Table 67 Storage stability of quinclorac in sorghum starch

Storage periods (months)	Procedural recovery % AR (mean)	Residues remaining % AR mean
0	na*	89, 88 (89)
7	98, 101 (100)	92, 95 (94)
14	72, 77 (75)	69, 80 (75)
20	89, 87 (88)	81, 86 (84)

* Data not available. The 0 day analysis, was extracted the day after fortification.

Nature of residue during processing

The hydrolysis of quinclorac during processing condition was investigated by Kennan, D and Brusky, M (2014 BASF/700909). ^{14}C-quinclorac was applied directly to a target concentration of 30 µg/mL to buffer solutions of pH 4, 5 and 6. Incubation was done at three representative sets of hydrolysis conditions: 90 °C, pH 4 for 20 minutes (pasteurization); 100 °C, pH 5 for 100 minutes (boiling) and 120 °C, pH 6 for 20 minutes (sterilization).

Parent compound and potential hydrolysis products were quantified by LSC and identified by HPLC using a radioactive detector (HPLC-RAD) and three replicates per sample. Quinclorac reference standard was chromatographed at the beginning of each sampling set. Material balance was established for each set of hydrolysis conditions. In the following tables recovered radioactivity is summarized.

Table 68 Hydrolysis of quinclorac under simulated processing conditions expressed as % TRR

Incubation time (minutes)	Hydrolysis conditions	Recovered % AR (average)	Quinclorac (average)	Total other (average)
0	pH 4, 90 °C	98.8, 98.9, 99.6 (99.1)	97.2, 97.1, 98.3 (97.5)	1.7, 1.9, 1.3 (1.6)
20		99.6, 100.2, 99.4 (99.7)	98.1, 98.6, 96.7 (97.8)	1.9, 1.6, 2.7 (2.1)
0	pH 5, 100 °C	100.1, 101, 99.8 (100.3)	98.2, 98.9, 97.2 (98.1)	1.8, 2.1, 2.6 (2.2)
20		100.6, 100.3, 99.8 (100.2)	97.5, 98.7, 97.4 (97.9)	3.1, 1.5, 2.3 (2.3)
0	pH 6, 120 °C	99.3, 98.6, 100 (99.3)	95.4, 96.6, 98.7 (96.9)	3.9, 2.0, 1.3 (2.4)
20		100.8, 100, 100.2 (100.3)	99.1, 97.0,98.8 (98.3)	1.8, 3.0, 1.4 (2.1)

Table 69 Hydrolysis of quinclorac under simulated processing conditions, expressed in concentrations µg/mL

Incubation time (minutes)	Hydrolysis conditions	Recovered µg/mL (average)	Quinclorac µg/mL (average)	Total other µg/mL (average)
0	pH 4, 90 °C	30.9, 29.7, 30.6 (30.4)	30.4, 29.1, 30.2 (29.9)	0.5, 0.6, 0.4 (0.5)
20		29.4, 30.3, 30.2 (29.9)	28.8, 29.8, 29.4 (29.3)	0.6, 0.5, 0.8 (0.6)
0	pH 5, 100 °C	29.9, 29.9, 29.8 (29.9)	29.4, 29.3, 28.9 (29.2)	0.6, 0.6, 0.8 (0.7)
20		29.8, 30.0, 20.8 (29.9)	28.9, 29.6, 29.2 (29.2)	0.6, 0.6, 0.8 (0.7)
0	pH 6, 120 °C	29.8, 29.8, 29.8 (29.8)	28.6, 29.2, 29.4 (29.1)	1.2, 0.6, 0.4 (0.7)
20		30.6, 30.6, 30.5 (30.6)	30.0, 29.7, 30.1 (29.9)	0.5, 0.9, 0.4 (0.6)

Within pH 4 and pH 5 none of the individually degradates exceeded 3.0% applied radioactivity (AR). Within pH 6 individual degradate did not exceed 4% AR. Therefore the products were not further analysed.

Residues after processing

The fate of quinclorac and its metabolite quinclorac methyl ester during processing of raw agricultural commodity (RAC) was investigated in rice, wheat, and sorghum and rape seed. As a measure of the transfer of residues into processed products, a processing factor (PF) was used, this is defined as:

$$PF = \frac{\text{Total residue in processed products (mg/kg)}}{\text{Total residue in raw agriculture commodity (mg/kg)}}$$

If residues in the RAC were below the LOQ, no processing factor could be derived.

Rice

In one field trial conducted in Texas and reported by Single, YH (1989, BASF/5003) rice samples were taken from field plots treated with a single foliar application of 1.68 kg ai/ha (3N GAP rate) and a pre-harvest interval of 79 days. 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 (10g) were analysed for quinclorac according to method A8902. The method is designed to determine residues of quinclorac expressed as its methyl ester. 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 70 Residues of quinclorac in rice and rice processed products

Commodity	Residues (mg/kg)	Mean residues (mg/kg)	Processing factor
Rice grain	0.43, 0.46	0.45	-
Hulls	0.50, 0.45	0.48	1.07
Brown rice	0.47, 0.45	0.46	1.02
Rice bran	1.4, 1.2, 1.5, 1.3	1.35	3
Milled rice	0.33, 0.35	0.34	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.

Wheat

In two independent field trials conducted in USA and reported by Burkey, JD and Riley, M (1994, BASF/5093) samples of spring wheat were taken from plots treated with three post emergence broadcast applications of quinclorac each at 0.56 kg ai/ha (6× GAP rate). The treatments were made in a sequence within growth stage BBCH 22–49 (from tillering to first awn visible). The samples (control and treated) were harvested at normal maturity (57–58 days after the last application) and then processed.

The spring wheat grain was first dried and cleaned to separate husks and other impurities from the grain. The seed were then conditioned by adding tap water to adjust the moisture content to 16%. The milling process followed. For analysis, samples of whole wheat, bran, middlings, shorts, low grade flour and patent flour was collected.

Samples were analysed for quinclorac according to method A8902. The LOQ was 0.05 mg/kg. Spiked samples were run concurrently and the overall average recovery was 76±9% (n=14). In the following table the residues found in the processed commodities are summarized.

Table 71 Residues of quinclorac in wheat and wheat processed products

Location, year	No	kg ai/ha total	DALT*	Commodity	Residues (mg/kg)	average mg/kg	PF calculated
Minnesota 1990	3	1.68	57-58	Wheat grain	0.21, 0.20	0.21	
				Bran	0.43, 0.44	0.44	2.1
				Middlings	0.17, 0.11	0.14	0.67
				Shorts	0.26, 0.26	0.26	1.24
				Low grade four	0.12, 0.14	0.13	0.62
				Patent flour	0.16, 0.15	0.16	0.76
North Dakota 1990	3	1.68		Wheat grain	1.01, 0.95	0.98	
				Bran	1.59, 1.45	1.52	1.55
				Middlings	0.92, 0.86	0.89	0.91
				Shorts	1.23, 1.28	1.26	1.29
				Low grade four	0.48, 0.58	0.53	0.54
				Patent flour	0.53, 0.57	0.55	0.56

DALT= days after last treatment

PF = processing factor

In one field trial in spring wheat conducted in USA and reported by Versoi, PL (1996, BASF/5208) samples of spring wheat were taken from plots treated with one pre emergence broadcast applications of quinclorac at 1.4 kg ai/ha (5× GAP rate). The treatment was made on bare soil on the date the wheat seed was later planted. Grain samples (control and treated) were collected as raw agricultural commodity at normal maturity 103 days post application and then processed.

