DIQUAT (031)

The first draft was prepared by Dr Dugald MacLachlan, Australian Government Department of Agriculture, Fisheries and Forestry

EXPLANATION

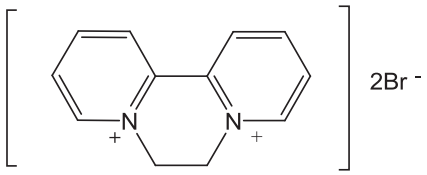
Diquat is an herbicide used in a variety of crops and was first reviewed by the 1970 JMPR. Diquat was scheduled at the Forty-fourth Session of the CCPR (2012) for periodic re-evaluation of toxicology and residues by the 2013 JMPR.

Diquat is a non-selective contact herbicide; the major use of which is for pre-harvest desiccation of a variety of crops. It is rapidly absorbed by green plant tissue and interacts with the photosynthetic process to produce compounds that destroy plant cells. It is inactivated on contact with soil and not taken up by plant roots. As a general herbicide diquat is used to control weeds before planting, before or just after crop emergence, and as a directed spray between the rows of established crops.

IDENTITY

Common name	Diquat
Chemical name	
IUPAC:	6,7 dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium dibromide
CAS:	6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium (8 & 9 CI)
CAS number:	2764-72-9 (diquat); 85-00-7 (diquat dibromide)
CIPAC Code:	55 (diquat); 55.303 (diquat dibromide)
Molecular formula:	$C_{12}H_{12}N_2Br_2$ (diquat)
Molecular mass	344.05 (diquat), 184.2 (diquat ion)

Structural formula:



Formulations

Formulations	Active ingredient content
SL diquat	150–240 g ai/L
SL diquat and paraquat mixtures	45–135 g ai/L

Specifications

Specifications for diquat have been developed by FAO (2008).

PHYSICAL AND CHEMICAL PROPERTIES

Pure diquat dibromide as the monohydrate

Property	Results (method)	Reference
Appearance	Pure diquat dibromide is a yellow crystalline solid with no known characteristic odour	Wollerton, 1987; PP901/0024
Melting point	325 °C with decomposition	Wollerton, 1987; PP901/0024
Relative density	1.61 g/cm	Wollerton, 1987; PP901/0024
Vapour pressure	less than 10^{-8} kPa at 25 °C	Wollerton, 1987; PP901/0024
Henry's Law constant	An absolute value for Henry's Law Constant (H) cannot be calculated since pure diquat dibromide has no measurable vapour pressure. The value of H is estimated to be less than 5×10^{-12} Pa/m^3/mol.	
Solubility in water including effect of pH	712 g/L at pH 5.2 (buffered water) 718 g/L at pH 7.2 (buffered water) 713 g/L at pH 9.2 (buffered water)	Wollerton, 1987; PP901/0024
Solubility in organic solvents (at 20 °C)	Methanol 25 g/L Acetone < 0.1 g/L Dichloromethane < 0.1 g/L Toluene < 0.1 g/L Ethyl acetate < 0.1 g/L Hexane < 0.1 g/L	Wollerton, 1987; PP901/0024
Partition coefficient n-octanol/water	log P_{ow} –4.6	Wollerton, 1987; PP901/0024
Hydrolysis	The hydrolysis of diquat was studied in the dark in sterile, aqueous buffered solutions at pH 4, pH 7 and pH 9 at 50 °C for 5 days. Diquat was shown to be hydrolytically stable under all the conditions tested in this study.	Dixon and Alderman, 2012; PP901_10823
Photolysis	The photolysis of diquat was investigated in sterile natural water under continuous irradiation from a xenon arc lamp simulating natural sunlight. Diquat was rapidly degraded, with only 15.8% parent compound remaining after 3 days irradiation. Degradation followed first-order kinetics with an estimated half-life of 31 hours (equivalent to 6.5 days of Tokyo spring sunshine, or 2 days summer sunlight at a latitude of 50 °N).	Oliver and Webb, 2005: PP901_1892
Dissociation constant	Not measureable	Wollerton, 1987; PP901/0024

Technical grade material

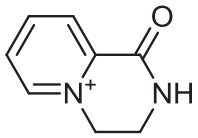
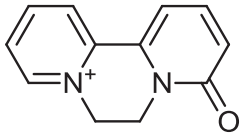
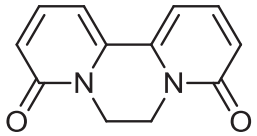
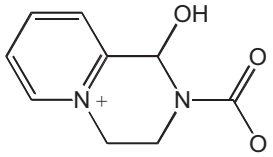
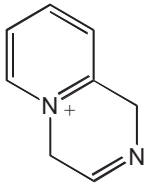
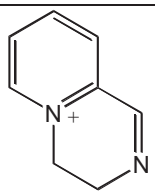
Property	Results (method)	Reference
Physical state, colour, and odour	Dark brown clear liquid with earthy odour	Wollerton, 1987; PP901/0024

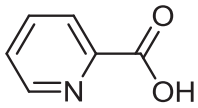
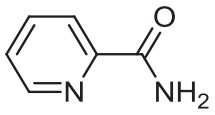
Property	Results (method)	Reference
Density at 25 ºC	1.26 g/cm^3	Wollerton, 1987; PP901/0024
pH at 20 ºC	6.68	Wollerton, 1987; PP901/0024
Surface tension at 20 ºC	41.0 mN/m	Wollerton, 1987PP901/0024

METABOLISM AND ENVIRONMENTAL FATE

Metabolites are given various abbreviations and code numbers in the studies. Structures and abbreviations and codes are shown below.

Degradation compounds from metabolism of diquat in plants, animals, soil, or water

Compound Name	Structure	Found in:
TOPPS 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion R032245		Livestock, plants
Diquat monopyridone SYN546442 R34908		Livestock, crops
Diquat dipyridone R030740		Livestock, crops
1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid		Photolysis
1,4-dihydro-pyrido[1,2-a]pyrazin-5-ylium		Photolysis
3,4-dihydro-pyrido[1,2-a]pyrazin-5-ylium		Photolysis

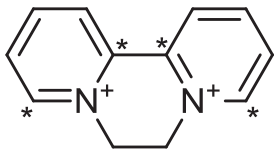
Compound Name	Structure	Found in:
Picolinic acid		Livestock, crops
Picolinamide		Livestock, crops

The identification of residue components in the animal and plant metabolism studies was achieved using authentic standards of the compounds involved.

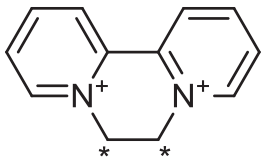
Animal metabolism

The Meeting received studies on the metabolism of diquat in rats, lactating goats and laying hens. The metabolism of only low levels of radioactivity are found in plant parts such as tubers that are not directly exposed to the spray in plants and animals was investigated using [^{14}C] diquat bromide. The structural formula and the positions of the ^{14}C label are shown below. The studies on rats were evaluated by the WHO Core Assessment Group.

*Label positions of diquat: marked as **



Ring-labelled diquat



Bridge-labelled diquat

Lactating goat

Wickstead and Lowrie (2012 PP901_10848) studied the metabolism of diquat in a lactating goat (53.5–58 kg bw; 2 kg milk/d) that was dosed orally via gelatin capsule once a day with ring labelled [^{14}C] diquat dibromide just after the morning milking for 7 consecutive days at the equivalent of 90 ppm in the feed (feed consumption 2.2 kg DM/d). Milk was collected twice daily and urine and faeces were collected daily. The goat was sacrificed approximately 12 h after the administration of the final dose and tissues taken post-mortem for quantification and analysis of radioactivity.

The radioactive residue in liquid samples was determined by direct liquid scintillation counting. Solid samples were homogenised frozen and the radioactive residue determined by combustion analysis followed by liquid scintillation counting. Milk, liver, kidney, composite muscle (forequarter, hindquarter and tenderloin in the ratio 4:4:1) and subcutaneous fat, sub-samples of were extracted three times (four times for fat) with 10% trichloroacetic acid. The resulting extracts were then further fractionated and subjected to chromatographic analysis by HPLC-MS/MS with concurrent radiodetection for identification/characterisation and quantification, respectively. The day 6 urine sample was analysed directly by LC-MS to provide further understanding of the biotransformation pathway.

The total recovery of dosed radioactivity was 97% with the majority of the radioactivity excreted in the faeces (84%) and only low levels (0.8%) in the urine. Approximately 12% remained in the gastrointestinal tract contents.

TRR in milk samples increased during the dosing period and reached a maximum of 0.015 mg equiv/kg in the milk collected at 156 hours (Day 7 pm) after the start of dosing. The large difference in TRR levels for samples collected at the morning and afternoon milkings is indicative of rapid elimination.

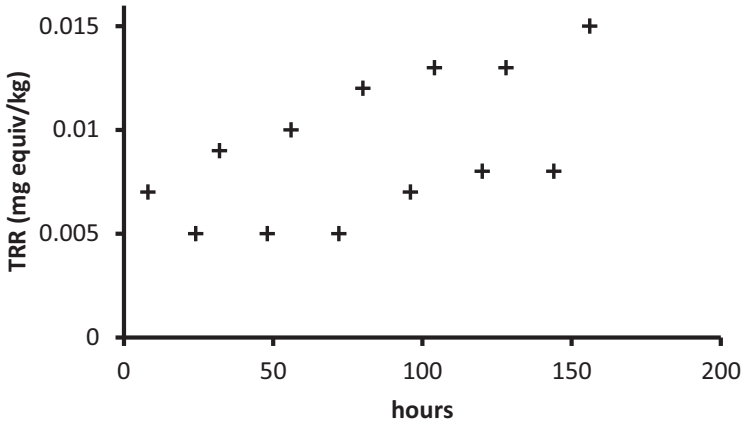


Figure 1 Radioactive residue in milk following dosing of a lactating goat once daily, equivalent to 90 ppm in the feed, for 7 consecutive days + morning samples, ● evening samples

Subsamples of day-4 to day-7 milk were separated by centrifugation into cream and skimmed milk; the fraction of cream residue to skimmed milk residue was between 0.57 and 0.67 in all samples suggesting the residues do not selectively partition into lipids.

Radioactive residues in tissues were low and ranged from 0.003 mg equiv/kg in the omental fat to 0.079 mg equiv/kg in the kidneys. Good extractability was achieved for the milk and muscle samples with greater than 90% TRR recovered in extracts. Extractability of radioactive residues from kidney and fat was approximately 80%TRR while the extractability from liver was slightly lower at 64% TRR.

The identified metabolites in the tissue, milk and urine samples are summarised in Table 1.

Table 1 Identification of radioactivity in goat tissue, milk and urine

Matrix	Milk	Liver	Kidney	Muscle	Subcutaneous Fat	Urine
TRR (mg equiv/kg)	0.012	0.052	0.079	0.010	0.016	–
			%TRR			
Extracted	94	64	83	91	80	

Matrix	Milk	Liver	Kidney	Muscle	Subcutaneous Fat	Urine
Diquat dipyridone	82	33	29	46	20	16
Diquat monopyridone	ND	13	21	13	ND	19
Diquat	ND	22	4.3	ND	3.5	19
Unextracted	6.2	36	17	9.1	20	–

ND = not detected

The radioactivity remaining in liver and kidney after extraction with 10% trichloroacetic acid was further investigated using molecular weight/size exclusion filtration following treatment of the debris with sodium dodecyl sulphate. In liver, 9.2% TRR (0.005 mg equiv/kg) was characterised as having a molecular weight of < 3 kDa and a further 9.8% TRR (0.005 mg equiv/kg) > 3 kDa. In kidney, 1.2% TRR (0.001 mg equiv/kg) was characterised as < 3 kDa and a further 2.5% TRR (0.002 mg equiv/kg) > 3 kDa.

Laying hens

The metabolism of diquat in laying hens was studied by Leahey and Hemingway (1973, PP901/0464). Doses of ^{14}C-bridge labelled diquat were applied to the hen feed pellets and were administered orally once daily. Three experiments were carried out in this study, as follows:

Experiment 1

One hen was given a single oral dose of [^{14}C] diquat at a rate equivalent to 4–5 ppm in the diet and excreta collected for 3 days post dosing. Expired air was collected for 4 hours on day 1 and 7 hours on day 2 by drawing the air through ethanolamine traps.

Experiment 2

One hen was given five daily oral doses of [^{14}C] diquat at a rate equivalent to 4–5 ppm in the diet. Excreta and eggs were collected daily. The hen was sacrificed 7 days after the final dose, and samples of meat, fat, liver, kidney and lungs collected.

Experiment 3

One hen was given 14 daily oral doses of [^{14}C] diquat at a rate equivalent to 0.4–0.5 ppm in the diet. Excreta and eggs were collected daily. The hen was sacrificed 4 hours after the final dose, and samples of meat, fat, liver, kidney and blood collected.

TRR levels in the samples were determined by oxidative combustion followed by liquid scintillation counting (LSC) or by direct liquid scintillation counting. Dose feed pellets were analysed 1 and 28 days after treatment with [^{14}C] diquat. Pellets were extracted with water followed by 1 N HCl, and the combined extracts analysed by paper chromatography and by isotope dilution. Faeces samples were extracted by boiling with 2 M HCl, and the extracts analysed by paper chromatography against reference standards and by isotope dilution for diquat, diquat monopyridone and TOPPS. Fat was dissolved in a xylene solution for analysis by LSC. All other tissues were dried and analysed by sample oxidation. Eggs were separated into yolk and albumen. The egg yolks from experiments 2 and 3 were extracted by refluxing with 2 M HCl. Diquat, diquat monopyridone and TOPPS were isolated and analysed by isotope dilution.

The majority of the administered residue was rapidly excreted in hens. Extremely low residues of diquat or its metabolites were found in the tissues and eggs of poultry after continuous oral dosing with diquat.

In Experiment 1 after 3 days, 98% of dose was recovered in the excreta with almost none recovered in expired air traps.

In Experiment 2 after 8 days, 94% of dose was recovered in the excreta, most of which was unchanged diquat. The residue levels in eggs during and after dosing are shown in Figure 2. One week

after the final dose, very low radioactive residues were found in the tissues, indicating that neither diquat nor its metabolites accumulate in the hen. TRR in egg yolks from days 5 and 6 comprised 36–39% diquat, 54–61% diquat monopyridone and 6–7% TOPPS.

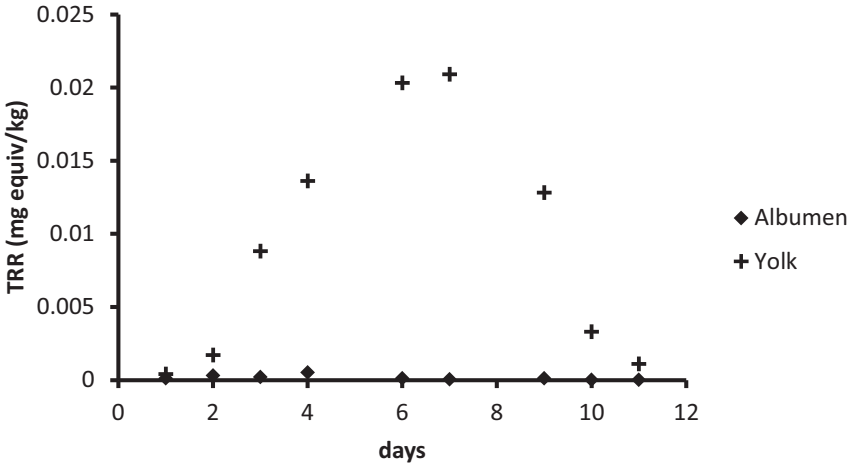


Figure2 Radioactive residues in eggs following dosing of hens once daily, equivalent to 4–5 ppm in the feed, for 5 consecutive days

Table 2 Radioactive residues in hen tissues following oral administration of [^{14}C] diquat to a laying hen for 5 consecutive days at 4–5 ppm in the diet

Sacrifice time	TRR (mg equiv/kg)				
	Muscle	Fat	Liver	Kidney	Lung
5 days dosing + 7 days depletion)	< 0.0001	0.0008	0.0004	0.0035	0.0008

Residues in excreta were profiled. During the dosing period, unchanged diquat accounted for 75–80% of the excreted radioactivity. TOPPS (2%) and diquat dipyridone (4%) were also detected.