The spring wheat grain was first dried and cleaned to separate husks and other impurities from the grain. 50 kg of cleaned grain from untreated control sample and 19 kg of treated grain were removed for germ recovery process. The yield of grain from treated plots was reduced due to the extreme rate of application. The 50 kg sample was divided into 25 kg batches. The entire sample of treated wheat and each batch of untreated control was lightly ground and separated over a 12 mesh screen. The resulting material was screened over a 46 mesh screen. The material that passed through the 46 mesh screen was discarded. The material that remained on the screen contained the germ fraction. The endosperm fragments were separated from the germ fraction by bulk density. The entire wheat germ samples recovered was stored frozen. The original plan for processing is presented below. Due to the low supply of treated grain, residues were only measured in the germ fraction.

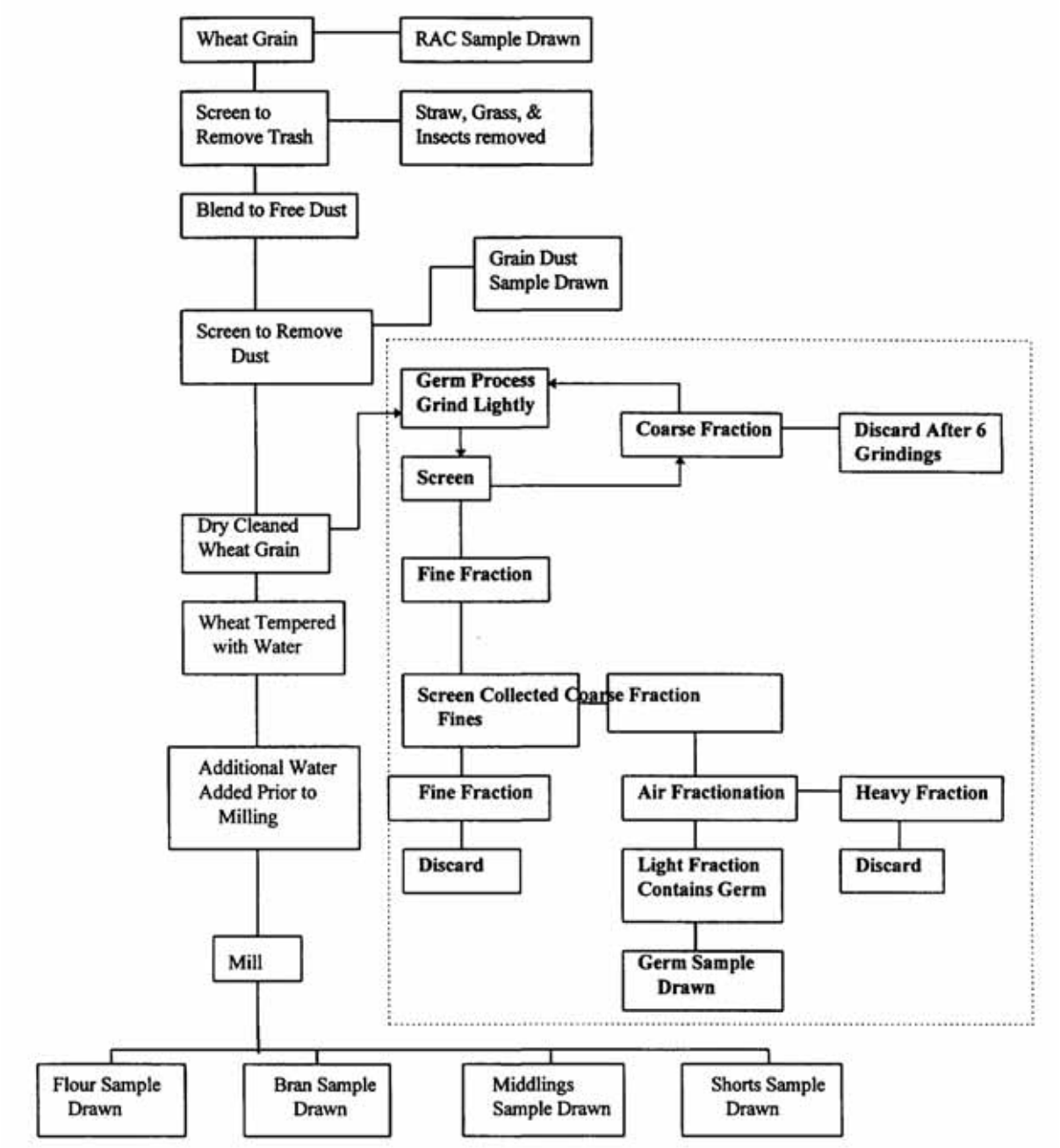


Figure 10 The original plan for processing into wheat germ

Samples were analysed for quinclorac according to method A8902. The LOQ was 0.05 mg/kg. Spiked samples were run concurrently and the overall average recovery was 79±7% (n=5). In the following table the residues found in the wheat germs are summarized.

Table 72 Residues of quinclorac in wheat and wheat germs

Commodity	Residues (mg/kg)	Mean residues (mg/kg)	PF
Wheat grain	0.221, 0.221	0.221	-
Germ	0.544, 0.683	0.614	2.8

PF = processing factor

Rape seed (canola)

In two independent field trials in rape seed one conducted in Canada and the other in USA reported by Guirguis, M (1998, BASF/5093) samples of rape seed were taken from plots treated with 0.1 kg ai/ha (1× GAP rate), 0.5 kg ai/ha and control plots. 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 canola. 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 (BH 514 ME) 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 73 Quinclorac resides in rape seed, meal and refined oil

Location, year	No	kg ai/ha	DALT	Sample	Quinclorac		Quinclorac methyl ester		Total Quinclorac + quinclorac methyl ester	
					mg/kg	PF	mg/kg	PF	mg/kg	PF
USA 1998	1	0.1	60	seed	0.05	-	0.054		0.1	-
		0.5	60	seed	0.19	-	0.30		0.49	-
		0.1	60	meal	< 0.05	<1	< 0.05	< 0.93	< 0.05	< 0.5
		0.5	60	meal	0.07	0.36	0.45	1.5	0.52	1.06
		0.1	60	refined oil	< 0.05	<1	0.055	1.02	0.06	0.6
		0.5	60	refined oil	< 0.05	< 0.26	0.20	0.33	0.25	0.5
Canada 1998	1	0.1	60	seed	0.13		0.24		0.37	-
		0.5	60	seed	0.36		1.0		1.36	-
	1	0.1	60	meal	0.28	2.15	< 0.05	< 0.21	0.33	0.89
		0.5	60	meal	0.58	1.61	0.08	0.08	0.66	0.49
		0.1	60	refined oil	< 0.05	< 0.39	0.29	1.21	0.34	0.92
		0.5	60	refined oil	0.08	0.22	1.36	1.36	1.44	1.06

DALT= days after last treatment

PF = processing factor

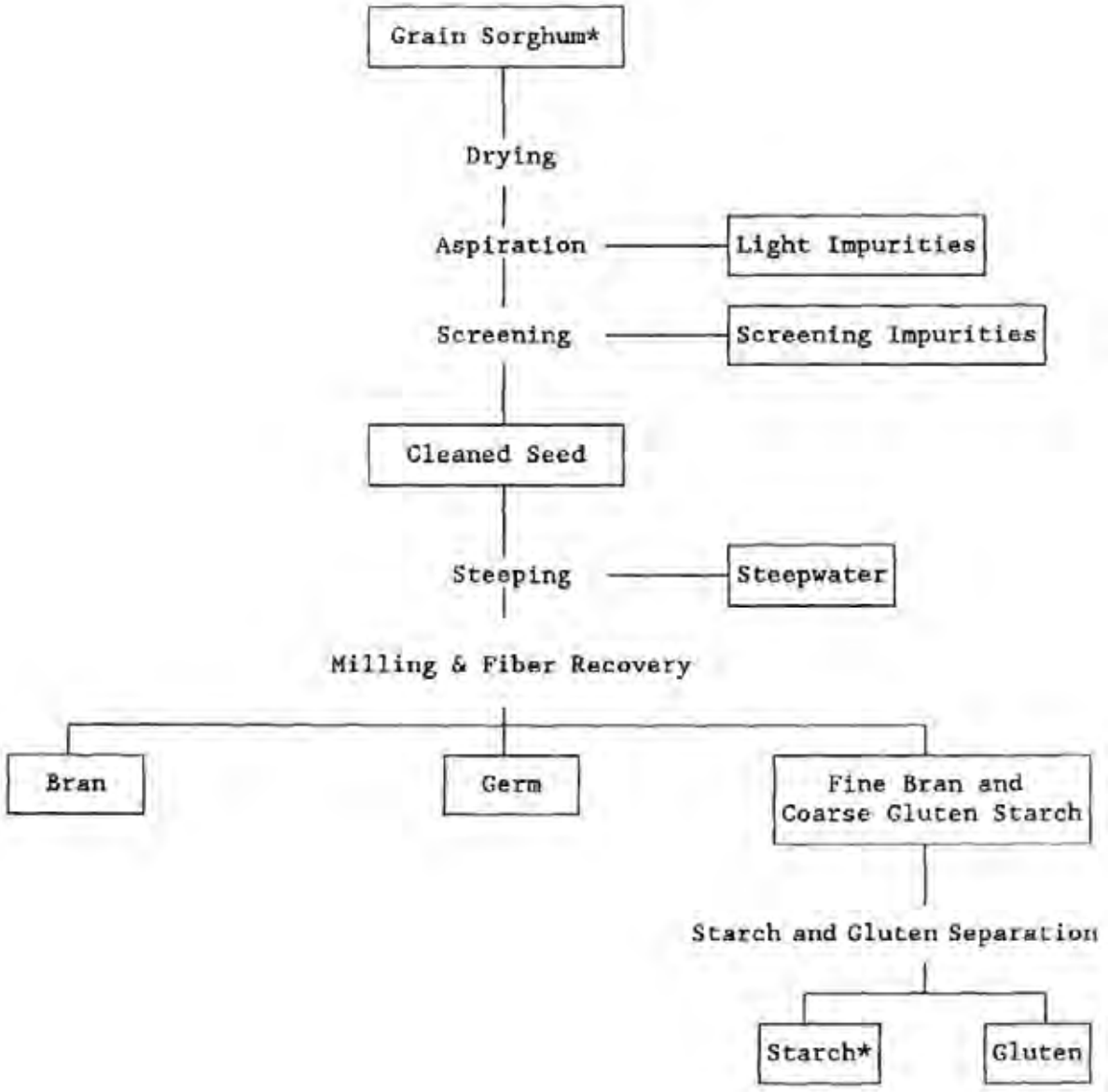
Sorghum

In two independent field trials conducted in USA and reported by Burkey, JD and Riley, M (1994, BASF 1994/5104) samples of sorghum grain were taken from plots treated with a pre-emergence application of 1.12 kg ai/ha followed by two sequential broadcast post emergence applications of 0.84 kg ai/ha. The applications were broadcast spray made when the sorghum was 3 to 5 leaf stage and again at the 8–10 leaf stage. Samples of sorghum grain were taken at normal maturity which was 89 days or 106 days after the last application and then processed.

The sorghum grain was dried until moisture content was 13% or less. After drying the grain was cleaned from light impurities (aspiration) and screened for large impurities (screening).

For dry milling of grain into flour, the hulls were first separated (decorticated) and then ground with a 2 mm screen and passed through a sifter

For wet milling of grain into starch, the cleaned grain was conditioned by steeping in a stainless steel tank with water, sodium bisulfite, and lactic acid at 50 °C. The steeped grain was ground, a majority of the germs were removed, the stock solution was passed over a shaker equipped with a 610µ (0.6 mm) screen. The material collected after screening was passed through a mill with 6 mm screen. The milled product was washed in a shaker equipped with a 43µ (0.043 mm) screen. The remaining process water with gluten and starch fraction was separated by centrifugation. The resulting fractions were starch, gluten and process water.



*fraction analysed

Figure 11 Flow chart of wet milling sorghum grain into flour and starch

Samples (duplicate) were analysed for quinclorac residues according A8902 (derivatized extracts analysed by GC). The LOQ was 0.05 mg/kg. Spiked samples were run concurrently and the average recoveries were 86% (n=2) for the grain, 81% (n=2) for the flour and 79% (n=2) for the starch. In the following table the residues found processed products are summarized.

Table 74 Quinclorac resides) in sorghum grain, flour and starch

Location, year	No	kg ai/ha total	DALT*	Sample	quinclorac		
Nebraska 1990	3	2.8	106		mg/kg	average	pf
				grain	0.33, 0.29	0.31	-
				flour	0.24, 0.28	0.26	0.83
				starch	< 0.05, < 0.05	< 0.05	< 0.16
Kansas 1990			89	grain	1.98, 1.91	1.95	-
				flour	1.67, 2.03	1.85	0.95

Location, year	No	kg ai/ha total	DALT*	Sample	quinclorac		
				starch	0.08, 0.08	0.08	0.04

DALT= days after last treatment

PF = processing factor

Table 75 Summary of quinclorac residues in processed commodities

		Calculated processing factors			
RAC	Commodity	Quinclorac	Quinclorac methyl ester	Total Quinclorac+quinclorac methyl ester	PF median or best estimate
Rice	RAC: grain				
	hulls			1.07	1.07
	brown rice			1.02	1.02
	bran			3	3
	milled			0.76	0.76
Wheat	RAC: grain				
	bran			2.1, 1.55	1.83
	middlings			0.67, 0.91	0.79
	shorts			1.24, 1.29	1.27
	low grade flour			0.62, 0.54	0.58
	patent flour			0.56,0.76	0.66
	germ			2.8	2.8
Rape seed	RAC: seed				
	meal	<1.0, 1.61, 2.15, 0.36,	0.08, < 0.21, < 0.93, 1.5	0.49, <,0.5, 0.89, 1.06	
	refined oil	0.22, < 0.26, < 0.39, <1.0,	0.33, 1.02, 1.21, 1.36	0.5, 0.6, 0.92, 1.06	
Sorghum	RAC: grain				
	flour			0.83, 0.95	0.89
	starch			0.16, 0.04	0.10

RESIDES IN ANIMAL COMMODITES

Farm animal feeding studies

For the estimation of residues of quinclorac in animal matrices laying hen and lactating cow feeding studies was submitted to the Meeting. Storage stability data was not provided in the studies.

Poultry

The magnitude of the residue of quinclorac has been studies in laying hens by Mayer, F (1989, BASF 89/5024)(Method 268). 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 no 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. Prior to dosing of quinclorac eggs collected contained no detectable residues of quinclorac. The results for those samples are not presented.