In Experiment 3 very low TRR were detected in the egg albumen (0.00001–0.00012 mg equiv/kg) and yolk (0.0002–0.0032 mg equiv/kg) of eggs collected throughout the 14 day dosing period. Very low TRR were found in the tissues collected 4 hours after the final dose.

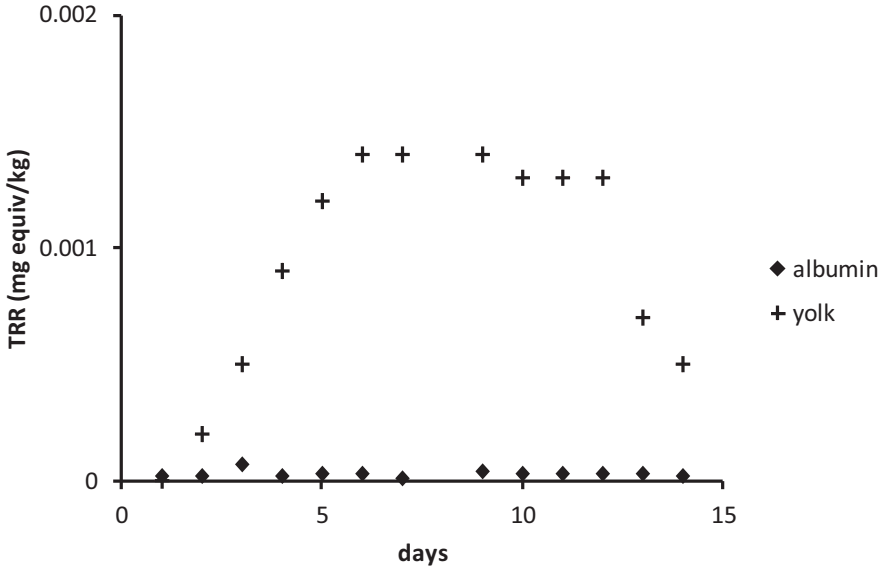


Figure 3 Radioactive residues in eggs following dosing of hens once daily, equivalent to 0.4–0.5 ppm in the feed, for 14 consecutive days (outlier at day 8 white 0.00012 mg equiv/kg and yolk 0.0032 mg equiv/kg not plotted)

The extractability of radioactivity from treated feed pellets declined with time after preparation and may have accounted in part for the unexpected decline in TRR for eggs. Yolk from day 9 + 10 eggs contained 26% diquat, yolks from day 7 contained 85% diquat monopyridone and egg yolks from day 11 contained 10% TOPPS.

Table 3 Radioactive residues in hen tissues following oral administration of [^{14}C] diquat to a laying hen for 14 consecutive days at 0.4–0.5 ppm in the diet

Sacrifice time	TRR (mg equiv/kg)					
	Muscle	Fat	Liver	Kidney	Lung	Blood
Day 14 (14 days dosing)	0.00019	0.00010	0.00042	0.00045	0.00016	0.00043

A later study French and Leahey (1988, RJ0622B Fujie 1988 addendum PP901/0470) also investigated the metabolism and distribution of [^{14}C] diquat in laying hens. Three laying hens were each given daily doses of ^{14}C-ring labelled diquat by oral gavage for 4 days at 2.4 mg/kg bodyweight/day equivalent to 32 ppm in the diet. Excreta and eggs were collected daily. The hens were sacrificed 18 hours after the last dose, and samples of liver, kidney, muscle and fat collected. Samples were stored at -18 ºC prior to analysis. TRR levels in the samples were determined by combustion followed by liquid scintillation counting (LSC) or by direct liquid scintillation counting (egg whites, extracts). Pooled tissue samples were extracted with acetonitrile. After solvent extraction, liver and kidney samples were subjected to a second extraction with 2 M HCl under reflux. Residues in liver and kidney extracts were characterized using HPLC and TLC against reference standards, and by isotope dilution.

Table 4 Radioactive residues in eggs and tissues following oral administration of [^{14}C] diquat to hens for 4 consecutive days at 32 ppm in the diet

Matrix	Radioactive residue (mg equiv/kg)
Egg yolk (day 2 [a])	< 0.001
Egg white (day 2 [a])	0.004
Liver	0.030–0.045
Kidney	0.042–0.058

Matrix	Radioactive residue (mg equiv/kg)
Muscle (leg and breast)	0.003
Fat (abdominal and subcutaneous)	0.004

[a] All hens laid eggs at day 2 only

Radioactive residues in the muscle, fat and eggs were all < 0.01 mg/kg and were not analysed further. For liver, 76% of the radioactive residue was extracted with acetonitrile/water, and a further 22% TRR was extracted with 2 M HCl, total extracted 97%. The residue comprised mainly diquat, with small amounts of TOPPS, diquat monopyridone and diquat dipyridone being identified. For kidney, 70% TRR was extracted with acetonitrile/water, and a further 28% TRR extracted with 2M HCl, total 98%. The residue in kidney was shown to comprise diquat and diquat monopyridone in similar amounts together with small amounts of TOPPS and diquat dipyridone.

Table 5 Identification of the radioactive residues in liver and kidney following oral administration of [^{14}C] diquat to hens for 4 consecutive days at 32 ppm in the diet

Matrix	liver	kidney
TRR (mg equiv/kg)	0.045	0.058
	%TRR	
Extracted	97	98
Diquat	48	12
TOPPS	1.8	3.9
Diquat monopyridone	3.9	15
Diquat dipyridone	3.1	6.6
Unidentified in acetonitrile/water extract	27	37
Unidentified in 2 M HCl extract	13	24
Unextracted	2.6	1.9

In an additional study, Hughes and Leahey (1975, PP901/0461) studied the absorption, metabolism and distribution of incurred residues of [^{14}C] diquat in laying hens. ^{14}C-ring labelled diquat was sprayed onto mature barley plants at a rate equivalent to 1.1 kg ai/ha. After 4 days, the barley plants were harvested and the dried grain powdered and pelleted for dosing. One laying hen (hen 1) was given a single oral dose of treated grain pellets. A further two laying hens (hens 2 and 3) were each given 11 consecutive daily doses of treated grain pellets at a rate equivalent to 1–1.5 ppm in the diet. Excreta and eggs were collected daily. Hen 2 was sacrificed 7 days after the final dose and hen 3 was sacrificed 4 hours after the final dose. At sacrifice, samples of heart, liver, kidney, lungs, muscle and fat were collected.

TRR levels in the samples were determined by oxidative combustion followed by LSC or by direct liquid scintillation counting (diluted egg yolk and albumen, extracts). Samples of the pelleted barley grain were extracted by refluxing with 2 N HCl, and the extracts analysed for diquat and its photoproducts by paper chromatography against reference standards and by isotope dilution. Faeces samples from hen 1 and hen 2 (day 10) were extracted by refluxing with 2 N HCl, and the activity in the extract determined by LSC. The hen 2 (day 10) sample was analysed by paper chromatography against reference standards and by isotope dilution. Faeces samples from hens 2 and 3 were analysed by combustion. Egg yolk (hen 2, day 8) was extracted with ethyl acetate, and the extract analysed by LSC to determine the amount of radioactivity associated with fat. The egg yolk residue was purified by washing with 1 N HCl, 1 N $NaHCO_3$ and water, and combusted to determine the amount of radioactivity associated with protein.

The majority of the administered dose was excreted in the faeces. The transfer of residues to eggs and tissues was very low following repeated daily oral dosing. The maximum residues found in eggs albumen and yolk was 0.0006 and 0.0039 mg equiv/kg respectively. Residue levels in tissues were very low, with the highest residues being found in kidney (0.014 mg equiv/kg) and liver (0.0046 mg equiv/kg) at 4 hours after the final dose).

Table 6 Recovery of total radioactivity following oral administration of [^{14}C] diquat (incurred residues) to laying hens at a dose level of 1–1.5 ppm in the diet

Matrix	Recovery of radioactivity (% of dose)		
	Hen 1 (sacrificed 5 days after a single dose)	Hen 2 (sacrificed 7 days after 11 daily doses)	Hen 3 (sacrificed 4 hours after 11 daily doses)
Faeces	96	89	84
Eggs	–	0.08	0.05
TOTAL	96	89	84

Table 7 TRR in eggs following daily oral administration of [^{14}C] diquat (incurred residues) to laying hens for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

	Radioactive residue (mg equiv/kg)			
	Hen 2 (sacrificed 7 days after 11 daily doses)		Hen 3 (sacrificed 4 hours after 11 daily doses)	
Day	Albumen	Yolk	Albumen	Yolk
1	0.0002	< 0.0005	< 0.0001	< 0.0005
2	0.0003	< 0.0005	0.0002	< 0.0005
3			0.0004	0.0009
5	0.0005	0.0011	0.0004	0.0017
6	0.0005	0.0019	0.0004	0.0025
7	0.0005	0.0034	0.0005	0.0030
8	0.0005	0.0037	0.0004	0.0033
10	0.0006	0.0038	am 0.0005 pm 0.0004	am 0.0035 pm 0.0034
11	0.0006	0.0038		
13	0.0004	0.0039		
14	0.0001	0.0030		
15	< 0.0001	0.0027		
17	< 0.0001	0.0025		
18 (inside hen)	< 0.0001	0.0015		

Table 8 Radioactive residues in tissues following daily oral administration of [^{14}C] diquat (incurred residues) to laying hens for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

Animal ID (Sacrifice time)	Radioactivity residue (mg equiv/kg)					
	Muscle	Heart	Kidney	Lung	Liver	Fat
Hen 2 (sacrificed 7 days after last dose)	0.0002	0.0003	0.0012	0.0007	0.0004	0.0011
Hen 3 (sacrificed 4 hours after last dose)	0.0009	0.0008	0.014	0.0014	0.0046	0.0022

The residue in the treated grain, used to prepare the dose, was characterized.

Table 9 Characterization of radioactive residues in treated barley grain and hen faeces

Component	Residue in treated grain (% TRR)	Residue in hen 2 day 10 faeces (% TRR)
Diquat	17	16
TOPPS	8.7	3.6
Diquat monopyridone	1.1	2.4
Diquat dipyridone	0.1	1.0
Picolinic acid	1.7	0.4
Picolinamide	1.0	0.5
Unidentified photoproducts	59	49
Unextracted	15	27

Analysis of the faeces from hen 2 (day 10) showed that the composition of the radioactivity in the faeces was fairly similar to the composition of the dose.

Radioactive residues in the egg albumen were very low and as a result no attempt was made to characterise the residue. The yolks from hen 2 (days 10, 11 and 13) were analysed. Diquat, TOPPS and diquat monopyridone were found to account for only a small part of the residue in egg yolk. The majority of the residue in egg yolk was found to be associated with fats and protein. This is in contrast to the study (French and Leahey, 1988; Report RJ0622B) where hens were dosed with [^{14}C] diquat only where diquat, TOPPS and diquat monopyridone accounted for almost all the radioactive residue in eggs.

Table 10 Characterization of radioactive residues in egg yolk following oral administration of [^{14}C] diquat and its photoproducts to a laying hen for 11 consecutive days at a dose level of 1–1.5 ppm in the diet

	Hen 2 Day 8 yolk	Hen 2 Day 10 yolk	Hen 2 Day 11 yolk	Hen 2 Day 13 yolk
TRR (mg equiv/kg)	0.0037	0.0038	0.0038	0.0039
		%TRR		
Diquat		0.9		
TOPPS			3.5	
Diquat monopyridone				3.0
Associated with fats	31			
Associated with protein	29			

Metabolic pathways in animals

Diquat is poorly absorbed following oral ingestion and is largely excreted in the faeces; residues in tissues, milk and eggs are low.

In the ruminant dosed with [^{14}C] diquat at the equivalent of 90 ppm in the diet for a period of 7 consecutive days and terminated 12 hours after the final dose, the recovery of ^{14}C was 97%. The majority of the radioactivity was found in the faeces and only 0.8% in the urine. Radioactive residues milk and tissues were low. In liver, diquat (22%), diquat monopyridone (13%) and diquat dipyridone (33%) were the major components of the ^{14}C residue. In kidney the major components were diquat (4.3%), diquat monopyridone (21%), and diquat dipyridone (29%). In milk the radioactive residue comprised almost entirely diquat dipyridone. Radioactive residues in muscle and fat were very low comprising of diquat dipyridone (20–46% TRR). Diquat represented 3.5% TRR in fat but was not found in muscle. In muscle diquat monopyridone represented 13% TRR and was not found in the fat sample.

In poultry dosed with diquat at 32 ppm in the diet for 4 days, the residues in eggs and tissues were low. The radioactive residue in liver was characterised as mainly diquat (48%), with small quantities of diquat monopyridone (3.9%), diquat dipyridone (3.1%) and TOPPS (1.8%), also present. The radioactive residue in kidney was mainly comprised of diquat (12%) and diquat monopyridone (15%). Small quantities of diquat dipyridone (6.6%) and TOPPS (3.9%) and were also present.

The metabolism of diquat in ruminants and laying hens is adequately understood. In both goats and hens diquat is oxidised to form diquat monopyridone and diquat dipyridone. TOPPS is found as a minor metabolite in hens but was not detected in studies of the metabolism of diquat by goats or rats.

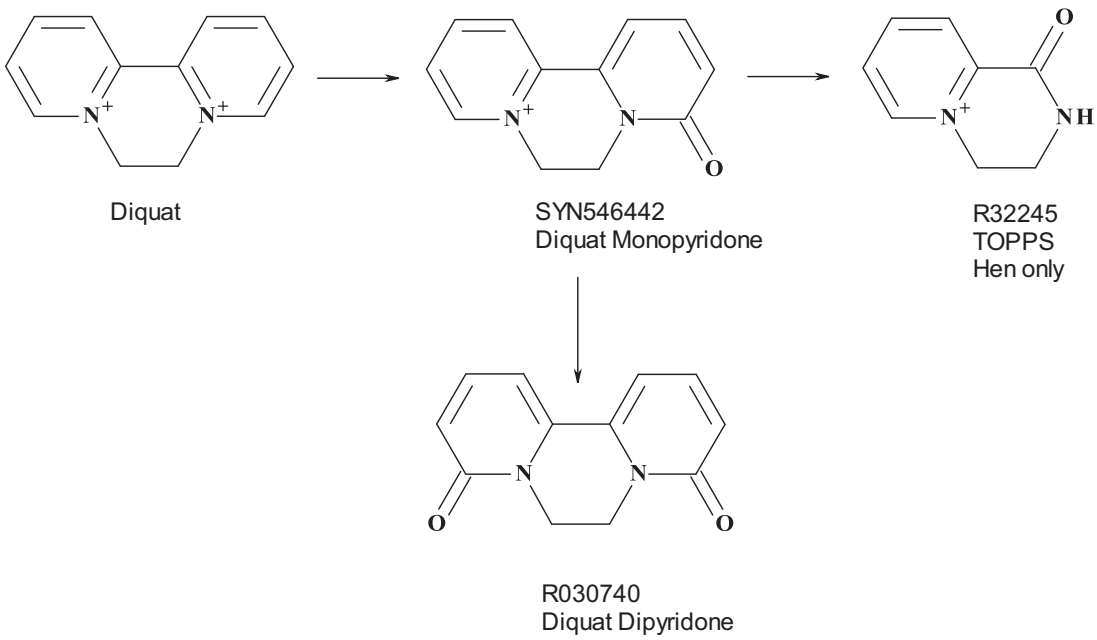


Figure 4 Proposed metabolic pathway for diquat in livestock (ruminant and poultry)

Plant metabolism

For weed control, diquat is applied either pre-emergent or inter row. On contact with the soil, diquat is strongly adsorbed by clay minerals and organic matter, reducing the availability of the chemical for degradation and uptake by plant roots. It is unlikely that soil residues will be taken up by the crops. Additionally diquat is used pre-harvest for crop desiccation with application at a time when plants are entering senescence and little diquat is expected to be translocated.

The metabolism of diquat in plants was studied in tomatoes (pre-emergent application) and in potatoes and rape plants (pre-harvest desiccation). Each study utilised ring-labelled diquat (as the dibromide salt).