Table 76 Residues of quinclorac in eggs of laying hens after daily administration of quinclorac for 28 days

Days	Residues* in mg quinclorac-equivalents per kg (mean)		
Dose level	1 ppm	10 ppm	100 ppm
-1	< 0.01 (2)	< 0.01 (2)	< 0.01
1	< 0.01 (2)		< 0.01
2	< 0.01 (2)		0.016, 0.013 [0.015]
3	< 0.01 (2)		0.020, 0.023 [0.025]
4	< 0.01 (2)		0.011, 0.019 [0.015]
5	< 0.01 (2)		0.017, < 0.01 [0.09]
6	< 0.01 (2)		0.024, 0.025 [0.025]
7	< 0.01 (2)	< 0.01 (2)	**0.032, 0.033 [0.033**]
10	< 0.01 (2)		0.016, 0.025 [0.021]
12	< 0.01 (2)		0.021, 0.032 [0.027]
14	< 0.01 (2)		0.030, 0.019 [0.025]
18	< 0.01 (2)		0.013, 0.016 [0.015]
21	< 0.01 (2)	< 0.01 (2)	0.015, 0.033 [0.024]
23	< 0.01 (2)		0.013, 0.031 [0.022]
25	< 0.01 (2)		**0.036, 0.041 [0.039]**
28	< 0.01 (2)	< 0.01	0.036, 0.024 [0.03]

*based on limit of detection LOD (0.01 mg/kg)

The bodyweight of the birds were not influenced, however the number of egg laid appeared to be lower in the highest dose group.

Table 77 Number if egg laid per diet group after administration of quinclorac at 0.07, 0.7 or 7 mg/kg bw/day

Days	Control	1 × (1 ppm, 0.07 mg/kg bw)	10 × (10 ppm, 0.7 mg/kg bw)	100 × (100 ppm, 7 mg/kg bw)
-1--7	82	91	66	53
1-7	78	78	90	49
8-14	67	69	85	46
15-21	68	59	73	42
22-28	59	65	65	44

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

Table 78 Residues of quinclorac in tissues of laying hens after daily administration of quinclorac for 28 days

Tissue	Residues* in mg quinclorac-equivalents per kg (mean)		
Dose level	1 ppm	10 ppm	100 ppm
Skin and fat	0.00, 0.013, 0.018 [0.01]	0.12, 0.13, 0.17 [0.14]	0.122, 0.475, 0.760 [0.452]
Muscle dark	0.005, 0.00, 0.00 [0.002]	0.00, 0.00, 0.00 [0]	0.022, 0.025, 0.045, [0.03]
Muscle light	0.005, 0.00, 0.00 [0.002]	0.002, 0.003, 0.004, [0.003]	0.018 ,0.039, 0.068 [0.042]
kidney	0.002, 0.02, 0.059 [0.027]	0.007, 0.011, 0.015 [0.011]	0.235, 0.456, 0.558 [0.412]
Liver	0,00, 0.009, 0.009 [0.006]	0.009, 0.012, 0.013 [0.011]	0.042, 0.054, 0.128 [0.075]

*based on limit of detection LOD (0.01 mg/kg)

Lactating cows

Residues in lactating cows were investigated by Mayer F (1989 BASF 89/5025)(Method 268). 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, omental 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 BASF method no 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:

Table 79 Residues* of quinclorac in milk after daily oral administration of quinclorac for 28 days

Days	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 **[0.013]**
2	< 0.01 (3)			< 0.01, 0.011 0.035 **[0.019**]
3	< 0.01 (3)			0.016, 0.026, 0.033 **[0.025]**
4	< 0.01 (3)			0.032, 0.027, 0.038 **[0.032]**
5	< 0.01 (3)			0.016, 0.018 0.030, **[0.021**]
6	< 0.01 (3)			0.018, 0.026, < 0.01 **[0.018]**
7	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	0.013, 0.023, 0.024 **[0.02]**
8				
9				
10	< 0.01 (3)			0.012, 0.014, 0.017 **[0.014]**
11				
12	< 0.01 (3)			0.01, 0.016, 0.02 **[0.015]**
13				
14	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01 (2) 0.013 **[0.011]**
15				
16				
17	< 0.01 (3)			
18				< 0.01, 0.011, 0.019 **[0.013]**
19				
20				
21	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01, (2), 0.01 **[0.01]**
22				
23	< 0.01 (3)			< 0.01, (2), 0.01 **[0.01]**
24				
25	< 0.01 (3)			< 0.01, (3) **[0.01]**
26				
27				
28	< 0.01 (3)	< 0.01 (3)	< 0.01 (3)	< 0.01, (2), 0.012 **[0.011]**

*based on limit of detection LOD (0.01 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 80 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 (mean)			
	1 ppm	10 ppm	50 ppm	500 ppm
Fat, subcutaneous fat	< 0.01, < 0.01, 0.013 [0.005]	< 0.01 (3)	< 0.01, 0.01 (2)	0.11, 0.122,1.38 [0.537]
Fat, peritoneal	< 0.01 (2), 0.01	< 0.01 (2), 0.023 [0.008]	< 0.01 (2), 0.014, [0.005]	0.195, 0.253, 0.269, [0.239]

Tissue	Residues* in mg quinclorac-equivalents per kg (mean)			
Muscle	< 0.01 (2), 0.01	< 0.01 (3)	< 0.01 (3)	0.010, 0.033, 0.037 [0.027]
kidney	< 0.010, 010, 0.016, [0.06]	0.062, 0.074, 0.082 [0.073]	0.144, 0.174, 0.186 [0.168]	1.188, 1.514, 2.634 [1.779]
Liver	< 0.01 (3)	0.010, 0.014, 0.020 [0.015]	0.022, 0.026, 0.029 , [0.026]	0.188, 0.276, 0.326 [0.263]

*based on limit of detection LOD (0.01 mg/kg)

National residue definitions

Country	MRL-compliance	Dietary intake	Exceptions/comment
Australia	quinclorac	quinclorac	
Canada	quinclorac	quinclorac	For rape seed quinclorac + quinclorac methyl ester
Europe	not registered	not registered	Import tolerance for rice: quinclorac
Korea	quinclorac	quinclorac	Import tolerance for rape seed: quinclorac + quinclorac methyl ester
Japan	quinclorac + quinclorac methyl ester for crops	quinclorac + quinclorac methyl ester for crops	
Japan	quinclorac for terrestrial animal	quinclorac for terrestrial animal	
USA	quinclorac	quinclorac	For rape seed quinclorac +quinclorac methyl ester expressed as quinclorac

APPRAISAL

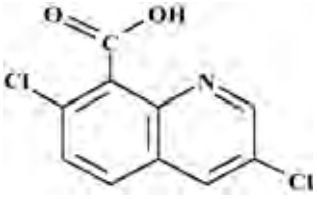
Quinclorac is a systemic herbicide with uptake through roots and foliage and used to control annual grass and broadleaf weeds. Quinclorac mode of action is similar to phenyl herbicides as it imitates the plant growth hormone auxin. The use of quinclorac results in the rupture of the cell membranes due to overstimulation of the growth of the plant.

It was scheduled by the Forty-sixth Session of the CCPR (2014) as a new compound for consideration by the 2015 JMPR. The manufacturer submitted studies on metabolism, analytical methods, supervised trials, processing, storage stability, environmental fate in soil and rotational crop studies.

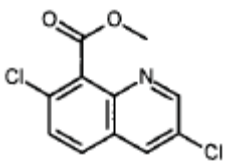
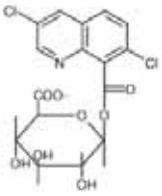
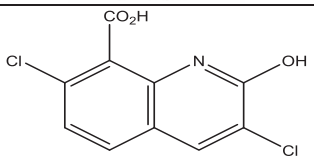
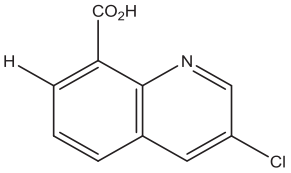
Quinclorac is registered for uses in berries and other small fruits stalk and stem vegetables, cereal grains and rape seed in Australia, Canada, China, Republic of Korea, South America and USA. Information on GAP with supporting labels from Canada and USA was provided to the Meeting.

Chemical name

Quinclorac: 3,7-dichloroquinoline-8-carboxylic acid
Structural formula:



Metabolites referred to in the appraisal with codes:

BH 514-Me Quinclorac methyl ester SES218	 methyl-3,7-dichloroquinoline-8-carboxylate
BAS 514 H M1 glucuronide (glucuronic acid) conjugate	
BH 514-2-OH 2 -hydroxyquinclorac	 3,7-dichloro-2-hydroxyquinoline-8-carboxylic acid
BH 514-1 3-chloroquinoline-8-carboxylic acid	 3-chloroquinoline-8-carboxylic acid

Animal metabolism

The Meeting received metabolism studies on laboratory animals, poultry and lactating goats using 2, 3, 4-[^{14}C]-quinclorac (quinoline label).

In rats quinclorac is widely distributed in the body, with highest concentrations of radiolabel present in the blood, kidney and plasma. The labelled material was excreted primarily via urine (50-90% in 24 hours). Absorbed quinclorac was metabolized to only a limited extent, with unchanged parent compound representing approximately 80% of the excreted radiolabel. The major bio-transformation product was quinclorac glucuronide conjugate at approximate 5% of the administrated dose.

One lactating goat received five daily doses of ^{14}C- quinclorac at a rate equivalent to 800 ppm in the diet (34 mg/kg bw). The animal was sacrificed approximately 6 h after the last dose.

A total 67% of the applied radioactivity was recovered. Excretion of radioactivity in urine and faeces accounted for 63 and 3.7% respectively of the total dose. In milk 0.003%, in liver 0.12% and kidney 0.1% of the administrated dose was recovered. The extraction efficiency using 1 M HCl) was generally > 80% TRR in muscle and liver. In milk and kidney it was above 95% TRR.

In milk the TRR levels reached a plateau after 48 hrs. Residues found in tissues at sacrifice were 0.16 to 0.19 mg eq/kg in muscle, 0.14 and 0.78 mg eq/kg in fat (omental and subcutaneous respectively), 10 mg eq/kg in kidney and 2.1 mg eq/kg in liver. Muscle and fat were not analysed

further. In milk, liver and kidney, parent quinclorac was the major residue at 86, 81 and 86% TRR respectively. Metabolite (M1) identified as the glucuronic acid conjugate of the parent was found at 4.0% TRR in milk and at 4.7% TRR in kidney.

Seven laying hens (1.8–2.4 kg) were orally dosed once daily for five days with 33–44 mg radiolabelled quinclorac per kg body weight per day corresponding to 800 ppm in the diet. The animals were sacrificed after 6 hours after the last dose. The major part of the radioactivity was recovered in the excreta (93%).

Extraction efficiency (including 1 M HCl) was generally above 80% for excreta, liver, breast muscle and skin. In eggs the TRR levels increased from < 0.06 mg eq/kg one day after first administration up to a plateau of 1.2 mg eq/kg after three days; however levels of TRR showed wide variation in eggs. TRR levels in tissues were 1.1–1.8 mg eq/kg in muscle (breast and leg respectively), 2.0 mg eq/kg in skin/fat, 3.7 mg eq/kg in kidney and 20 mg eq/kg in liver. The unextracted residues were from 2.0–21.1% of TTR.

Parent quinclorac was the major residue in poultry tissues and eggs (78–92% of the TRR). The only metabolite identified was M1, present up to 3% TRR in a combined concentration with two other fractions.

In summary from data presented quinclorac is not significantly metabolized in animals. Parent quinclorac is the major residue found in tissues, milk and eggs, making up from 78–92% TRRs, with the only identified metabolite being M1 present at low levels (< 5% TRR) and also identified in the rat. Since the extraction methods used for lactating goat and poultry tissues included 1 M HCl, it is not clear whether parent compound represents parent only or includes parent released from conjugates and whether the M1 is the fraction of conjugates that remained uncleaved.

Plant metabolism

The Meeting received plant metabolism studies for quinclorac following pre- and/or post-emergent foliar application of 2,3,4-^{14}C-quinclorac to rice, or with 3-^{14}C-quinclorac to wheat, rape seed sorghum and strawberry.

Rice plants were treated in the growth chamber with one foliar application at 1.5 kg ai/ha, and with one application at 0.84 kg ai/ha in the field at the 4 and 3-5 leaf stage, respectively. Samples were collected from whole plant (28 days after application), straw (97 days after application) and grain (97 and 118 days after application from growth chamber and field respectively). Total radioactive residues were 0.49 mg eq/kg from whole plant, 13 mg eq/kg from straw and 1.5 mg eq/kg and 0.12 mg eq/kg from grain in growth chamber and field respectively. Extraction rates were in general above 80% TRR.

Quinclorac was the major residue identified (85–94% TRR) in rice straw, whole plant, and grain in growth chamber and the field. Since rice grain was extracted by reflux with 1 M HCl, the quinclorac detected in rice grain might be released from conjugates. Metabolites present at low levels were not identified.

Wheat plants were treated in the greenhouse with one foliar application of 0.125 kg ai/ha or 0.5 kg ai/ha at the 3–5 leaf stage. Samples were collected of forage (early to late boot stage, 37 days before harvest), straw and grain (92 days after application). Total radioactive residues following the low application rate were 3.3 mg eq/kg (forage), 1.9 mg eq/kg (straw) and 1.1 mg eq/kg (grain) and following the high application rate were 13 mg eq/kg (forage), 8.2 mg eq/kg (straw) and 3.9 mg eq/kg in grain. Extraction with acetone/water and subsequent treatment with NaOH for forage, grain and straw in general was above 80% TRR.

In all plant parts parent quinclorac was the major residue identified at 24% and 45% TRR in forage, 12 and 22% TRR in straw and 62 and 68% TRR in grain from low and high application rate respectively. Metabolites characterized as hydroxyquinclorac conjugates were present in forage at 6.8% TRR (0.22 mg/kg) in the low application rate and 6.4% TRR (0.84 mg/kg) in the high application rate, straw at 14% TRR (0.26 mg eq/kg) and 13% TRR (1.83 mg eq/kg), in grain at 4%

TRR (0.05 mg eq/kg) and 4%TRR (0.14 mg eq/kg) in low and high rate application respectively. Other metabolites identified in forage and straw were quinclorac conjugates and hydroxyquinclorac, each < 5% TRR.

Sorghum plants were grown outdoor and treated with a pre-emergence spray application to the soil followed by a foliar treatment (post-emergence) when sorghum plants were 15–25 cm tall. The pre-emergence treatment was 0.525 kg ai/ha and the post-emergence at 0.504 kg ai /ha (total 1.03 kg ai/ha. Residue analysis was done on forage (whole plants) collected at 25 days after the last treatment and on mature fodder and grain collected at 95 days after last treatment.