Tomatoes

Derz (2012, A1412A_10298) studied the metabolism of diquat in tomatoes (var "Vitella") following a single pre-emergence application to soil for the control of weeds. A single pre-emergence application at a nominal application rate of 1.0 kg diquat/ha (spray volume 300 L/ha) of an SL formulation was made to sandy loam soil into which tomato seeds had previously been sown. The tomato plants were maintained in a container in a glasshouse until maturity. Mature fruits, immature fruits, leaves and stems were harvested 112 days after application and were separately were homogenised and radioactivity determined by combustion/LSC. TRR were 0.002 mg equiv/kg in tomato leaves and < 0.001 mg equiv/kg in mature fruits and due to the low levels were not analysed further.

The low levels detected in mature fruits and in leaves suggest that uptake of residues from soil into crops is negligible.

Potatoes

The metabolism of diquat in potato plants (var Belana") following a desiccant use pattern was studied by Derz (2012 A1412A_10304). A single foliar application of an SL formulation of [^{14}C] diquat dibromide was made to potato plants at growth stage BBCH 44–48 and at an application rate of 0.97 kg ai/ha in a spray volume of 400 L/ha. The potato plants were grown outdoors in a sandy loam soil and the tubers and haulm harvested 10 days and 20 days after application. Tubers were gently

wiped to remove the adhering soil, were washed with water and then peeled. After peeling, the potato flesh was washed again and the radioactivity in all wash solutions determined by LSC. The tuber flesh and skins were separately homogenised in a frozen state and the radioactivity determined by combustion/LSC.

The wash solutions were not analysed further since the radioactive residue present was determined to be extremely low, i.e., 0.0003 mg equiv/kg potato.

TRRs in tuber flesh were 0.029 and 0.032 mg equiv/kg for the samples taken after 10 and 20 days after application respectively. TRRs in tuber skins harvested after 10 and 20 days amounted to 0.044 and 0.039 mg equiv/kg, respectively. Sub-samples of tuber flesh and skins were extracted under reflux with water/sulphuric acid. Aliquots of the water / sulphuric acid extracts were centrifuged, adjusted to pH 9 and subjected to solid phase extraction.

The total extractability for all samples was very high with > 95% TRR extracted by a single water/sulphuric acid reflux. The levels of radioactivity that remained unextracted were low in all samples (≤ 4.7% TRR; ≤ 0.002 mg equiv/kg) and were not investigated further.

The principal component of the residue in the extracts was parent diquat representing ≥ 71.7% TRR. No postulated metabolites of diquat were detected. A minor unassigned metabolite was observed during TLC analysis but only in potato flesh from the samples harvested 10 days after treatment and at very low levels, corresponding to 0.5% TRR (< 0.001 mg equiv/kg). No individual fraction contained > 9.0% TRR (0.003 mg equiv/kg).

The extracted radioactivity was analysed by chromatography. The identified components for tuber flesh and skins at each sampling interval are summarised in Table 11.

Table 11 Identification of radioactivity in potato tubers

	flesh		skins	
Days after application	10	20	10	20
TRR (mg equiv/kg) [a]	0.029	0.032	0.044	0.039
		%TRR		
Extracted	97	97	95	96
Diquat	79	74	72	73
Unassigned [b]	0.5	ND		
Baseline [c]	3.9	4.0	2.5	3.6
Remainder [d]	1.9	1.6	2.0	1.6
Other fractions [e]	9.1	6.6	7.2	4.1
Unextracted [f]	2.9	2.9	4.7	3.7
Losses/gains on fractionation [g]	2.9	11	12	14
Total	100	100	100	100

[a] mg equiv/kg calculated directly from radioactivity extracted, radioactivity in the debris and specific activity.

[b] Unassigned components which chromatographed away from the origin in 1D-TLC. In the 10 day sample this comprises of a single discrete component.

[c] Polar material on origin of the radio-chromatogram using 1D-TLC.

[d] The remainder comprises diffuse areas of radioactivity within the chromatogram which cannot be assigned to discrete radioactive components.

[e] Extractable residues in 2–3 fractions per harvest timepoint that were not analysed and produced during processing that were too low for analysis. No single fraction comprised > 9.0% TRR (> 0.003 mg equiv/kg) in either harvest timepoint.

[f] Radioactivity remaining in the debris after the water/sulphuric acid reflux extraction procedure.

[g] The net cumulative incremental losses or gains during analysis, calculated as 100%—sum of all components.

The presence of diquat in tubers suggests translocation occurs though the levels are low.

Oilseed Rape

Derz (2012, A1412A_10305) also studied the metabolism of diquat in oilseed rape plants following use of diquat for pre-harvest crop desiccation. An SL formulation of [^{14}C] diquat was applied as a single foliar application to oilseed rape plants (var “Belinda”) at growth stage BBCH 80–87 at an

application rate of 0.58 kg ai/ha and in a spray volume of 300 L/ha. The rape plants were grown outdoors in a sandy loam soil and the seed, pods and foliage were harvested 5 days after application. The seeds were homogenised in a frozen state to a powder and the radioactive residue determined by combustion/LSC. A sub-sample of seed was extracted sequentially once with hexane, using a Soxhlet-extractor, to remove the oil and then the remaining meal twice with water / sulphuric acid under reflux. Aliquots of the combined water / sulphuric acid extracts were centrifuged, adjusted to pH 9 and subjected twice to solid phase extraction (SPE) procedures.

TRR in the oilseed rape seed was 0.97 mg equiv/kg. Extractability was high with 82% TRR extracted from the seed. Significant radioactive residues were only extracted into the water/sulphuric acid extracts (82% TRR), while the initial hexane which contained the oil fraction only extracted 0.3% TRR.

The principal component of the residue in the meal, after extraction of the oil with hexane, was parent diquat representing 48% TRR. Diquat metabolites TOPPS and diquat monopyridone were observed at low levels corresponding to 7.8 and 2.0% TRR respectively. Minor unassigned components were observed representing in total 3.9% TRR (0.038 mg equiv/kg) but no individual component accounted for > 2% TRR (0.019 mg equiv/kg).

Unextracted radioactivity amounted to 17.9% TRR. A sub-sample of post-extraction solids was subjected sequentially to further extraction with acetonitrile/water (80/20), diluted acid and a surfactant solution. Each separate treatment step released radioactivity representing ≤ 2.0% TRR and in total only a further 3.5% TRR was extracted leaving 10.1% TRR (0.098 mg equiv/kg) which was not investigated further.

The principal component of the residue in the meal after extraction of the oil was parent diquat with two diquat metabolites, TOPPS and diquat monopyridone, observed at low levels.

Table 12 Summary of total radioactive residues and extractability in rape seed treated with [^{14}C] diquat dibromide

TRR (mg equiv/kg) [a]	0.969
	%TRR
Extracted	73
Diquat	48
TOPPS	7.8
diquat monopyridone	2.0
Unassigned [b]	3.9
Baseline [c]	1.9
Remainder [d]	5.5
Other fractions [e]	4.2
Unextracted [f]	18
Losses/gains on fractionation [g]	8.9
Total	100

[a] TRR determined by summation of radioactivity present in the extracts, filter and debris following solvent extraction.

[b] Unassigned components which chromatographed away from the origin in 1D-TLC comprising at least three discrete components, none > 2% TRR; 0.019 mg equiv/kg.

[c] Polar material on origin of the radio-chromatogram using 1D-TLC

[d] The remainder comprises diffuse areas of radioactivity within the chromatogram which cannot be assigned to discrete radioactive components.

[e] Extractable residues in 4 fractions produced during processing that were too low for analysis. No single fraction comprised > 2.2% TRR (> 0.021 mg equiv/kg).

[f] Radioactivity remaining in the debris after the initial hexane and water/sulphuric acid reflux extraction procedures.

[g] The net cumulative incremental losses or gains during analysis, calculated as 100%—sum of all components.

Table 13 Further characterisation of radioactive residues in rape seed post-extraction solids

Percentage of TRR in PES	17 (Sub-sample)
TRR (mg equiv/kg)	0.164

Percentage of TRR in PES	17 (Sub-sample)
Radioactive residues released by	% TRR
Acetonitrile/water 80/20	2.0
Dilute acid reflux (water/sulphuric acid)	1.4
2% (w/v) SDS solution in water	0.1
Filters used	1.0
Remaining unextracted	10
Losses on fractionation	2.4
Total	17

Metabolic Pathways in Crops

For weed control use, diquat is applied pre-emergent or as an inter-row spray; in this use diquat will inevitably reach the soil. There is no deliberate application to crop plants, and accidental application is avoided so far as possible by careful spraying and/or the use of shielded sprayers. There is effectively no direct application to plants. Once on the soil, diquat is strongly adsorbed by clay minerals and organic matter and largely unavailable for metabolism by soil organisms or uptake by plant roots. It is not expected that there would be any residues in crop commodities following weed control use of diquat.

In the tomato metabolism study where [^{14}C] diquat was applied to the soil as a single pre-emergent application, radioactive residues in leaves and mature fruits were very low, 0.002 and < 0.001 mg equiv/kg respectively.

Where diquat is used for desiccation of crops, the residues found in commodities that are not exposed to the spray (i.e. tubers) show only low levels of parent diquat with no degradation products were observed. Where direct spray could result in application to the commodity, other metabolites/degradates, i.e. TOPPS and diquat monopyridone are also found albeit at low levels (< 7.8% and 2.0% TRR respectively). The proposed transformation pathway for diquat following desiccation use is shown in Figure 5.

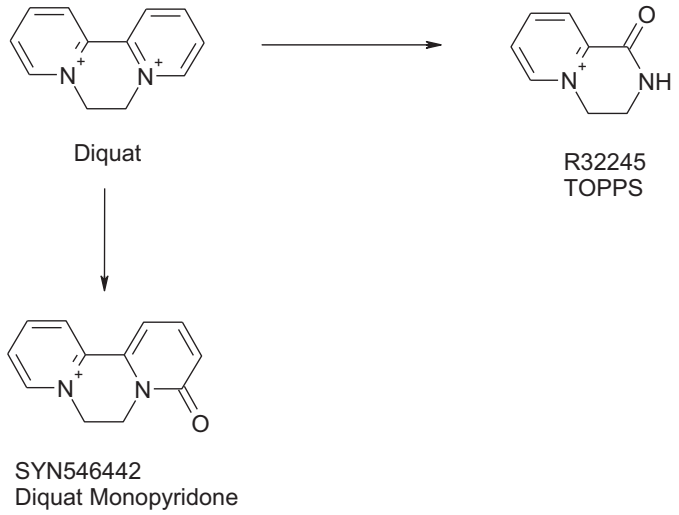


Figure 5 Proposed metabolic pathway for diquat in plants following pre-harvest desiccation use

Confined rotational crop studies

A confined rotational crop study was conducted on a sandy loam soil treated at 1.12 kg ai/ha with ^{14}C ring-labelled diquat (Lee 1989 PP901/0451). After intervals of 30, 120, and 365 days, carrots (var

Imperator), lettuce (var "Parris Island Romaine") and wheat (var "Anza") were planted and grown under greenhouse conditions to maturity. Plant samples were harvested at immature and mature stages for analysis. In most cases, the TRR in the mature plant were below the LOD (< 0.008 mg equiv/kg). The TRR was above the LOD in the carrot leaf at 365-days post- treatment (0.017 mg equiv/kg) and the wheat straw at 120- and 365-days post-treatment (0.022 and 0.024 mg equiv/kg, respectively). It is likely the radioactive residue in these plants, identified as parent diquat, is due to contamination with soil though not all the residues were removed with rinsing. Immature plants contained TRRs above LOD (0.035–0.090 mg equiv/kg) but these residues were not characterized since the immature plants are not a typical raw agricultural commodity. The bulk of the radioactivity was contained in the soil, mostly in the 0–7.6 cm soil depth (TRR 0.13–1.15 mg equiv/kg) with little observed in the 7.6–15 cm soil cores (0–0.047 mg equiv/kg).

Crops grown in soil containing [^{14}C] diquat showed negligible uptake of radioactivity. As such, crops grown in rotation with diquat-treated crops are not expected to contain residues of diquat or diquat degradation products.

Field Crop Rotational Studies

No field crop rotational studies were made available to the meeting. However, no residues are expected in rotational crops.

Environmental fate in soil

Route of Degradation in Soil

Aerobic degradation in soil

The rate and route of degradation of [^{14}C] diquat was investigated in four soils under aerobic conditions by Dixon (2012, PP901_10824). [^{14}C] Diquat was applied at a nominal rate equivalent to a single application of 0.54 kg ai/ha. The soil samples were incubated under aerobic conditions in the laboratory and maintained under moist, dark conditions at 20 °C for up to 120 days. Extraction was sequentially using calcium chloride solution, sulphuric acid (6 M) and finally water and acetone solutions. Additional samples for each soil type were incubated up to 364 days and the volatile radioactivity recovered in the liquid traps quantified to investigate the potential for further mineralisation to $^{14}CO_2$ beyond the normal study duration.

The mean total recoveries of radioactivity for the 0 to 120 DAT soil samples were between 93 and 103% of applied radioactivity (AR). The total extracted was high throughout the incubation period (from 97 to 99% AR at 0 DAT and 96 to 101% AR at 120 DAT). Of the extraction solutions, minimal radioactivity was extracted using calcium chloride solutions (≤ 0.3% extracted at 0 DAT).

Levels of parent compound decreased slowly over the incubation period from initial values of 96% to be 86–98% AR at 120 DAT. In addition to parent, four minor metabolites were present at levels < 5% AR; diquat monopyridone and three unknown compounds.

The unextracted radioactivity remained constant throughout the 120 DAT incubation period for the Gartenacker loam and 18 Acre sandy clay loam soils, ranging from 0.4 to 3.2% AR. Unextracted radioactivity at 7 days in the Marsillargues silty clay and North Dakota sandy clay loam soils were 9.5 and 8.1% AR, respectively, declining thereafter. Limited degradation to volatile products was observed with levels of $^{14}CO_2$ in traps totalling < 5% AR by the end of the study 36 DAT.

The rate of degradation was estimated using single first-order (SFO) kinetics. The DT_{50} values obtained are presented in Table 14.

Table 14 Summary of DT_{50} for diquat in the various culture systems at 10 mg diquat/L

Soil	DT50 (days)	Chi^2	r^2

Gartenacker (Switzerland, loam)	662	0.81	0.9109
18 Acres (UK, sandy clay loam)	> 1000 [a]	1.46	0.0702
Marsillargues (France, silty clay)	> 1000 [a]	4.16	0.0034
North Dakota (USA, sandy clay loam)	> 1000 [a]	3.05	0.0017

[a] Although there was a small amount of degradation, calculated DT_{50} values could not be differentiated from zero using SFO kinetics and therefore a default of 1000 days is proposed.

A number of studies assessed the degradation of diquat by soil bacteria and fungi and to enhance the understanding of the intrinsic biodegradability of diquat (Ricketts, 1997 PP901/0876); Kuet *et al.,* 2001a P901/1321; Kuet and Pinheiro, 2001 PP901/0741; Kuet *et al.,* 2001b PP901/1244). The studies used a range of techniques including isolated soil bacterial cultures, aqueous soil extracts, isolated soil fungal species and a soil yeast culture (*Lipomyces starkeyi*). Diquat is rapidly and extensively degraded by soil micro-organisms, normally found in soil pore water, in the absence of soil, to give a small number of non-volatile degradation products (not identified), with mineralisation to CO_2. The DT_{50} for degradation in soil solution is rapid at < 1 week.

Addition of clay minerals to the bacterial test system proportionately decreased the rate of diquat degradation, and $^{14}CO_2$ evolution, until the point when virtually all the diquat had adsorbed onto the clay, when degradation apparently ceased. This finding confirms that sorbed diquat is not available to biological degradation processes.

Mônego (2006, PP901/1977) studied the rate of degradation of [^{14}C] diquat in four viable Brazilian soils: Argissolo Vermelho from Eldorado do Sul (sandy clay loam), Latossolo Vermelho from Nova Prata (clay), Neossolo from Osório (sand) and Gleissolo from Viamão (sandy loam) under aerobic laboratory conditions. The test was performed at 20 °C in the dark under aerobic conditions with soil moisture content at 40% of the maximum water holding capacity (MWHC). Diquat was applied to the soils at the rate of 0.5 kg ai/ha. The dissipation half-lives were calculated using nonlinear first-order regression and are summarised in Table 15.

Table 15 Dissipation half-lives (DT_{50}) for diquat in four soils from Brazil

Soil	k	Half-life (days)
Argissolo (sandy clay loam),	0.00071	976
Latossolo (clay)	0.00239	290
Neossolo (sand)	0.00148	468
Gleissolo (sandy loam)	0.00122	568
Mean		576

Diquat dissipation proceeded slowly in each soil. Unchanged diquat accounted for an average of 99%, 101%, 104% and 99% at day 0 to 86%, 77%, 80% and 83% at day 119 for Argissolo, Latossolo, Neossolo and Gleissolo soils, respectively. Other than diquat, only a single minor compound was detected in Argissolo, Neossolo and Gleissolo soils but accounted for less than 2.8% of the applied radioactivity at the end of the study.

The soil dissipation of diquat occurs at a very slow rate and is dependent on the equilibrium between sorbed and dissolved phases.

Aerobic degradation of TOPPS

Dixon and Dove (2012, CGA130327_10007) investigated the rate of degradation of [^{14}C]-TOPPS in four soils under aerobic conditions. [^{14}C]-TOPPS was applied at a nominal rate equivalent to a single application rate of 0.15 kg ai/ha. The microbial biomass at the end of the incubation period (120 DAT) was in the range 1.6 to 2.7% of organic carbon indicating that the soil supported a viable microbial population. The soil samples were maintained under moist, dark aerobic conditions at 20 °C for up to 120 days.

Levels of TOPPS decreased over the incubation period from initial values of 93–94% to 3.8–46% AR (Gartenacker and Marsillargues) and from 94–95% to 82–85% AR (18 Acres and White Swan). Limited mineralisation to $^{14}CO_2$ was observed in 18 Acres and White Swan soils, with maximum levels reaching 2.2% AR by the 120 DAT timepoint. However, significant levels of $^{14}CO_2$ were formed during the incubation period for Gartenacker and Marsillargues soils, with levels reaching 53 and 46% AR at 120 DAT, respectively, indicating that mineralisation is potentially a major route of degradation.

The TOPPS degradation data were modelled to obtain DT_{50} and DT_{90} values using SFO kinetics as listed in the table (Patterson 2012 CGA130327_10009). DT50 values range from 28 to 757 days with a geometric mean of 224 days.

Table 16 Dissipation half-lives for TOPPS in soil

Soil	DT_{50} (days)	DT_{90} (days)
18 Acres	750	> 1000
Gartenacker	27.8	92.4
Marsillargues	159	529
White Swan	757	> 1000

Anaerobic degradation

A number of studies have investigated the long-term dissipation of diquat in field soils (Wilkinson 1980 PP148/0662; Gowman *et al.*, 1980 PP148/0576; Cole *et al.,* 1986 PP148/0014; Dyson and Chapman 1986 PP901/0017). Dissipation of diquat was monitored following application of either a single dose of diquat at exaggerated application rates (UK and USA), or of repeat annual doses of diquat applied at normal field application rates (USA). These long-term studies indicate that the DT_{50} for the total diquat residue was in the range 10–20 years in the UK and 1–4 years in the USA.

Monitoring studies on diquat residues in soil after long-term treatment of various crops with diquat showed that soil residues were considerably lower than the 'theoretical' maximum that would be anticipated on the basis of the amount of diquat known to have been applied and assuming no degradation (Devine 2004, PP901/1604).

Surveys on sites using diquat as a desiccant in various crops were also carried out in Europe (Anderson and Earl 1996, PP901/0522). In a series of 39 trials, diquat residues were determined in a variety of soils 184–280 days after a single application of diquat in an SL formulation as a desiccant to a variety of crops (potatoes, oilseed rape, peas and sunflowers) at rates up to 1 kg ai/ha. The amount of diquat reaching the soil was substantially below the theoretical deposition rate based on the amount of diquat applied. The average loss of applied diquat by degradation on the plant and soil between application and sowing of the following crop was 75%. German trials (on potatoes, oilseed rape and fodder peas, treated at 0.5–0.6 kg ai/ha) showed a loss of diquat 268 days after application of 45–75%. Following application at rates of 0.5–1.0 kg ai/ha, the increases in diquat soil residues the following spring were less than 0.11 mg/kg and averaged only 0.03 mg/kg in the top 30 cm of soil.

Diquat in soil adsorbs strongly to clay materials, and is not bioavailable leading to persistence in soils. However, when released into solution diquat is available for microbial degradation. Diquat degrades very slowly in standard aerobic soil studies. Mineralisation to form CO_2 was demonstrated with the extent varying between soils. Diquat is persistent in the environment.

Soil photolysis

The photolysis of diquat was investigated on both dry and moist soil surfaces of one soil, Gartenacker (Switzerland, loam) by Dixon and Gilbert (2012, PP901_10832). Ring-labelled [^{14}C] diquat was applied at a rate equivalent to 0.54 kg ai/ha, to thin layers of either dry or moist soil in individual photolysis vessels. The treated soils were maintained at about 20 °C and continuously irradiated using light from a xenon arc lamp filtered to provide a spectral distribution close to natural sunlight, with a

mean light intensity of 24.3 W/m^2 for periods up to the equivalent of approximately 30 days summer sunlight.

The mean mass balance ranged from 97 to 101% for the irradiated samples and from 98 to 101% for the dark controls.

Dry layer tests

Only slight degradation occurred in the light and dark dry soil samples. Two minor degradation products, TOPPS and diquat monopyridone, were observed in the irradiated samples, individually accounting up to 0.9% AR.

Moist layer tests

Degradation was more significant in the light moist soil samples with only a small degree of degradation occurring in the dark moist soil samples. The major photolytic degradation product was TOPPS which reached a maximum of 9.9% AR after 30 days. Diquat monopyridone was also detected but was generally present at levels < 1% AR. A number of other minor degradation products were also detected. Unknown SP-1, present at between 5.2 and 5.4% after 30 days, was found to be composed of two components by TLC. The maximum level of either single component was 4.0% AR. Volatile radioactivity, confirmed as CO_2, resulted mainly from irradiation of moist soil with levels of $^{14}CO_2$ reaching 7.2% AR by 30 DAT.

The maximum levels of unextracted residues were observed under light and moist conditions and were present up to a level of 3.1% AR after the 30-day incubation period.

In soil exposed to light, the main degradation pathway involved oxidation to diquat monopyridone and TOPPS. In dark samples, only oxidation to diquat monopyridone was observed. There was also photodegradation to a number of minor unknowns under moist light conditions. There was a small amount of mineralization to carbon dioxide.

The rate of degradation was estimated using single first-order (SFO) kinetics. Under the experimental conditions, photolytic DT_{50} values in dry soil and in moist soil were 237 and 37 days respectively (equivalent summer days for Europe and North America at latitudes 30 ° and 50 °N). Degradation in the dark controls was significantly slower with DT_{50} for the dry and moist soils being 857 and > 1000 days, respectively.

Soil photolysis is not expected to be a significant route of diquat degradation.

Aqueous Photolysis

Oliver and Webb (2005, PP901/1892) studied the photolysis of diquat in sterile natural water (Middle Row Pond). Solutions containing 10 µg [^{14}C] diquat/mL were continuously irradiated using light from a xenon arc lamp filtered to give a spectral distribution close to that of natural sunlight. The samples were maintained at 25 °C and were irradiated for periods up to the equivalent of approximately 15 days Tokyo spring sunlight (equivalent to approximately 5 days of summer sunlight at latitude of 50 °N).

The mean mass balance (across all samples) was 94% of the applied radioactivity. Diquat was rapidly degraded accounting for 16% AR after 3 days of continuous irradiation. The photo-degradation of diquat followed first-order kinetics with an estimated half-life of 31 hours under continuous irradiation, equivalent to approximately 6.5 days of Tokyo spring sunlight (or approximately 2 days of summer sunlight at a latitude of 50 °N).

A number of photo-degradates were formed (> 8 HPLC peaks in samples at 2 and 3 days of irradiation). The most significant identified metabolite formed was TOPPS, reaching a level of 23% AR at 15 days irradiation. Traces of diquat monopyridone were also detected (maximum 4.3% AR after 3 days). A mixture of 1,4 dihydropyrido[1,2a]pyrazin-5-ylium and 3,4 dihydropyrido[1,2a]pyrazin-5-ylium was detected by LC-MS/MS analysis although levels were not determined. The majority of the remainder consisted of a polar component (representing a maximum

of 12% AR after 2 days of irradiation) identified as 1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid. Trapped volatiles ($^{14}CO_2$) accounted for up to 3.8% AR during the irradiation period. No significant degradation was apparent in the dark controls indicating that the degradation in irradiated samples was the result of photodegradation only.

Aqueous photolysis of diquat is expected to be a significant route of degradation under environmental conditions.

RESIDUE ANALYSIS

Analytical methods

The analysis of diquat is complicated by its polar nature and similarity in properties to paraquat. Several different analytical methods have been reported for the analysis of residues of both compounds in plant materials, animal tissues, milk and eggs. Early methods used in field trials generally involve extraction of residues by reflux with sulphuric acid with clean-up on cation exchange columns. Detection was initially achieved spectrophotometrically following reduction with alkaline dithionite or sodium borohydride. In more recent methods, the diquat recovered from the cation exchange column is subjected to HPLC with NPD or UV detection. In the case of animal commodities, trichloroacetic acid is sometimes used in place of sulphuric acid for the extraction step.

The efficiency of the acid extraction step has been demonstrated during the metabolism studies where the majority of the total radioactive residue (TRR) was recovered in the aqueous acid extracts.

The most recent advance in methods has been the use of LC-MS/MS which allows for the clean-up steps to be omitted.

A brief description of the methods used in the residue trials is given in Table 17.

Table 17 Summary of major analytical methods used for the determination of diquat and metabolites in various matrices

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
PPRAM 1	Plant commodities	Reflux 0.5 M H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.1–0.5 mg/kg
PPRAM 005/RAM 005	Plant commodities	Oil seeds: Remove oil by extracting with hexane. Then proceed as for other crops. Other crops: Reflux 0.5 M H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.05–0.1 mg/kg
RM5/RM5.5	Plant commodities	Reflux 18 N H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection, 350–450 nm LOQ 0.02–0.05 mg/kg
RM5C	Plant commodities	Reflux 18 N H_2SO_4	Filter extract, percolate through cation exchange column, wash 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with sodium borohydride.	GC-NPD LOQ 0.02 mg/kg
PPRAM 007	Liquid	Mix with cation	Place resin in a column and	Spectrophotometric detection

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
	commodities (milk, water)	exchange resin and roll for 2 hours, decant the liquid and wash the resin 3× with deionised water	wash 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite.	(350–450 nm) LOQ 0.001–0.01 mg/kg
RAM 252 RAM 252/01 RAM 252/02	Plant commodities	Reflux 0.55 to 1 N H_2SO_4 depending on matrix	Precipitation with EDTA may be used prior to clean-up using cation exchange. Filter extract, percolate through cation exchange column, sequentially wash with deionised water, 2 M HCl and 2.5% NH_4Cl. Elute using saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite. If using HPLC, clean-up using C18 SPE cartridge	Spectrophotometric detection 350–450 nm (RAM 252) 2nd derivative spectrophotometric detection (RAM 252/01) HPLC-UV 310 nm (RAM 252/02) LOQ 0.02–10 mg/kg
RAM272	Plant commodities	Reflux 0.55 to 1N H_2SO_4 depending on matrix	For oilseeds: precipitation with EDTA is required prior to clean-up using cation exchange. For all crops: Filter extract, percolate through cation exchange column, sequentially wash with deionised water, 2M HCl and 2.5% NH_4Cl. Elute using saturated NH_4Cl. Clean-up the eluate on a preconditioned SPE cartridge.	Reversed-phase ion-pair HPLC-UV (310 nm) LOQ 0.01–0.05 mg/kg.
POPIT MET.021 Rev00	Citrus	Reflux 1 M H_2SO_4	Filter extract, adjust to 100 mL. An aliquot is derivatised using potassium ferricyanide/NaOH and partitioned against CH_2Cl_2. The organic phase is evaporated and redissolved in CH_3CN/H_2O (1:1).	LC-MS/MS LOQ 0.02 mg/kg
GRM012.03A	Plant commodities	Oilseeds: Reflux 1M H_2SO_4 Other: Reflux 1M H_2SO_4 + octan-2-ol	Centrifuge if required. Aliquots (0.01 µL) are diluted with ammonium formate (250 mM) and CH_3CN.	LC-MS/MS LOQ 0.01 mg/kg
RM5B	Animal commodities	Reflux 18 N H_2SO_4	Fat: Partition against hexane. All samples: Filter extract, percolate through cation exchange column, wash with H_2O, 2.5% NH_4Cl, elute saturated NH_4Cl. A portion is reduced with sodium borohydride.	GC-NPD LOQ 0.02 mg/kg
PPRAM 7	Animal commodities	Homogenise in ten times the volume CCl_3COOH (10%), centrifuge. Retain the liquid. Resuspend the pellet in CCl_3COOH (10%) and	Percolate through cation exchange column. Sequentially wash with H_2O, 2 N HCl, H_2O, 2.5% NH_4Cl, H_2O. Elute saturated NH_4Cl. A portion is reduced with alkaline sodium dithionite.	Spectrophotometric detection (350–450 nm) LOQ 0.01 mg/kg

Method/reference	Matrix	Extraction	Clean-up	Detection, LOQ
		centrifuge retaining the liquid.		
GRM012.02A	Animal commodities	Homogenise in ten times the volume CCl_3COOH (10%)	Centrifuge, aliquots (75 uL) are diluted with ammonium formate (250 mM) and CH_3CN.	LC-MS/MS LOQ 0.005 mg/kg

Plant materials

PPRAM 1 (developed for paraquat and extended to diquat, PP148/0910, PP148/0972, PP148/0349, PP901/0478)

Samples are extracted by reflux in dilute (0.5 M) sulphuric acid solution to which a small amount of octan-2-ol is added (about 1:500 v/v). The filtered digest is percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite (0.2% w/v in 0.3 M NaOH) to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically between 350 and 450 nm. The absorption is compared to a reference solution prepared from saturated ammonium chloride and sodium dithionite. The spectra must be measured within 5 minutes of adding the dithionite. The LOQ was 0.01–0.05 mg/kg for diquat in crop matrices, depending on the crop.

Table 18 Recovery data for the determination of diquat obtained during carrot residue analysis (PP901/0636)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)
Carrot	0.10	97, 78, 82	3	86	12
Lettuce	0.50	75, 102, 75	3	84	19
Onion	0.10	74, 99, 76	3	83	17

Residue Analytical Method PPRAM 005/RAM 005(PP901/0230, PP901/0220)

For oil seeds: a preliminary hexane extraction is performed to remove oil before the acid extraction. All commodities: Samples are extracted by reflux in dilute (0.5 M) sulphuric acid solution. The filtered digest is neutralised and percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite (0.2%w/v in 0.3 M NaOH) to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm). The LOQ was 0.01–0.1 mg/kg for diquat in crop matrices, depending on the crop.