Extraction with acetone/water and subsequent treatment with HCl were in general above 80% TRR for forage, grain and straw. In all plant samples, unchanged parent quinclorac was the major residue being present at levels of 73% TRR (2.9 mg eq/kg) in forage, 22% TRR (0.19 mg eq/kg) and 74% (0.61 mg eq/kg) in grain. This residue included the quinclorac that was released from remaining solids (4% in grains to 9% TRR in forage and fodder) under hydrolysis conditions. The only other metabolite identified was quinclorac methyl ester present at 3.6% TRR in forage, 5.9% in fodder and 1.7% in grain. A large amount of unidentified residues was present in forage and fodder in organic and aqueous fractions, maximum 19% TRR (0.75 mg eq/kg in forage and 52% TRR (0.46 mg eq/kg) in fodder.

Rape seed plants were grown in a growth chamber and treated with one foliar post emergence application of 0.2 kg ai/ha at 30 days after sowing at 5th true leaf stage. Whole plants were sampled 1 and 29 days after treatment. Seed and straw were sampled 60 days after treatment. Extraction with acetone/ phosphate buffer and subsequent treatment with 0.1M NaOH was above 90% TRR in seed and straw.

Residues in seed were identified as parent quinclorac at 37% TRR (0.18 mg eq/kg) and the quinclorac methyl ester 37% TRR (0.18 mg eq/kg). Metabolites characterized as ‘aqueous soluble’ were present at 8.7% TRR (0.042 mg eq/kg) and those characterized as ‘organo soluble’ were found at 8.6% TRR (0.041 mg eq/kg). Residues in straw (0.64 mg eq/kg) and forage (0.68 mg eq/kg) were not further identified

Strawberry plants were grown outdoor and treated with one foliar post-emergence application at growth stage BBCH 73 (seeds clearly visible). The treatment rate was 1.12 kg ai/ha. Foliage and fruits were sampled at three harvest times 21, 37 and 61 days after treatment.

In foliage, unchanged parent quinclorac accounted for 67% TRR (10 mg eq/kg) at first harvest 21 DAT and at 57% TRR (4.4 mg eq/kg) at the last harvest 61 DAT. Conjugated quinclorac released by acid hydrolysis ranged from 27%TRR (4.2 mg eq/kg) at first harvest to 29%TRR (2.3 mg eq/kg) in the last harvest. Extraction efficiency was above 90% TRR in fruit and foliage.

In fruit, unchanged parent quinclorac accounted for 79% TRR (9.1 mg eq/kg) at first harvest and at 51% TRR (1.7 mg eq/kg) at third harvest 61 DAT. Conjugated quinclorac released by acid hydrolysis increased from 11%TRR (1.3 mg eq/kg) at first harvest to 47%TRR (1.6 mg eq/kg) in the last harvest. Quinclorac methyl ester accounted for 9.6% TRR (1.1 mg eq/kg) at first harvest, to 4.9% TRR (0.42 mg eq/kg) at second harvest and was not detected at the last harvest.

In summary the Meeting concluded that in cereals (rice, wheat and sorghum), and in strawberry quinclorac is not significantly metabolized and parent quinclorac including conjugates is the major residue > 80% TRR in both food and feed matrices. A number of identified quinclorac conjugates were identified in amounts below 5% TRR in cereals and up to 47% TRR in fruit. Quinclorac levels reported in cereal metabolism studies may already include the quinclorac released from conjugates. Other metabolites were not found in tested crop matrices above 10% TRR except quinclorac methyl ester which was found at 37% TRR (0.18 mg eq/kg) in rape seed. Quinclorac methyl ester was found as a minor metabolite in strawberry fruit at a maximum of 9.6% TRR (1.1 mg eq/kg), in sorghum at a maximum of 1.7% TRR (0.014 mg eq/kg) and in forage at 3.6% TRR (0.14 mg eq/kg).

Environmental fate in soil

The Meeting received studies on hydrolysis, photolysis, terrestrial and aquatic soil metabolism and field dissipation for the investigation of the environmental fate.

In the photolysis study it was shown that quinclorac degraded slowly with a half-life of 162 days. The soil hydrolysis study showed that quinclorac was stable during the testing period 30 days and at the temperature 25 °C.

In aerobic soil metabolism studies in silt loam soils under laboratory conditions and an application rate of 0.375 kg ai/ha, quinclorac degraded slowly; no degradation was indicated 120 days after treatment. In another study at an application rate of 3.9 to 4.1 kg/ha, the half-life (DT_{50}) for quinclorac was estimated at 391 days in loamy sand and 168 days in a clay soil. In this study two major soil metabolites were detected; 2-hydroxyquinclorac, at a maximum of 12% AR and quinclorac methyl ester at a maximum of 7.8% AR. Other metabolites were present at levels below 10% AR.

In one tested aerobic aquatic system (rice field) at an application rate 3.75 kg ai/ha, quinclorac degraded to the metabolite 3-chloro-8-quinolilne carboxylic acid (BH 514-1) up to a maximum of 55.7% AR. Three additional fractions were present (not characterized) but present at less than 10% AR. The half-life of quinclorac in this system was 4.7 months and for the metabolite 3-chloroquinoline-8-carboxylic acid, 7.4 months. Under anaerobic conditions at the same application rates the same metabolites were formed but at a slower rate; there was 50% conversion of quinclorac to 3-chloroquinoline-8-carboxylic acid.

In one field dissipation study using a loamy sand soil, quinclorac was applied to bare soil with two applications of 2.8 kg ai/ha. DT_{50} and DT_{90} values for parent quinclorac were 126 days and > 360 days respectively following the first application (autumn), and DT_{50} and DT_{90} of 8 days and 26 days respectively following the second application (summer). The maximum of the two metabolites were less than 5% TRR. The results indicate that quinclorac is tightly bound to the loamy sand soil.

One confined rotational metabolism study from crops rotated after flooded and non-flooded rice grown on silty clay was available. Quinclorac [2, 3, 4-^{14}C] was applied to flooded and non-flooded rice (primary crop) at a rate of 0.84 kg ai/ha in Mississippi, USA. After harvest of mature rice, the first rotational crops (wheat, mustard green and turnips) were planted 120 DAT followed by the second crops (sorghum, mustard green, soya beans and turnip) 360 DAT. The extractable radioactive residues were analysed for quinclorac and the metabolite 3-chloroquinoline-8-carboxylic acid (BH 514-1).

For the first rotational crops, maximum TRRs were 0.028 mg eq/kg for mustard plant, wheat seed, 0.025 mg eq/kg and turnip plant, 0.012 mg eq/kg. For the annual rotational crops, maximum TRRs were 0.014 mg eq/kg for mustard top, soya bean seed 0.017 mg eq/kg and for root and turnip root, 0.02 mg eq/kg. The metabolism of quinclorac by soya bean was qualitatively similar, although up to 62% TRR (0.01 mg eq/kg) was not extractable.

Quinclorac was the only major residue (>10% TRR but less than 0.05 mg eq/kg) detected in the examined rotational crops. Furthermore in the first rotational crops as well as the second rotational crops, TRRs were higher from crops grown under non-flooded conditions.

Another confined rotational metabolism study with one interval (120 days) was also available from crops planted after sorghum. Treatment levels to sorghum plants with 3-^{14}C-quinclorac were 0.53 kg ai/ha pre-emergence and 0.50 kg ai/ha post-emergence giving a total of 1.03 kg ai/ha (2 times GAP). The rotational crops mustard green, turnip and barley were planted 120 days after the last treatment of sorghum. The parent quinclorac was the major (up to 0.1 mg/kg) residue in all matrices. Quinclorac methyl ester was a minor metabolite below 5% in mustard green, turnip roots, and barley.

One field rotational crop study with rape seed planted after barley treated at 0.2 kg ai/ha the previous year was available. The application rate was below -25% critical GAP for cereals (0.29 kg ai/ha, wheat). The residues in rape seed at harvest analysed for parent quinclorac were below the LOQ of 0.05 mg/kg.

In the confined rotational studies, uptake of quinclorac and quinclorac methyl ester was observed in both first and second rotational crops. Residues were no more than 0.01 mg/kg (0.012 mg eq/kg) at the GAP rate.

In summary quinclorac is persistent in some soils and the amount, dependent on the season; residues from quinclorac in rotational crops may be found but generally at levels <.05 mg/kg.

Methods of residue analysis

The Meeting received analytical methods for the analysis of quinclorac residues in plant and animal matrices.

The extraction in lactating goat and laying hen was with acetone/0.1M NaOH. After clean-up, residues of parent quinclorac are determined by GC-ECD. The method is suitable for measuring residues of quinclorac in animal commodities with a LOQ of 0.05 mg/kg. It is not clear whether identified quinclorac represents quinclorac only or also includes quinclorac released from conjugates by the alkaline extraction method used.

The extraction in strawberry was with 1% acetic acid, in rice and wheat with acetone/0.1 M NaOH, in rape seed with acetone. After clean-up, residues of parent quinclorac in wheat, sorghum, rape seed, and strawberry were determined by HPLC-MS/MS or GC-ECD. Methods used for analysis of quinclorac in cereals may hydrolyse any quinclorac conjugates present. The LOQ ranged between 0.01–0.05 mg/kg.

The metabolite quinclorac methyl ester identified as a metabolite in rape seed and sorghum matrices is extracted with acetone and after clean-up determined by HPLC-MS/MS. The LOQ was 0.05 mg/kg.

A radiovalidation study showed that extraction with acetone/0.1 M NaOH converts quinclorac methyl ester partly into parent compound. For this reason, the parent is overestimated in samples containing quinclorac methyl ester. Methods D9708/1 (quinclorac) and R0036 (quinclorac) use acetone/0.1 M NaOH and are therefore not suitable of the determination of parent compound in oilseed rape seed and possibly other pulses and oilseeds, where the quinclorac methyl ester can be expected to be present.

In summary analytical methods are available for determining parent quinclorac in plant (cereals and fruit) and animal (lactating goat and hen) matrices and for the quinclorac methyl ester in plant (fruit and sorghum) matrices. However the methods for animal and cereal commodities use a hydrolysis step; indicating that the quinclorac residues measured may actually include quinclorac released from conjugates. Current analytical methods presented for oil seed rape are likely to overestimate quinclorac residues as the determination of quinclorac may also include some of its methyl ester.

Stability of residues in stored analytical samples

The Meeting received information on the storage stability of quinclorac and quinclorac methyl ester in plant matrices. Quinclorac (> 80% of spiked levels remained) was stable in rice and sorghum matrices for 38 months, in wheat grain for 26 months, and in cranberry fruit for 14 months. For quinclorac and quinclorac methyl ester no significant degradation was observed within 22 months in oilseed meal and oil.

For animal matrices no storage stability studies were provided.

Definition of the residue

In wheat and rice the parent quinclorac is the major residue present (above 80% TRR). Glucose conjugates, hydroxylated conjugates of quinclorac and hydroxyquinclorac were identified as minor metabolites (< 10% TRR) in wheat. In sorghum parent was also the major (> 73% TRR) residue present. The metabolite quinclorac methyl ester was also present (< 6% TRR) in sorghum.

In rape seed besides the parent, the metabolite quinclorac methyl ester was found as a significant metabolite (37%TRR).

In strawberry the parent quinclorac was the major residue present (> 98% TRR). Quinclorac methyl ester accounted for 9.6% TRR in fruit at the first harvest and was not detected in the third harvest

In rotational crop studies including mustard, barley and turnip in first rotation, uptake of residues identified as quinclorac (major) and quinclorac methyl ester (minor) was observed when analysed and resulted in residues near the LOQ at GAP rate.

Thus based on available metabolism data parent quinclorac is the major residue in examined crops. The metabolite quinclorac methyl ester was a significant residue in rape seeds and was a minor residue in other primary and subsequent rotational crops analysed.

Analytical methods are available for determining parent quinclorac in plant (cereals and fruit) and quinclorac methyl ester in fruit and sorghum matrices.

Current analytical methods determining quinclorac and quinclorac methyl ester in rape seed is not suitable as they overestimate the level of parent present.

Taking into account that the methodology measuring quinclorac is also accounting for conjugates derived from hydrolysis during the extraction process, and that quinclorac is the major residue measured in plants, the Meeting decided that the residue definition should be as follows:

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

The Meeting noted that quinclorac methyl ester has a toxicological potency up to 10 times that of quinclorac and decided to include it in the residue definition for dietary intake.

Definition of the residue for estimating dietary intake for plant commodities: Quinclorac plus quinclorac conjugate plus quinclorac methyl ester expressed as quinclorac

In calculating residue values for dietary intake estimation the Meeting agreed to use the following formula: residues = (quinclorac +conjugate) + 10 × quinclorac methyl ester.

In lactating goat the major residue was quinclorac and the highest residues were found in liver and kidney with small amounts of other metabolite also found (less than 5% TRR).

For laying hen, the available data show that quinclorac is the only major residue in tissues and eggs.

In both species, measurement of the parent in the metabolism studies probably also includes conjugates of quinclorac as the extraction method used strong acid or alkali. This conclusion is supported by partitioning of residues in the animal feeding studies where quinclorac residues are more than ten times higher in fat tissue compared to muscle tissue.

The Meeting noted however that quinclorac residue was more than ten times higher in fat tissue compared to muscle tissue.

For quinclorac, a log Kow of -0.72 at pH 7 was reported suggesting residues of free quinclorac are water soluble.

The fact that the residue is generally found in the fat suggests that the actual tissue residue is not the parent molecule but may be a fatty acid conjugate of quinclorac.

Based on the above the Meeting decided the residue definition for compliance with MRLs and estimating the dietary intake should be as follows:

Definition of the residue for compliance with MRL and estimating the dietary intake for animal commodities: Quinclorac plus quinclorac conjugates.

The residue is fat soluble

Results of supervised residue trials on crops

Quinclorac is registered for use as a herbicide in many countries. The Meeting received supervised trial data for foliar application of quinclorac to rice, wheat, rape seed, sorghum, cranberry and rhubarb. The trials were conducted in USA and Canada. Frozen samples from the trials presented are covered by storage stability studies. The residue trials did not measure the methyl ester required for estimating dietary intakes.

The Meeting noted quinclorac methyl ester in oilseed equal level to quinclorac in the rape metabolism study and for cereals and fruit at levels up to10 percent of the parent, and agreed to use to the following formula to estimate levels for use in dietary intake calculations:

Plants except oilseed:

HR/STMR = (quinclorac + conjugate) + 10 x 0.1 (quinclorac + conjugate) = 2 × (quinclorac + conjugate)

Oil seed:

HR/STMR = (quinclorac + conjugate) + 10 x (quinclorac + conjugate) = 11 × (quinclorac + conjugate)

Cranberry

Data from supervised trials on cranberry from USA were presented to the Meeting. The critical GAP in USA is two foliar post-emergent applications of 0.28 kg ai/ha, with a 30 day interval and a PHI of 60 days.