Table 19 Recovery data for the determination of diquat using method PPRAM 5A/RAM 005 (PP901/0240, PP901/0671)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.05	100, 80, 82, 76, 98	5	87	13	76–100
	0.10	95, 91, 84, 71, 92, 82, 76, 84, 68, 70, 81, 79, 76, 69, 81, 69	16	79	11	68–95
	0.20	61, 62, 69, 71, 68, 77, 60, 72, 76	9	68	9.2	60–77
	Overall		30	77	14	60–100
Grapes	0.05	87	1	–	–	–
	0.10	89	1	–	–	–

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	Overall		2	88	–	87–88
Rape seed	0.05	87, 69	2	78	–	69–87
	0.10	89, 59	2	74	–	59–89
	0.20	88	1	–	–	–
	0.50	108	1	–	–	–
	Overall		6	83	21	59–108
Rape seed oil	0.10	87, 77	2	82	–	–
	0.20	80, 82, 88	3	83	5.0	80–88
	0.50	70	1	–	–	–
	Overall		6	81	8.3	70–88
Potatoes	0.01	89, 101	2	95	–	89–101
	0.10	84, 84	2	84	–	84
	0.50	88, 88	2	88	–	88
	Overall		6	89	7.0	84–101
Peas (seeds, fresh)	0.05	84, 85	2	85	–	84–85
	0.10	87, 84	2	86	–	84–87
	0.50	89, 92	2	91	–	89–92
	Overall		6	87	3.8	84–92
Beans (seeds, fresh)	0.05	88, 87	2	88	–	87–88
	0.10	81, 80, 85, 78	4	81	2.9	78–85
	0.50	84, 85, 91, 93	4	88	4.4	84–93
	Overall		10	85	5.6	78–93
Rape seed cake	0.10	72, 85	2	79	–	72–85
	2.0	70, 70	2	70	–	70
	10	73, 72	2	73	–	72–73
	Overall		6	74	7.7	84–92
Rape seed oil	0.05	88, 71	2	80	–	71–88
	0.10	81, 72	2	77	–	72–81
	0.50	73, 77	2	75	–	73–77
	Overall		6	77	8.5	71–88

Residue Analytical Method RM-5 (PP901/0594)

Samples are extracted by reflux in concentrated (18 N) sulphuric acid solution for 15 minutes. A small volume of octan-2-ol may be added to reduce foaming. Filter the digest. For oily crops, extract the filtered digest three times with benzene, retaining the aqueous phase. The filtered digest/aqueous phase is neutralised using 50% NaOH, EDTA (1 g) is added and the solution adjusted to pH 9 (10 M NaOH) and percolated through a column of cation-exchange resin. The column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. In method versions RM-5 and RM-5-5, a portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm).

In method version RM-5C, reduction with dithionite was replaced by reduction with sodium borohydride and determination of the reduced diquat product was by GC-NPD in place of spectrophotometry.

The LOQ of the method was 0.02 mg/kg for diquat in crop matrices.

Table 20 Recovery data for the determination of diquat using method RM-5C, Report PP901/0238

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.02	111, 117, 99	3	109	8.4	99–117
	0.10	88, 80, 86	3	85	4.9	80–88
	Overall		6	97	15	80–117
Tomatoes	0.02	109, 99, 106	3	105	4.9	99–109
	0.10	85, 86, 82	3	84	2.5	82–86
	Overall		6	95	12	82–109

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Lettuce	0.02	101, 119, 118	3	113	9.0	101–119
	0.10	85, 86, 82	3	84	2.5	82–86
	Overall		6	99	17	82–119
Oranges	0.02	98, 108, 97	3	101	6.0	97–108
	0.10	94, 92, 99	3	95	3.8	92–99
	Overall		6	98	5.7	92–108
Wheat grain	0.02	116, 107, 110	3	111	4.1	107–116
	0.10	74, 94, 102	3	90	16	74–102
	Overall		6	101	15	74–116

Residue Analytical Method PPRAM 007 (PP901/1005)

Aliquots of milk or water are mixed with cation-exchange resin by rolling for 2 hours. After allowing the resin to settle, the milk or water is decanted away from the resin and the resin washed three times with deionised water. The resin is then packed into a burette and the water allowed to percolate through. The resin column is washed with aqueous ammonium chloride (2.5%) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured spectrophotometrically (350–450 nm). The LOQ of the method was reported to be 0.001 to 0.01 mg/kg for diquat in liquid matrices, depending on the sample volume used, however no data to support the LOQ was supplied.

Table 21 Diquat analytical method recovery data for method PPRAM 007 (PP901/1005)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Milk	0.001	85 88 90 94 100 85 100 100 100 100 100 100 100 91 108 100	16	96	7.1	85–108
	0.002	100 91 85 88 92 91 93 100 100 100 85 100 100 97	14	94	6.2	85–100
	0.003	83 90 93 89	4	89	4.7	83–90
	0.004	94 84	2			84–94
	0.008	80 81	2			80–81
Tissues [a]	0.01–0.2	NR	12	90		75–100

[a] Tissues fortified and individual recovery values were not reported

Residue Analytical Method RAM 252 (PP901/0589)

Samples are extracted by reflux in dilute (0.55–1 M, depending on sample type) sulphuric acid solution. The filtered digest is neutralised using NaOH and percolated through a column of cation-exchange resin. For some crops an additional clean-up i.e. required where 5% (w/v) EDTA solution is added after the neutralisation step and the solution filtered prior to loading onto the cation exchange column. The column is washed with deionised water, hydrochloric acid (2 M), aqueous ammonium chloride (2.5%) and deionised water to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured using a scanning spectrophotometer in second-derivative mode (350–450 nm). Oilseeds may be analysed directly as whole, seeds or extracted with hexane and the cake and oil (from evaporation of the hexane extract) determined separately. The LOQ of the method ranged from 0.01 mg/kg to 10 mg/kg, depending on the matrix.

In an extension to the method (RAM 252/02) the sample is cleaned up using a C_{18} SPE cartridge prior to analysis using HPLC-UV.

Table 22 Diquat procedural recovery data obtained in residue trials during 1989–1994 (PP901/0589, PP148/0350)

Matrix	Fortification Range (mg/kg)	n	Mean Recovery (%)	RSD (%)
Grape	0.05–0.1	2	100	5
Banana	0.05–0.2	10	92	3
Carrot	0.05–0.1	2	97	3
Onion	0.05–0.1	2	87	2
Lettuce	0.05–0.1	2	92	1
Pea seed	0.05–0.1	6	88	15
Pea haulm	0.1–20	6	90	6
Lentils	0.1	2	85	2
Linseed oil	0.1	2	72	8
Linseed cake	0.5–2.0	2	69	1
Sunflower oil	0.05–0.1	2	89	3
Sunflower cake	0.1–0.4	2	72	6
Potato	0.05–0.2	32	94	6
Barley grain	0.5–3.0	4	97	2
Barley straw	10–25	4	98	2
Oat grain	0.5–3.0	2	93	1
Oat straw	10–25	2	98	2
Wheat grain	0.1	4	82	4
Wheat straw	0.1–0.2	3	68	6
Rice grain	0.05–0.1	2	90	3
Rice straw	0.05–0.1	2	95	2
Maize cob	0.05–0.1	2	89	2
Maize silage	0.05–0.1	2	82	5
Coffee bean	0.05–0.5	8	80	4

The methods also refer to validation studies (M4895B and CEMR-322) conducted with earlier versions of the method and which remain applicable. These data are summarised above (under Method PPRAM 005).

Table 23 Recovery data for the determination of diquat using method RAM 252 (PP901/0742)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.02	113, 69	2	91	–	69–113
	0.10	63, 72	2	68	–	63–72
	Overall		4	68	6	63–113
Pea seed	0.05	81, 79	2	80	–	79–81
	0.10	85, 77	2	81	–	77–85
	Overall		4	80	4	77–85
Bean seed	0.05	71, 73	2	72	–	71–73
	0.10	71, 71	2	71	–	71
	0.50	81, 82	2	82	–	81–82
	Overall		6	75	7	71–82

Residue Analytical Method RAM 272 (PP901/0226, PP901/0225)

Crop samples are extracted by reflux in dilute (0.55–1 M, depending on sample type) sulphuric acid solution. The filtered digest is neutralised and percolated through a column of cation-exchange resin. The column is washed with deionised water, hydrochloric acid (2 M), aqueous ammonium chloride (2.5%) and deionised water to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. An additional clean-up step using precipitation with EDTA is required prior to ion-exchange clean-up for oilseed crops. A portion (10 mL) of the eluate from the resin column is transferred to a pre-conditioned SPE cartridge (C_{18}) and eluted, collecting a portion of the second 5 mL for final determination. The analytical standards are cleaned-up in the same way to remove interferences arising from ammonium chloride. Diquat residues in the clean-up extracts are

determined using reversed-phase ion-pair HPLC with UV detection (310 nm). The LOQ of the method ranged from 0.01 to 0.05 mg/kg, depending on the matrix.

Table 24 Recovery data for the determination of diquat using method RAM 272, (PP901/0689, PP901/0244, ASF378/0002, PP901/1438)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Potatoes	0.01	93, 94, 94, 110	4	98	8	93–110
	0.10	88, 93, 106, 102	4	97	8	88–106
	0.5	95, 95	2	95	–	95
	Overall		10	97	7	88–106
Barley grain	0.02	95, 90, 90, 85	4	90	5	85–95
	0.10	80, 88, 83, 113	4	91	17	80–113
	1.0	91, 87	2	89	–	87–91
	Overall		10	90	10	80–113
Beans	0.05	88, 84, 86, 74	4	83	7	74–88
	0.10	86, 90, 90, 94	4	90	4	86–94
	0.50	96, 96	2	96	–	96
	Overall		10	88	7	74–96
Rape seed	0.05	78, 98, 92, 96	4	91	10	78–98
	0.10	95, 99	2	97	–	95–99
	0.50	92, 85	2	89	–	85–92
	2.0	93, 97	2	95	–	93–97
	Overall		10	93	7	78–99
Potatoes	0.01	89, 89, 90, 85	4	88	2.5	85–90
	0.05	69, 96	2	83	–	69–96
	0.2	94, 76	2	85	–	76–94
	Overall		8	86	11	76–96
Rape seed	0.05	67, 76, 78, 65	4	72	9.0	65–78
	0.25	58, 78, 87, 88	4	78	18	58–88
	1.0	80, 81	2	81	–	80–81
	Overall		10	76	13	78–99
Orange	0.01	99, 95, 94, 96, 88	5	94	3.6	88–99
	0.10	92, 91, 91, 92, 93	5	92	0.9	91–93
	Overall		10	93	2.7	88–99
Tomato	0.01	104, 78, 94, 100, 88	5	93	11.1	78–104
	0.10	97, 97, 98, 96, 94	5	96	1.6	94–98
	Overall		10	95	7.6	78–104
Rape seed	0.05	87, 92, 90, 91, 87	5	89	2.6	87–92
	0.50	89, 89, 87, 88, 88	5	88	0.9	87–89
	Overall		10	89	2.0	87–92
Straw	0.05	77, 71, 76, 75, 76	5	75	3.1	71–76
	0.50	72, 87, 78, 76, 85	5	80	7.9	72–87
	Overall		10	77	6.6	71–87
Potatoes	0.0025	91, 90	2	91	–	90–91
	0.005	84, 86	2	85	–	84–86
	0.01	89, 91	2	90	–	89–91
	Overall		6	89	3.3	84–91

Residue Analytical Method POPIT MET.021.Rev00 (PP148/3146)

Diquat is extracted from crop samples by reflux in dilute (1 M) sulphuric acid solution. After cooling, the extract is filtered and adjusted to a volume of 100 mL before an aliquot of the extract solution is derivatized with potassium ferricyanide/sodium hydroxide. The resulting solution is partitioned against dichloromethane. The organic phase is evaporated and redissolved in acetonitrile:water (1:1, v / v) for quantification by liquid chromatography with mass-selective triple-quadrupole mass-spectrometric detection (LC-MS/MS). The LOQ of the method was 0.02 mg/kg.

Table 25 Recovery data for the determination of diquat using method POPIT MET.021.Rev00 (*PP148/3146)*

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Orange fruit	0.02	91, 88, 89, 89, 92, 96, 98	7	91	4.1	88–98
	0.2	83, 78, 79, 76, 74	5	78	4.3	74–83
	Overall		12	86	9.2	74–98
Orange juice	0.02	107, 104, 107, 91, 106, 86, 108	7	101	8.8	86–108
	0.2	97, 100, 106, 106, 109	5	104	4.8	97–109
	Overall		12	102	7.2	86–109

Residue Analytical Method GRM012.03A (PP901/0478, PP901/2096)

Samples are extracted by reflux in dilute sulphuric acid solution (3.75% v/v). Octan-2-ol may be added to reduce foaming. Extracts are centrifuged (if required) and aliquots (100 µL=0.01 g) are diluted with aqueous ammonium formate (250 mM) and acetonitrile. Final determination is by LC-MS/MS, primary 183–157 m/z and confirmatory 183–130 m/z transition data. The detector response was linear for solution concentrations ranging from 0.000005 to 0.005 µg/mL corresponding to sample concentrations of 0.005 to 0.16 mg/kg (r^2 1.000). Sample extracts (3.75% v/v H_2SO_4) were stable for at least 15 days when stored at < 7 °C. Final extracts (CH_3CN: pH 3.7 aqueous ammonium formate buffer 30:70 v/v) were stable for at least 8 days when stored at < 7 °C. Stock solutions of diquat in water were stable for at least 51 days when stored at < 7 °C. No significant enhancement or suppression of MS/MS response was detected for the matrices in Table 26. The LOQ of the method is 0.01 mg/kg for diquat in crop matrices.

It was noted that diquat absorbs strongly to glass and it is imperative to use disposable polypropylene labware (not Teflon). LC systems should be fitted with PEEK tubing rather than stainless steel to avoid Teflon or derivatized the glass silanols using trimethylsilane.

Table 26 Recovery data for the determination of diquat using method GRM012.03A (PP148/3147)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Primary transition m/z 183–157						
Sunflower seeds	0.01	93, 101, 100, 99, 93	5	97	4	93–101
	0.10	103, 105, 100, 97, 99	5	101	3	97–105
	Overall		10	99	4	93–105
Sunflower oil	0.01	87, 86, 90, 116, 89	5	93	13	86–116
	0.10	89, 119, 89, 89, 83	5	94	15	83–119
	Overall		10	94	14	83–119
Lettuce leaves	0.01	84, 80, 80, 87, 88	5	84	4	80–88
	0.10	86, 84, 92, 88, 83	5	87	4	83–92
	Overall		10	85	4	80–92
Cereal grains	0.01	112, 112, 98, 105, 100	5	105	6	98–112
	0.10	111, 111, 107, 108, 114	5	110	3	107–114
	Overall		10	108	5	98–114
Orange whole fruits	0.01	76, 76, 81, 79, 81	5	79	3	76–81
	0.10	83, 79, 85, 82, 78	5	82	4	78–85
	Overall		10	80	4	76–85
Hop fresh cones	0.01	81, 82, 77, 79, 77	5	79	3	77–82
	0.10	78, 82, 78, 80, 80	5	80	2	78–82
	Overall		10	79	2	77–82
Cabbages	0.01	91, 84, 84, 90, 89	5	88	4	84–91
	0.10	91, 95, 99, 100, 106	5	98	6	91–106
	Overall		10	93	8	84–106
Confirmatory Transition m/z 183–130						

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Sunflower seeds	0.01	96, 101, 109, 94, 90	5	98	7	90–109
	0.10	98, 99, 96, 97, 98	5	97	1	96–99
	Overall		10	98	5	90–109
Sunflower oil	0.01	88, 82, 87, 118, 75	5	90	18	75–118
	0.10	84, 122, 92, 89, 84	5	94	17	84–122
	Overall		10	92	17	75–122
Lettuce leaves	0.01	81, 78, 84, 88, 101	5	86	11	78–101
	0.10	82, 79, 80, 85, 82	5	81	3	79–85
	Overall		10	84	8	78–101
Cereal grains	0.01	110, 101, 96, 92, 110	5	102	8	92–110
	0.10	113, 109, 106, 110, 116	5	111	4	106–116
	Overall		10	107	7	92–116
Orange whole fruits	0.01	79, 77, 86, 84, 81	5	81	5	77–86
	0.10	84, 81, 82, 82, 79	5	82	2	79–84
	Overall		10	81	3	77–86
Hop fresh cones	0.01	78, 80, 75, 81, 79	5	79	3	75–81
	0.10	79, 85, 81, 77, 83	5	81	4	77–85
	Overall		10	80	4	75–85
Cabbages	0.01	96, 91, 97, 96, 112	5	98	8	91–112
	0.10	87, 94, 97, 97, 103	5	95	6	87–103
	Overall		10	97	7	87–112

In addition, a range of methods have been published in the scientific literature for the analysis of diquat in various crops that are similar to those reported above (Worobey 1993; Chichila and Walters 1991; Chichila and Gilvydis 1993; Aramendía *et al.*, 2006; King 1978; Calderbank and Yuen 1966; Tadeo *et al.,* 2000).