In four independent trials from USA matching the critical GAP residues of quinclorac in cranberry fruit for MRL estimation were (n=4): 0.16, 0.17, 0.18, 0.67 mg/kg. The highest residue of 0.68 mg/kg was measured in an individual cranberry sample.

Residues for dietary intake estimation in cranberry fruit were (n=4): 0.32, 0.34, 0.36 and 1.34 mg/kg

Based on a data set from USA the Meeting estimated a maximum residue level, an STMR value and an HR value for quinclorac in cranberry fruit of 1.5 mg/kg, 0.35 mg/kg and 1.36 mg/kg, respectively.

Rhubarb

Data from supervised trials on rhubarb from USA were presented to the Meeting. The critical GAP in USA is two foliar post-emergence applications of 0.42 kg ai/ha, with a 30 day interval and a PHI of 30 days.

In three independent trials from USA matching the critical GAP residues in rhubarbs for MRL estimation were (n=3) 0.11, 0.18, 0.21 mg/kg. The highest residue of 0.23 mg/kg was measured in an individual rhubarb sample.

Residues for dietary intake estimation in rhubarbs were (n=3): 0.22, 0.36 and 0.42 mg/kg.

Based on a data set from USA the Meeting estimated a maximum residue level, an STMR value and an HR value for quinclorac in rhubarb of 0.5 mg/kg, 0.36 mg/kg and 0.46 mg/kg, respectively.

Rice

Data from supervised trials on rice from USA were presented to the Meeting. The critical GAP in USA is one application of 0.29-0.54 kg ai/ha and a PHI of 40 days. The use can be soil application, pre-planting or pre-emergence (dryland rice) or post-emergence broadcast application after the 2-leaf stage (but before heading) on dryland and water seeded rice. Only six trials matched the GAP and an estimation of maximum residue level was not made.

Wheat

Data from supervised trials on wheat from USA and Canada were presented to the Meeting. The critical GAP in Canada is one post-emergent foliar application of 0.135 kg ai/ha and a PHI of 80 days. Only six trials matched the GAP and an estimation of maximum residue level was not made.

Sorghum grain

Data from supervised trials from USA were presented to the Meeting. The critical GAP is one application pre- and /or post-emergence (at maximum 12 cm height limit) as long as the seasonal maximum amount of 0.7 kg ai/ha is not exceeded. The maximum post-emergent application rate is 0.56 kg ai/ha. The trials did not match the critical GAP and an estimation of maximum residue level was not made.

Rape seed (canola)

A registered use with a supporting label from Canada was presented with one foliar application at 2-6 leaf stage of 0.1 kg ai/ha and a PHI of 60 days. Data from seventeen independent supervised trials from Canada (16) and USA (1) supporting this GAP were presented to the Meeting.

The analytical method used in the trials method D9708/1 for determining quinclorac and method D9806 for determining quinclorac methyl ester (BH514-Me) overestimates the level of the parent. Therefore the trials cannot be used for estimating the maximum residue level.

Animal feeds

Strawberry and rhubarbs are not used as animal feeds.

Fate of residues during processing

The Meeting received information on the fate of incurred residues of quinclorac during the processing of rice, wheat, rape seed and sorghum. Supporting trials with matching GAPs were not available and therefore the studies were not considered by the current Meeting.

Residues in animal commodities

Farm animal feeding studies

The Meeting received feeding studies on residue levels of quinclorac plus quinclorac conjugates in laying hens and lactating cows.

For lactating cows three groups of were dosed daily at levels of 1, 10, 50, or 500 ppm in the diet (0.002, 0.02, 0.09 and 0.9 mg/kg bw) for 28 consecutive days.

In milk residues were only detected in the 500 ppm group. A plateau level was reached in this group after 4 days (mean: 0.032 mg/kg).

In muscle residues were only detected in the 500 ppm group, 0.01–0.037 mg/kg (mean: 0.027 mg/kg).

In fat two different tissues were analysed (peritoneal and subcutaneous fat). The highest residues were found in subcutaneous fat with < 0.01–0.013 (mean: 0.005 mg/kg) for the 1 ppm group, < 0.01 mg/kg for the 10 ppm group. In peritoneal fat with < 0.01–0.01 mg/kg for the 1 ppm group, < 0.01–0.023 mg/kg for the 10 ppm group.

In liver residues were < 0.01–0.01 mg/kg for the 1 ppm group, 0.01-0.02 mg/kg for the 10 ppm group.

In kidney residues were < 0.01–0.016 mg/kg for the 1 ppm group, 0.062-0.082 mg/kg for the 10 ppm group.

For laying hens three groups of animals were dosed with rates of 1, 10 and 100 ppm by dry weight in the feed (0.07, 0.7 and 7 mg/kg bw/day) for 28 consecutive days. Eggs were collected throughout the whole study and tissues were collected on day 29 after the last dose.

In eggs a clear plateau level was not reached in any dosing group. For the 1 and 10 ppm the residues were below 0.01 mg/kg during the whole experiment.

In dark and light muscle residues were 0.0–0.005 mg/kg (max mean: 0.002 mg/kg) for the 1 ppm group.

In skin + fat total residues in fat for the 1 ppm group was 0.0–0.018 mg/kg.

In liver residues were: 0.0–0.009 mg/kg for the 1 ppm group. In kidney residues were 0.002–0.059 mg/kg for the 1 ppm group.

Animal commodities residue levels estimation

Strawberry and rhubarbs are not used as animal feed and therefore estimation of residue levels was not made for animal commodities.

RECOMMENDATIONS

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

Definition of the residue for compliance with MRL for plant commodities: quinclorac plus quinclorac conjugates

Definition of the residue for estimating dietary intake: quinclorac plus quinclorac conjugate plus quinclorac methyl ester expressed as quinclorac

Definition of the residue for compliance with MRL and estimating the dietary intake for animal commodities: quinclorac plus quinclorac conjugates

The residue is fat soluble.

CCN	Commodity	Recommended Maximum residue level (mg/kg)		STMR or STMR-P mg/kg	HR or HR-P mg/kg
		New	Previous		
FB 0265	Cranberry	1.5		0.35	1.36
VS 0627	Rhubarb	0.5		0.36	0.46

DIETARY RISK ASSESSMENT

Long-term intake

The International Estimated Daily Intake of quinclorac for the 17 GEMS/Food regional diets based on estimated STMRs were 0% of the maximum ADI of 0.4 mg/kg bw for the sum of quinclorac, its conjugates plus 10× quinclorac methyl ester, expressed as quinclorac (see Annex 3 of the 2015 Report). The Meeting concluded that the long-term dietary intake of residues of quinclorac is unlikely to present a public health concern.

Short-term intake

The International Estimated Short Intake (IESTI) for quinclorac was calculated for commodities for which STMRs or HRs were estimated and for which consumption data were available. The results are shown in Annex 4 to the 2015 Report. The ARfD for quinclorac, its conjugates plus 10 × quinclorac

methyl ester, expressed as quinclorac is 2 mg/kg bw and the IESTIs varied from 0–1% of the ARfD for children and the general population.

The Meeting concluded that the short-term intake of residues of quinclorac when used in ways that have been considered by the JMPR is unlikely to present a public health concern.

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