An LC-MS/MS method has been developed by Kolberg *et al.,* (2012). Homogenised samples (10 g for potato and 5 g for barley, pulses and other dry commodities are weighed into 50 mL centrifuge tubes and 100 µL of a 10 µg/mL internal standard mixture added. For the dry commodities, water (10 mL) is added and the slurry was allowed to stand for 10 min to allow the water to thoroughly wet the sample. Then 10 mL of extraction solution (MeOH (50%) + HCl 0.1 M in H_2O (50%)) is added and the mixture shaken for 2 min followed by heating at 80 °C in a water bath for 15 min after which the extracts are shaken vigorously and then cooled prior to centrifugation for 5 min at 4000 rpm. An aliquot is filtered through a syringe filter (0.45 µm) and analysed directly by LC-MS/MS (m/z 183/157). LOQs were 0.006 mg/kg for diquat in potatoes and barley. Mean recoveries in three different laboratories were 94 to 120% (n=5).

RESIDUES IN FOOD OF ANIMAL ORIGIN

Residue Analytical Method RM-5B

Samples are extracted by reflux in concentrated (18 N) sulphuric acid solution. Fat samples are initially cleaned-up by hexane partition. For all sample types, the filtered digest is then percolated through a column of cation-exchange resin. The column is washed with water and aqueous ammonium chloride (one-tenth saturated) to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. Diquat is reduced with sodium borohydride and determination of the reduced diquat product is by GC-NPD. The LOQ of the method is 0.02 mg/kg for diquat in animal matrices.

Table 27 Recovery data for the determination of diquat using method RM-5B-1 (PP901/0868)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Beef muscle	0.02	110, 115, 90	3	105	13	90–115
	0.10	101, 111, 101	3	104	5.5	101–111

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	Overall		6	105	8.7	90–115
Beef liver	0.02	105, 50, 85	3	80	35	50–105
	0.10	103, 99, 114	3	105	7.4	99–114
	Overall		6	93	25	50–114
Beef fat	0.02	80, 90, 70	3	80	13	70–90
	0.10	76, 82, 66	3	75	11	66–82
	Overall		6	77	11	66–90
Beef kidney	0.02	120, 90, 100	3	103	15	90–120
	0.10	107, 84, 174 [a]	3	121	47	84–174
	Overall		5	100	14	84–120
Beef heart	0.02	87, 77, 89	3	84	7.6	77–89
	0.10	83, 88, 94	3	88	6.2	83–94
	Overall		6	86	6.7	77–94

[a] Possibly double-fortified

Residue Analytical Method PPRAM 7 (PP901/1005)

Tissue samples (10–20 g) are homogenised in ten times the volume of trichloroacetic acid (10%). The homogenates are centrifuged and then the supernatant liquid decanted and retained. The precipitate is re-suspended in trichloroacetic acid (10%, 50 mL) and centrifuged again, decanting the supernatant and combining with the first. The de-proteinised extracts are then percolated through a column of cation-exchange resin. The column is washed with water, hydrochloric acid (2 N), water, aqueous ammonium chloride (2.5%) and water again to remove co-extractives. Diquat is then eluted with saturated ammonium chloride solution. A portion of the eluate is treated with alkaline sodium dithionite to reduce diquat to a free radical. Light absorption of the radical is measured colourimetrically (350–450 nm). The LOQ of the method was 0.01 mg/kg for diquat in animal tissues.

Residue Analytical Method GRM012.02A (PP148/3006)

Samples are extracted by homogenisation in 10% w/v aqueous trichloroacetic acid. Extracts are centrifuged and aliquots (75 µL=0.005 g) are diluted with ammonium formate (250 mM) and acetonitrile (CH_3CN: pH 3.7 aqueous ammonium formate buffer 30:70 v/v). Final determination is by LC-MS/MS. The detector response was linear for the range 0.000025–0.015 µg/mL. No significant matrix effects were observed. Primary extracts were stable for at lead 14 days when stored at < 7 °C. Final extracts were stable for at least 7 days under the same storage conditions. The LOQ of the method is 0.005 mg/kg for diquat in milk, eggs, muscle tissue, liver, kidney, fat and blood.

Table 28 Recovery data for the determination of diquat using method GRM012.02A(PP901/2097, PP148/3005)

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
Primary Transition m/z 183–157						
Cows' milk	0.005	108, 108, 102, 106, 113	5	107	4	102–113
	0.05	107, 108, 111, 112, 109	5	109	2	107–112
	Overall		10	108	3	102–113
Cow muscle	0.005	86, 92, 92, 92, 94	5	91	3	86–94
	0.05	87, 89, 86, 94, 91	5	89	4	86–94
	Overall		10	90	3	86–94
Cow liver	0.005	93, 97, 100, 92, 100	5	96	4	92–100
	0.05	106, 103, 110, 112, 112	5	108	3	103–112
	Overall		10	102	7	92–112
Cow kidney	0.005	85, 92, 89, 91, 95	5	90	4	85–95
	0.05	95, 96, 96, 91, 93	5	94	2	91–96
	Overall		10	92	4	85–96
Cow fat	0.005	88, 94, 90, 92, 85	5	90	4	85–94

Matrix	Fortification Level (mg/kg)	Recovery (%)	n	Mean (%)	RSD (%)	Range (%)
	0.05	95, 94, 93, 88, 90	5	92	3	88–95
	Overall		10	91	4	85–95
Cows' blood	0.005	113, 112, 108, 101, 113	5	109	5	101–113
	0.05	110, 104, 109, 110, 113	5	109	3	104–113
	Overall		10	109	4	101–113
Hens' eggs	0.005	95, 100, 108, 102, 97	5	100	5	95–108
	0.05	106, 100, 107, 107, 114	5	106	5	100–114
	Overall		10	103	5	95–114
Confirmatory Transition m/z 183–130						
Cows' milk	0.005	104, 101, 105, 90, 108	5	102	7	90–108
	0.05	107, 106, 111, 116, 105	5	109	4	105–116
	Overall		10	105	6	90–116
Cow muscle	0.005	93, 80, 102, 94, 100	5	94	9	80–102
	0.05	101, 89, 89, 93, 89	5	92	6	89–101
	Overall		10	93	7	80–102
Cow liver	0.005	98, 105, 103, 108, 114	5	106	5	98–114
	0.05	110, 100, 110, 117, 108	5	109	5	100–117
	Overall		10	107	5	98–117
Cow kidney	0.005	93, 102, 95, 84, 90	5	93	7	84–102
	0.05	94, 93, 96, 87, 88	5	92	4	87–96
	Overall		10	92	6	84–102
Cow fat	0.005	84, 86, 93, 95, 83	5	88	6	83–95
	0.05	91, 92, 90, 87, 86	5	89	3	86–92
	Overall		10	89	5	83–95
Cows' blood	0.005	113, 107, 111, 106, 105	5	109	3	105–113
	0.05	109, 109, 98, 116, 105	5	107	6	98–116
	Overall		10	108	5	98–116
Hens' eggs	0.005	99, 112, 101, 107, 102	5	104	5	99–112
	0.05	104, 101, 110, 110, 117	5	109	5	101–117
	Overall		10	106	5	99–117

Extraction of residues from incurred residue samples

Potatoes

In the metabolism study employing a similar extraction procedure as analytical methods PPRAM 1, PPRAM005, RAM 252 and GRM012.03A (with the exception that the water content of the samples were not taken into consideration), the extractability of the radioactive residues from both potato flesh and skin was very high (> 95% TRR). Diquat was the only significant component present in the extracted material. The extraction using reflux with sulphuric acid/water is suitable for use in analytical methods for determining diquat.

Rape seed

In the metabolism study, the first water/sulphuric acid reflux extraction recovered approximately 70% TRR. Diquat accounted for 48% of the TRR.

Milk and tissues

The metabolism study utilised three sequential extractions (four for fat) with 10% trichloroacetic acid. The extraction procedure extracted 94% of radioactivity in milk with diquat accounting for 82% of the radioactivity. In tissues ≥ 80% of the radioactivity was extracted with the exception of liver which was lower at 63%. In tissues diquat was 20 to 46% of the radioactive residue. The extraction procedure is suitable for use in analytical methods and has been employed in PPRAM7 and GRM012.02A.

Chicken liver

A sub-sample of composited chicken liver from metabolism study was used for the radio-validation of method RM-5B-1. Extraction of diquat involves reflux with 18 N H_2SO_4. Diquat measured using method RM-5B-1 was 0.012 and 0.013 mg/kg. Recoveries for samples spiked at 0.05 and 0.1 mg/kg were 80 and 85% respectively. The metabolism study reported diquat level in liver to be 0.022 mg/kg which is similar to the values measured using method RM-5B-1 after correction for recovery (0.015–0.016 mg/kg).

Applicability of multi-residue methods

Incorporation of diquat into multiresidue screen is unlikely as extraction from crops generally requires reflux in an acid solution.

Stability of residues in stored analytical samples

The freezer storage stability of diquat in fortified plant, animal tissues, milk and eggs samples was studied. Residues were generally stable for the duration of the studies.

Stability of residues in plant products

Langridge (2007) studied the stability of diquat in spinach, wheat grain, oilseed rape seed, lentil, orange, potato and wheat straw under freezer storage conditions for up to 24 months. These include representatives of the four crop types, predominantly water-, oil-, protein- and starch-containing materials. Crop samples (10 g of spinach, wheat grain, oilseed rape seed, lentil, whole orange, potato and wheat straw) were separately weighed into polypropylene extraction vessels and fortified with known amounts of a standard solution of diquat in water at a target rate of 0.2 mg/kg. The fortified samples were sealed (after allowing any solvent to evaporate) and gently shaken to distribute the analyte before being stored in a temperature monitored freezer at < -18 °C. Method GRM012.03A was used to determine diquat in the crop commodities.

There was no significant decrease (> 30% as compared to the initial value) in the observed residues of diquat in spinach, wheat grain, oilseed rape seed, lentil, whole orange, potato and wheat straw when stored deep frozen at < -18 °C for a period of at least 24 months.

Table 29 Storage stability results for samples spiked with diquat at 0.2 mg/kg.

Commodity	Storage Period (months)	Concentration (mg/kg)	Mean Procedural Recovery (%) [a]
Spinach	0	0.22, 0.21, 0.22	107
	3	0.18, 0.18	98
	6	0.21, 0.20	94
	12	0.24, 0.22	116
	18	0.19, 0.21	105
	24	0.17, 0.18	91
Wheat grain	0	0.22, 0.22, 0.20	104
	3	0.19, 0.20	95
	6	0.19, 0.19	94
	12	0.19, 0.23	109
	18	0.18, 0.19	88
	24	0.19, 0.18	97
Wheat straw	0	0.21, 0.21, 0.21	110
	3	0.18, 0.17	85
	6	0.18, 0.19	100
	12	0.23, 0.22	110
	18	0.19, 0.17	97
	24	0.18, 0.17	91
Rape seed	0	0.21, 0.21, 0.22	104
	3	0.23, 0.25	107
	6	0.20, 0.19	92

Commodity	Storage Period (months)	Concentration (mg/kg)	Mean Procedural Recovery (%) [a]
	12	0.23, 0.22	109
	18	0.21, 0.19	105
	24	0.15, 0.15	69
Lentils	0	0.21, 0.23, 0.22	104
	3	0.14, 0.15	70
	6	0.17, 0.17	80
	12	0.18, 0.19	90
	18	0.17, 0.19	94
	24	0.16, 0.15	69
Orange fruit	0	0.21, 0.21, 0.21	107
	3	0.18, 0.18	95
	6	0.20, 0.20	103
	12	0.22, 0.22	114
	18	0.19, 0.19	86
	24	0.17, 0.17	80
Potato tubers	0	0.22, 0.19, 0.20	100
	3	0.18, 0.21	92
	6	0.20, 0.21	103
	12	0.17, 0.19	78
	18	0.19, 0.20	98
	24	0.20, 0.19	89

[a] Mean of two recoveries

USE PATTERNS

Diquat is a non-volatile herbicide with two principal modes of use:

desiccant use as a harvest aid

weed-control use, before planting or around and between the rows of established crops.

Diquat is fast-acting and effectiveness varies with weed species; repeat applications may be necessary on certain perennial weeds while annual weeds are generally destroyed with one application.

Table 30 presents a summary of relevant GAP. The table is divided into two parts, desiccation uses where diquat is applied deliberately and directly to the target crop and weed-control uses where diquat is applied to weed plants and is not allowed to come into contact with the crop plants.

Table 30 Selected registered uses of diquat (SL formulations)

Crop	Country	Application				PHI
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	(days)
Desiccant or	harvest aid					
Beans	Austria	Broadcast	0.6		1	5
Beans	Brazil	Broadcast	0.3–0.4	200–300	1	7
Beans	Canada	Broadcast	0.30–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Beans	France	Broadcast	0.6	> 300	1	
Beans	Germany	Broadcast	0.6	400–800	1	5
Beans	Slovakia	Broadcast	0.5–0.8	200–600	1	6–10
Beans	UK	Broadcast	0.60	200–500	1	7–10
Lentils	Canada	Broadcast	0.3–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Peas	Slovakia	Broadcast	0.5–0.8		1	6
Peas	Canada	Broadcast	0.30–0.41	225–550	1	4
	Canada	Aerial	0.41–0.55	45		
Peas	France	Broadcast	0.6	> 300	1	4
Peas	UK	Broadcast	0.40–0.60	200–500	1	7–10

Crop	Country	Application				PHI
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	(days)
Potato (consum.)	Austria	Broadcast	0.5		1	10
Potato	Brazil	Broadcast	0.3–0.5	200–300	1	7
Potato	Canada	Broadcast	0.41–0.84	550–1000	2	
Potato	Germany	Broadcast	0.5 –1.0	400–800	1 at 0.5 or 2 max 1.0/year	10
Potato	Netherlands	Broadcast	0.5–0.8	200–500	1/ max 0.8 or 2/max 1.0/year	
Potato	Spain	Broadcast	0.6–0.8	300–1000	1	15
Potato	UK	Broadcast	0.80–1.0	200–400	1/ max 0.8;or 2/ max 1.0/year	0, 14 (if potatoes to be stored)
Potato	USA	Broadcast	0.28–0.56	47–187	2/1.12	7
Rape seed	Austria	Broadcast	0.4– 0.6	500–1000	1	5
Rape seed	Canada	Broadcast	0.30–0.41	225–550	1	14
Rape seed	UK	Broadcast	0.60	250–500	1	7–10
Rape seed	USA	Broadcast	0.42–0.56	140	1	7
Rape seed	Germany	Broadcast	0.4–0.6	400–800	1	5
Soya bean	Brazil	Broadcast	0.2–0.4	200–300	1	7
Soya bean	Bulgaria	Broadcast	0.6		1	7
Soya bean	Canada	Broadcast	0.41–0.56	225–500	1	4
Soya bean	Slovakia	Broadcast	0.6		1	6
Sunflower	Slovakia	Broadcast	0.3–0.6	200–600	1	6
Sunflower	Canada	Broadcast	0.30–0.41	225–550	1	15
Weed control						
Apple (and other fruit trees)	Canada	Broadcast	1.1	225–675	1	0
Apple (and other fruit trees)	USA	Foliar	0.42–0.56	> 140	1	365
Banana/plantain	Belize	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Costa Rica	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Dominican Republic	Broadcast	0.2–0.6	250–300		0
Banana/plantain	El Salvador	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Guatemala	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Nicaragua	Broadcast	0.2–0.6	250–300		0
Banana/plantain	Panama	Broadcast	0.2–0.6	250–300		0
Cashew	Dominican Republic	Broadcast	0.2–0.6	250–300		0
Carrot	Slovakia	Broadcast	0.8	200–600	1	7
Carrot	Spain	Broadcast	0.3–0.8		1	0
Citrus	Brazil	Broadcast	0.3–0.5	200–300	1	14
Citrus	Costa Rica	Broadcast	0.2–0.6	325–570		0
Citrus	Dominican Republic	Broadcast	0.2–0.6	325–570		0
Coffee	Belize	Broadcast	0.2–0.6	325–570		0
Coffee	Brazil	Broadcast	0.3–0.5	200–300	1	16
Coffee	Costa Rica	Broadcast	0.6	325–570		0
Coffee	Dominican Republic	Broadcast	0.2–0.6	325–570		0
Coffee	El Salvador	Broadcast	0.2–0.6	325–570		0
Coffee	Guatemala	Broadcast	0.2–0.6	325–570		0
Coffee	Nicaragua	Broadcast	0.2–0.6	325–570		0
Coffee	Panama	Broadcast	0.2–0.6	325–570		0
Pome fruit	Slovakia	Broadcast	0.6–1.0		1	
Row crops	Spain	Broadcast	0.3–0.45	300–600	1	15 [a]
Strawberry	Sweden	Broadcast	0.5		1 before flowering or after harvest	n/a [b]
Stone fruit	Slovakia	Broadcast	0.8–1.0		1	

Crop	Country	Application				PHI
		Method	Rate kg ai/ha	Water L/ha	No or/ Season max kg ai/ ha	(days)
General weed control (pre-plant or post-emergence incl carrots)	Spain	Broadcast	0.3–0.8	300–600	1	–

[a] Use a spray protector (shield)

[b] Use a spray shield

RESULTS OF SUPERVISED RESIDUE TRIALS ON CROPS

Diquat is a non-selective herbicide that is highly active against growing weeds. The Meeting received information on supervised field trials for diquat on the following crops or crop groups:

Commodity	Table No.
Citrus fruit	Table 32
Pome fruit	Table 33
Strawberries	Table 34
Banana	Table 35
Tomato	Table 36
Pulses	Tables 38–45
Carrots	Table 46
Potato	Tables 47–48
Rape seed	Tables 49–50
Sunflowers	Table 51
Coffee (beverage seeds)	Table 52
Animal feed	Tables 53–56

Trials were generally well documented with laboratory and field reports; trials from the 1980s followed the standards of those times. Laboratory reports included method validation with procedural recoveries from spiking at residue levels similar to those occurring in samples from the supervised trials. Dates of analyses or duration of residue sample storage were also provided. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOQ. Control samples are indicated in the summary tables with a "c". Unless stated otherwise, residue data are recorded unadjusted for recovery.

Residues and application rates have generally been rounded to two significant figures or, for residues near the LOQ, to one significant figure. Residue values from the trials conducted according to maximum GAP have been used for the estimation of maximum residue levels. Those results included in the evaluation are underlined.

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

Table 31 Summary of sprayers, plot sizes and field sample sizes in the supervised trials

Crop	Location	Year	Sprayer	Plot size	Sample size	Sample to analysis interval (days)
Orange	Brazil	1987-2003	CO_2 backpack sprayer	4×15 m^2 to 100 m^2	Not reported to 3 kg	294-346 d
Apple	UK	1998-1999	CO_2 backpack sprayer with lance, Motor knapsack sprayer with single nozzle lance	4.1×2.0 m^2 (4 trees) to 2×5.8 m^2	Not reported	98 to < 215 d
Apple	Austria, France, Hungary, Spain, Italy	2010	CO_2 backpack sprayer, air-assisted backpack sprayer	4-10 trees	2.0-3.0 kg (12-30 fruit)	< 149 d
Banana	Costa Rica, Guatemala, Ecuador	1992	Hand held knapsack sprayer	2.3×2.5 m^2 - 30×50 m^2	12 fruit	< 4 months
Strawberry	UK	2000	CO_2 backpack sprayer with lance + shield	6×5 m^2 - 7.5×5 m^2	Not reported	< 30 d
Coffee	Costa Rica, Guatemala	1993	Hand held knapsack sprayer	Not reported to > 10 plants	1 kg beans	< 5 months
Tomato	Spain, france, Italy	2009	Air-assisted backpack sprayer, flat fan nozzle	10×2.4 m^2 - 25×3 m^2	1.6-3.5 kg	< 8 months
Tomato	France, Italy, Spain	2010	Air-assisted backpack sprayer, flat fan nozzle	10×2.4 m^2 - 20×5 m^2	1.6-3.5 kg	< 7 months
Bean fodder dry	Germany	1984-1985	Boom sprayer, knapsack sprayer, tractor mounted sprayer	2×4 m^2, 4 reps - 4.5×150 m^2	0.8-1.3 kg	< 243 d
Bean	USA	1994	Broadcast	3×9.1 m^2 - 4.9×61 m^2	1.1-1.8 kg	212-347d
Pea	France	1981	Not reported	Not reported	Not reported	< 173d
Pea fodder	Germany	1984	Knapsack sprayer, tractor mounted sprayer	2.5×10 m^2 6 reps	1 kg	< 508 d
Pea fodder	Germany	1984	Knapsack sprayer	1.5×10 m^2 4 reps - 25×25.2 m^2	1 kg	< 508 d
Pea	Denmark	1986	Knapsack sprayer	37.5m^2 - 5×12m^2	Not reported	< 170 d
Pea	UK	1990			> 0.5kg	< 242 d
Pea	UK	1992	Knapsack sprayer		0.5-1kg	< 126 d
Pea	USA	1994	Broadcast	3×30 m^2 - 4.9×61 m^2	> 1.1kg	145 - 357 d
Lentil	Canada	1989	Not reported to aerial	Not reported	> 1 kg	7 months
Lentil	USA	1994	Broadcast	3.7×9.1 m^2 - 6.1×15 m^2	> 1kg	< 318 d
Soy bean	France	1985	Knapsack sprayer (Cristal)	30×2.2 m^2	Not reported	< 10 months
Soy bean	France	1994	Knapsack sprayer	15×2 m^2 - 20×3.5 m^2	> 1kg	< 246 d
Soy bean	USA	1987	CO_2 backpack sprayer, farm sprayer, Tractor mounted offset sprayer	1.5×15 m^2- 780 m^2	Not reported	< 136 d
Carrot	Germany	1983-1984	Knapsack sprayer with bar, sprayer with shield, Sprinkler watering can, sprinkler with shield, Sprinkler bar	20 m^2-2.8×20 m^2	> 0.8kg	< 179 d
Carrot	Italy	1993	Knapsack sprayer with bar, sprayer with shield	Not reported	> 02kg	< 179 d
Potato	Austria, France	2009	Backpack sprayer	17×3 m^2 - 25×3 m^2	> 2kg	< 7 months
Potato	UK, France, Austria	2010	Backpack sprayer	10×3 m^2 - 30×3 m^2	> 2.4kg	< 3 months

Crop	Location	Year	Sprayer	Plot size	Sample size	Sample to analysis interval (days)
Potato	France, Italy, Spain	2009	Backpack sprayer	17×3 m^2 - 10×6 m^2	> 2kg	< 3 months
Potato	France, Italy, Spain	2010	Backpack sprayer	Not reported - 20×2.25 m^2	> 2kg	< 6 months
Potato	USA	1994	Backpack sprayer	3×15 m^2 - 4×37 m^2	Not reported	196-260 d
Rape	Austria, France, Italy	2009	Backpack sprayer	20×6 m^2	> 0.5kg	< 365 d
Rape	Austria	2009	Backpack sprayer	17×3 m^2 - 80×3 m^2	> 0.5kg	< 365 d
Rape	Spain, France, Italy	2010	Backpack sprayer	10×3 m^2 - 10×6 m^2	> 0.5kg	< 185 d
Rape	USA	2009-2010	Backpack sprayer, tractor mounted sprayer, bicycle sprayer	8.2×12.2 m^2 to 136×26 m^2		< 789 d
Sunflower	France	1993-1994	Backpack sprayer			< 266 d
Sunflower	France	2004	Backpack sprayer			< 76 d

Where duplicate field samples from an unreplicated plot were taken at each sampling time and were analysed separately, the mean of the two analytical results was taken as the best estimate of the residues in the plot and only the means are recorded in the tables. Similarly where samples were collected from replicate plots the mean result is reported (see general consideration JMPR 2010).

Citrus fruits

Two trials in 1988 and 1989 were conducted using diquat formulated as a soluble concentrate (SL). Applications were made close to commercial harvest of the citrus fruit, as appropriate for weed control. Orange fruit were sampled 14 days after application. Sample size and storage conditions were not reported.

Table 32 Residues of diquat in orange fruit (directed sprays for weed control)

Location, year, variety	Form	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Gelria–Holambra-SP Brazil 1988 (Pera Natal)	200SL	1	0.5	400		fruit	14	< 0.01	A1412A_10320
	200SL	1	1.0	400		fruit	14	< 0.01	
Sr. Geraldo Van Broke –Holambra SP Brazil 1989 (Pera Natal)	200SL	1	0.5	300		fruit	14	< 0.01	A1412A_10321
	200SL	1	1.0	300		fruit	14	< 0.01	
Estrada da Cachoeira, Holambra-SP Brazil 2003 (Pera Coroa)	200SL	1	0.5	100	BBCH 81–89	Fruit Juice	14	< 0.02 < 0.02	A1412A_10251
	200 SL	1	1.0	100	BBCH 81–89	Fruit Juice	14	< 0.02 < 0.02	

Pome fruits

Twelve supervised residue trials with diquat on apples were conducted in Europe between 1998 and 2010. In these trials, diquat was formulated as an SL formulation applied once at a rate of 1.0 kg ai/ha to the area around the base of the trees, well away from the fruit. All applications included an appropriate locally-typical adjuvant (wetter) at the recommended rate. In four trials from 1998–1999,

applications were made late in the growing season, at the time of harvest (0-day PHI). In eight trials from 2010, applications were made early in the growing season of the apples, as appropriate for weed control. Consequently, PHIs ranged from 0 to 171 days. Mature apple fruit were sampled at normal commercial harvest (BBCH growth stages 85–89) and stored frozen until analysis. Samples of apples were stored for a maximum of 215 days. Residues of diquat in apple samples were determined using methods RAM 272/02 or GRM012.03A.

Table 33 Residues of diquat in apple fruit (directed sprays for weed control)

Location, year, variety	Form	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
West Malling, Kent UK 1998 Discovery	200SL	1	1.0	200	BBCH 87	Fruit	0	< 0.05	PP901/0345 + 0.1% v/v Agral 90
Sittingbourne, Kent UK 1998 Bramley	200SL	1	1.0	200	BBCH 87	Fruit	0	< 0.05	PP901/0345 + 0.1% v/v Agral 90
Blean, Kent UK 1999 Cox	200SL	1	1.0	310	BBCH 87	Fruit	0	< 0.01	PP901/0349 + 0.1% v/v Agral 90
Little Witley, Hereford & Worcester UK 1999 Golden Delicious	200SL	1	0.96	288	BBCH 87	Fruit	0	< 0.01	PP901/0349 + 0.1% v/v Agral 90
Buchkirchen, Upper Austria, Austria 2010 Golden Delicious	200SL	1	1.1	328	BBCH 11–56	Fruit	150	< 0.01	A1412A_10290 + Neowett (Isotridecanol-polyglycolether) was used at a rate of 0.04% v/v
Burgundy France 2010 Gloster	200SL	1	0.95	332	BBCH 11	Fruit	171	< 0.01	A1412A_10290 LI700 added as a wetter (0.5% v/v)
Burgundy France 2010 Pinova	200SL	1	1.0	356	BBCH 11	Fruit	161	< 0.01	A1412A_10290 LI700 = added as a wetter (0.5% v/v)
Horvátzsidány Vas Vas, Hungary 2010 Gala Must	200SL	1	0.974	341	BBCH 11–15	Fruit	137	< 0.01	A1412A_10290 Silwet L-77
Lleida Spain 2010 Granny Smith	200SL	1	1.03	350	BBCH 11	Fruit	149	< 0.01	A1412A_10294 Agral 0.3%
Lleida Spain 2010 Golden Reinders	200SL	1	1.0	350	BBCH 11	Fruit	148	< 0.01	A1412A_10294 Agral 0.3%
Nîmes Languedoc-Roussillon France 2010 Fuji	200SL	1	1.1	372	BBCH 10–11	Fruit	145	< 0.01	A1412A_10294 LI700 added as a wetter (0.5% v/v)
Verzuolo (CN) Piedmont Italy 2010 Gala	200SL	1	0.94	330	BBCH 11	Fruit	137	< 0.01	A1412A_10294 Etravon used as an adjuvant.

Strawberry

Three supervised trials were carried out on protected strawberries during 2000 in the UK. In each trial one application of an SL formulation was made at a rate of 0.85 to 0.92 kg ai/ha at BBCH 57–60.

Samples of strawberries were taken at normal harvest 47 to 50 days after the application and were stored frozen for up to one month prior to analysis. Residues of diquat in strawberries were determined by ion-pair high performance liquid chromatography using method RAM 272/02.

Table 34 Residues of diquat in strawberries [a] grown under cover (inter-row directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Sevenoaks Kent UK 2000 Elsanta	1	0.85	213	BBCH 57–60	Fruit	50	< 0.05	PP901/0724
Maidstone Kent UK 2000 Elsanta	1	0.92	230	BBCH 57–60	Fruit	48	< 0.05	PP901/0724
Hereford Herefordshire UK 2000 Elsanta	1	0.86	215	BBCH 58–60	Fruit	47	< 0.05	PP901/0724

[a] Applications pre-flowering and used a spray shield

Banana

Eight supervised trials were conducted on bananas during 1992 and 1993, three in Costa Rica, three in Guatemala and two in Ecuador. Trials in Costa Rica and Guatemala consisted of two plots, one receiving three applications of diquat a SL formulation at a rate of 0.6 kg ai/ha and the other receiving two applications of a formulation also containing paraquat at a rate of 0.15 kg diquat/ha, at intervals of 29 to 33 days. The trials in Ecuador also consisted of two plots, both treated three times at intervals of 28 days at rates of either 0.2 or 0.4 kg ai/ha. The three trials conducted in Guatemala included an adjuvant "Agral" in each application and the two trials in Ecuador included "Agral 90" in each application according to local practice. Applications were sprayed directly to the soil around the plants according to commercial practices. Samples of mature banana bunches were collected immediately after the spray dried and also after 3 days for the trials in Costa Rica and Ecuador. On sampling, bananas were washed by immersion in water for 5–10 minutes according to local practices. All samples were stored frozen until analysis. Residues of diquat in banana samples were determined using method RAM 005/01.

Table 35 Residues of diquat in banana (directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
San Jose, Costa Rica 1992	3	0.15 0.15 0.15	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 05CR
	3	0.60 0.60 0.60	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	
San Jose, Costa Rica 1992	3	0.15 0.15 0.15	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 21CR
	3	0.60 0.60 0.60	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	
San Jose, Costa Rica 1992	3	0.15 0.15 0.15	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 24CR
	3	0.60 0.60 0.60	168 168 168	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Morales Izabel Guatemala 1992 Grand Nine	3	0.15 0.15 0.15	444 444 444	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 + Agral 0.1% 109GUA
	3	0.60 0.60 0.60	444 444 444	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	
Morales Izabel Guatemala 1992 Grand Nine	3	0.15 0.15 0.15	444 444 444	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 + Agral 0.1% 110GUA
	3	0.60 0.60 0.60	444 444 444	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	
Morales Izabel Guatemala 1992 Grand Nine	3	0.15 0.15 0.15	220 220 220	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	PP901/0359 + Agral 0.1% 111GUA
	3	0.60 0.60 0.60	220 220 220	250 cm 250 cm 250 cm	Fruit Fruit	0 3	< 0.05 < 0.05	
Guayas Ecuador 1992 Giant Cavendish	3	0.20 0.20 0.20	400 400 400		Fruit	0	< 0.05	PP901/0358 + Agral 0.1% RESREG1
	3	0.40 0.40 0.40	400 400 400		Fruit	0	< 0.05	
Guayas Ecuador 1992 Giant Cavendish	3	0.20 0.20 0.20	400 400 400		Fruit	0	< 0.05	PP901/0358 + Agral 0.1% RESREG2
	3	0.40 0.40 0.40	400 400 400		Fruit	0	< 0.05	

Tomato

Eight supervised residue trials were conducted in Europe during 2009 and 2010 where diquat was applied for weed control between the rows of tomato plants (inter-row application). In the trials, diquat as a SL formulation was applied once at a rate of 0.8 kg ai/ha. All applications included an appropriate adjuvant (wetter) at the recommended rate. Four of the trials contained additional plots treated with diquat pre-emergence with tomatoes sampled at normal commercial harvest 92 to 118 days after application. Samples of tomatoes were stored frozen for a maximum of 8 months. Tomato samples were analysed for residues of diquat using method GRM012.03A.

Table 36 Residues of diquat in field tomato (inter-row directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Trajano, Sevilla Spain 2009 Juncal	1	0.85	431	BBCH 74–76	Fruit Fruit Fruit Fruit Fruit	0 3 7 15 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10282 + 0.3% v/v Agral
Lebrija Sevilla Spain 2009 Juncal	1	0.88	444	BBCH 74–76	Fruit Fruit Fruit Fruit Fruit	0 3 7 15 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10282 + 0.3% v/v Agral
Languedoc-Roussillon France 2009 Valina	1	0.85	850	BBCH 73–82	Fruit Fruit Fruit Fruit Fruit	0 3 7 15 20	0.05 < 0.01 0.04 < 0.01 < 0.01 < 0.01	A1412A_10282 + 0.5% v/v LI 700

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Castagnito d'Alba Cuneo Piedmont Italy 2009 H3402	1	0.82	308	BBCH 83	Fruit Fruit Fruit Fruit Fruit	0 3 7 14 21	0.20 0.06 0.03 < 0.01 < 0.01 < 0.01	A1412A_10282 + 0.3% v/v Etravon
Languedoc-Roussillon France 2010 Valina	1	0.81	354	BBCH 71–81	Fruit	15	< 0.01	A1412A_10296 + 0.5% v/v LI700
Castagnito d'Alba Piedmont Italy 2010 Red Pear	1	0.87	380	BBCH 83	Fruit	15	< 0.01[A]	A1412A_10296 + Etravon
Losa del Obispo Valencia Spain 2010 Sahel	1	0.84	367	BBCH 72–76	Fruit	15	< 0.01	A1412A_10296 + 0.3% v/v Agral
Lliria Valencia Spain 2010 Valenciano	1	0.83	363	BBCH 74–79	Fruit	15	< 0.01	A1412A_10296 + 0.3% Agral

[a] Spray screen used during application to protect tomato plants

Table 37 Residues of diquat in field tomato (pre-emergent use for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Languedoc-Roussillon France 2009 Valina	1	0.84	368	BBCH 00	Fruit	116	< 0.01	A1412A_10282 + LI 700
Castagnito d'Alba Cuneo Piedmont Italy 2009 H3402	1	0.78	293	BBCH 07	Fruit	102	< 0.01	A1412A_10282 + Etravon
Languedoc-Roussillon France 2010 Valina	1	0.86	375	BBCH 01–07	Fruit	92	< 0.01	A1412A_10282 + LI 700
Castagnito d'Alba Piedmont Italy 2010 Red Pear	1	0.82	358	BBCH 03	Fruit	118	< 0.01	A1412A_10282 + Etravon

Pulses

Beans, dry

Eight supervised trials were conducted on dried beans without pods (field and fodder beans) in Germany during 1984 and 1985. Each trial received a single application of a diquat SL formulation at 0.6 kg ai/ha. Mature beans were collected from 3 to 13 days after treatment. The seeds were separated from the pods and samples were frozen until analysis. Storage periods ranged up to 243 days (8 months). Residues of diquat were determined using method PPRAM 5. Mean procedural recoveries were 59–64% for samples fortified at 0.1–0.2 mg/kg. The data are not suitable for estimating maximum residue levels.

Table 38 Residues of diquat in bean (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Oldenburg Germany 1984 Hara	1	0.60	600	PH [a]	Seed	5 8 13	< 0.02 < 0.02 < 0.02	PP901/0312
Wankendorf Germany 1984 Hara	1	0.60	600	PH	Seed	5 7 9	< 0.02 < 0.02 0.03	PP901/0312
Mörstadt Germany 1984 Kristal	1	0.60	600	PH	Seed	4	< 0.02	PP901/0312
Rheinhessen Germany 1984 Kristal	1	0.60	600	PH	Seed	5 7	< 0.02 < 0.02	PP901/0312

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Wankendorf Germany 1984 Hara	1	0.60	600	BBCH 88	seed	5 7 11	0.08 0.07 0.09	PP901/0312
Lüneburg Germany 1985 Hara	1	0.60	600	BBCH 88	seed	5 7 10	0.15 0.09 0.14	PP901/0312
Bottenbach Germany 1985 Kristall	1	0.60	600	BBCH 86–88	seed	3 5 8	< 0.02 0.03 0.05	PP901/0312
Kappellen-Drusweiler Germany 1985	1	0.60	600	BBCH 88	seed	3 5 7	0.04 0.08 0.06	PP901/0312

[a] PH Pre-harvest

Eight supervised trials were conducted in the USA in 1994 where diquat SL formulation was applied to mature bean plants as a desiccant 4 days prior to harvest of bean seeds. Dry bean samples were taken by hand or mechanically and maintained frozen until analysis. The maximum period of storage was 338 days. Samples were analysed for residues of diquat using method RAM 252/01.

Table 39 Residues of diquat in bean (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Greencrop	1	0.42	91	PH crop fully mature, pods drying	seed	4	< 0.05	PP901/0325
Ault CO USA 1994 Bill Z	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Jerome ID USA 1994 Pinto Vofi 196	1	0.42	76	PH crop mature	seed	4	< 0.05	PP901/0325
Bridgeport MI USA 1994 Blackhawk	1	0.42	92	PH crop mature	seed	4	< 0.05 [a]	PP901/0325
Hutchinson MN USA 1994 Montcalm	1	0.42	89	PH crop mature, pods yellow	seed	4	< 0.05	PP901/0325
Madrid NE USA 1994 Vaccaro	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Fabius NY USA 1994 Light Red Kidney	1	0.42	93	PH crop mature	seed	4	< 0.05	PP901/0325
Northwood ND USA 1994 Norstar	1	0.42	94	PH crop near maturity, 70% defoliated	seed	4	< 0.05	PP901/0325

[a] Bridgeport MI USA site received 18 mm rain on the day after application

Peas, dry

Seventeen supervised trials on dry peas were conducted in Europe from 1981 to 1992. One trial was carried out in France, seven in Germany, five in Denmark and four in the UK. A single application of an SL formulation of diquat was applied to dry pea plants 4 to 14 days prior to harvest. Mature peas were collected and the seeds were separated from the pods. Seeds, haulm and pods were analysed for residues of diquat using method PPRAM 5 or PPRAM 5A. Samples were stored frozen at about –20 °C prior to analysis. The maximum period of frozen storage was reported as 508 days (16 months). Mean procedural recoveries for the 1981 France trials were approximately 61% for samples fortified at 0.5 mg/kg. The data from the 1981 trials are not suitable for estimating maximum residue levels.

Table 40 Residues of diquat in peas dry (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Saint Vigor Bernay France 1981 Final	1	0.60	500	Dry pod	seed	5	< 0.05 [a]	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 41% pods Corrected recovery
Emanville Bernay France 1981 Final	1	0.60	500	Dry pod	seed	4	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 41% pods Corrected rec + Sporader
Matougues Rheims France 1981 Amino	1	0.60	500	Dry pod	seed	8	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 60% vines. Corrected rec. no control
	1	0.60	500	Dry pod	seed	17	< 0.05	+ Sporader
Neuflize Rheims France 1981 Rondo	1	0.60	500	Dry pod	seed	17	< 0.05	PP901/0306 0.5 mg/kg 61% seed; 2 mg/kg 60% vines Corrected rec. + Sporader
Wankendorf Germany 1984	1	0.60	600	PH	seed	4 7 10	0.05 0.03 0.05	PP901/0311
Neustadt/Holst Germany 1984	1	0.60	600	PH	seed	5 7 11	< 0.02 0.03 < 0.02	PP901/0311
Morstadt bei Worms Germany 1984 Stehgold	1	0.60	600	PH	seed	5 7 12	0.10 0.10 0.07	PP901/0311
Bröthen/Büchen Germany 1985 Columba	1	0.60	600	PH	seed	5 7 9	0.06 0.04 0.04	PP901/0311
Neustadt/Holst Germany 1985 Birte	1	0.60	600	PH	seed	5 7 10	0.05 0.04 0.04	PP901/0311
Dierbach Germany 1985 Stehgolt	1	0.60	600	PH	seed	3 5 7	0.07 0.06 0.06	PP901/0311
Kapellen-Drusweiler Germany 1985 Bodil	1	0.60	600	PH	seed	3 6 8	0.12 0.13 0.15	PP901/0311
Oberndorf-Hochmössingen Germany 1985 Stehgold	1	0.60	600	PH	Seed	7	0.04	PP901/0311
Slagelse Denmark 1986 Bodil (app 28/7)	1	0.60	400	yellowing	seed	0 3 7 9 14	0.10 0.03 0.04 0.05 0.05	PP901/0315 Day 0 seed 54% moisture
Slagelse Denmark 1986 Bodil (app 6/8)	1	0.60	400	yellowing	seed	0 3 7 9 13	0.03 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 32% moisture
Slagelse Denmark 1986 Bodil (app 8/8)	1	0.60	400	yellowing	seed	0 3 7 11 14	0.02 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 14% moisture
Olstykke Denmark 1986 Bodil (app 5/8)	1	0.60	400	yellowing	seed	0 3 7 10 14	0.09 0.03 0.02 0.03 0.03	PP901/0315 Day 0 seed 51% moisture

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Olstykke Denmark 1986 Bodil (app 8/8) unclear not two apps? Subsampled for analysis	1	0.60	400	yellowing	seed	0 3 7 10 14	0.09 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0315 Day 0 seed 25% moisture
Dorrington Lincolnshire UK 1990 Helka	1	0.53	300	PGRO/Knott 301–302	seed	5	0.04	PP901/0319 + Agral
Warwickshire UK 1990 Princess	1	0.53	300	PGRO/Knott 301–303	seed	10	0.04	PP901/0319 + Agral
Icklingham East Anglia UK 1990 Solara	1	0.53	300	PGRO/Knott 301–302	seed	8	< 0.03	PP901/0319 + Agral
Dorrington Lincolnshire UK 1992 Baroness	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral
Welton Cuff Lincolnshire UK 1992 Progreta	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral
Sandy Gate Lincolnshire UK 1992 Princess	1	0.26	200	PGRO/Knott 301–302	seed	4	< 0.05	PP901/0322 + Agral
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	
	1	0.53	200	PGRO/Knott 301–302	seed	4	< 0.05	+ Agral

Six supervised trials were conducted in the USA in 1994. Diquat was applied as a single application of an SL formulation at 0.42 kg ai/ha. Diquat applications were made to mature pea plants as a desiccant, 4 days prior to harvest of pea seeds. Dry pea samples were taken by hand or mechanically and maintained frozen at –20 °C until analysis. The maximum period of storage was 356 days. Samples were analysed for residues of diquat using method RAM 252/01.

Table 41 Residues of diquat in peas dry (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Progress #9	1	0.42	90	Mature	Seed	4	0.05	PP901/0324 + NIS
Nezperce ID USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.09	PP901/0324 + NIS
Milton-Freewater OR USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.56	PP901/0324 + NIS
Mercedes TX USA 1994 Tracer	1	0.42	84	Mature	Seed	4	0.40 c0.06	PP901/0324 + NIS small sample size 0.23 kg
Walla Walla WA USA 1994 Columbia	1	0.42	93	Mature	Seed	4	0.11	PP901/0324 + NIS
Ridgefield WA USA 1994 Yellow Spring	1	0.42	82	Mature	Seed	4	0.05	PP901/0324 + NIS

Lentils, dry

Fourteen trials on lentils were conducted in Canada and the USA. All trials received one application of diquat as an SL formulation at 0.4 or 0.42 kg ai/ha for broadcast application or 0.55 kg ai/ha for aerial applications. In some trials, a separate plot was treated with 2× application rates. Samples of lentil seeds were collected mechanically or by hand and stored frozen until analysis. The maximum period of frozen storage was about 12 months, though storage duration was not reported for study CRR114. Residues of diquat on lentil seeds from trials in the US were analysed using method RAM 252/01 while PPRAM 5A (modified as method 107) was used for the Canadian trials. Field trial reports were not available and analytical recoveries for the 1989 Canadian trials were 52–71%, mean 60% and, as such, the trials are not suitable for estimation of maximum residue levels. The description of the 1982 field trials was not adequate and there were no reports for the analytical phase. The trials are not suitable for use in maximum residue estimation.

Table 42 Residues of diquat on lentils—ground application (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.40	225	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	0.80	225	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Manitoba Canada 1989	1	0.55	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
	1	1.1	110	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	
Worley ID USA 1994 Brewers	1	0.42	90	Harvest aid	Seed	4	0.54	PP901/0323
	1	0.42	90	Harvest aid	Seed	4	0.21	PP901/0323

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Northwood ND USA 1994 Eston	1	0.42	94	Harvest aid	Seed	4	< 0.05	PP901/0323 pods still yellow, not mature at application. 14 mm rain between application and harvest
Waitsburg WA USA 1994 Baby Brown-Brewers	1	0.42	93	Harvest aid	Seed	4	0.06	PP901/0323
	1	0.42	93	Harvest aid	Seed	4	0.13	PP901/0323

Table 43 Residues of diquat on lentils—aerial application (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	6	< 0.05	PP901/0318 [a]
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	3	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	5	< 0.05	PP901/0318
Saskatchewan Canada 1989 Aerial	1	0.55	45	Swathing (lowermost pods yellow-brown)	Seed	7	< 0.05	PP901/0318
Davidson, Saskatchewan Canada 1982 Chilean	1	0.28 [b]	20		Seed	12	0.16	
Davidson, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	8	0.113	
Rocanville, Saskatchewan Canada 1982 Laird	1	0.42	34		Seed	8	0.095	
Rocanville, Saskatchewan Canada 1982 Eston	1	0.42	34		Seed	10	0.09	
Delmas, Saskatchewan Canada 1982 Chilean	1	0.55	45		Seed	4	0.045	
North Battleford, Saskatchewan Canada 1982 Laird	1	0.55	45		Seed	6	0.043	
North Battleford, Saskatchewan Canada 1982 Laird	1	0.55	45		Seed	9	0.036	
Moose Jaw, Saskatchewan Canada 1982 Eston	1	0.56	45		Seed	6	0.135	
Moose Jaw, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	7	0.11	
Rosetown, Saskatchewan Canada 1982 Laird	1	0.56	45		Seed	10	0.08	
Wisetown, Saskatchewan Canada 1982 Chilean	1	0.56	23		Seed	19	0.133	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Cupar, Saskatchewan Canada 1982 Laird	1	0.63	45		Seed	6	0.10	
Sedley, Saskatchewan Canada 1982 Laird	1	0.63	45		Seed	14	0.093 c0.06	

[a] No field report just protocol summary

[b] Data sheet suggests two applications made by aircraft from opposite directions so 0.56 kg ai/ha?

Rocanville, application dates about 1 week apart

North Battleford—different farms, dates

Moose Jaw—different variety, applications different as 1 week apart

Davidson—different variety, applications different as 1 week apart

Soya beans, dry

Four supervised trials on soya beans using diquat as a desiccant were conducted in Europe (France) during 1985 and 1994. Samples were maintained at -20 °C for periods up to 246 days, though the storage interval was not included in report R 2-FP. Diquat residues were determined by analytical method PPRAM 5 or RAM 252/01.

Table 44 Residues in soya beans (pre-harvest desiccation) Europe

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Villemur France 1985 Sloan	1	0.60	300	Yellow leaves	Seed	0 2 5 6 8	0.63 0.37 < 0.1 < 0.1 < 0.1	PP901/0310
	1	0.80	300	Yellow leaves	Seed	0 2 5 6 8	0.91 0.21 < 0.1 < 0.1 < 0.1	
	1	0.60	300	Yellow leaves	Seed	0 2 5 6 8	0.62 < 0.1 < 0.1 < 0.1 < 0.1	
	1	0.80	300	Yellow leaves	Seed	0 2 5 6 8	0.59 < 0.1 < 0.1 < 0.1 < 0.1	
Avignon France 1994 Goldor	1	0.60		Mature	Oil Cake Seed	4	< 0.05 0.06 0.06 [a]	PP901/0328
Blois France 1994 Maple Arrow	1	0.60		Mature	Oil Cake Seed	4	< 0.05 < 0.05 < 0.05[A]	PP901/0328

[a] Calculated residue (from separate oil and meal determinations)

Seven supervised trials using diquat as a desiccant on soya beans were conducted in various locations in the US in 1987. Samples were maintained in freezers at -20 °C for periods up to 136 days until analysis. Diquat residues were determined by analytical method RM-5C.

Table 45 Residues in soya beans (pre-harvest desiccation) USA

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) [a]	Reference
Proctor AR USA 1987 Asgrow 5980	1	0.56	187	Harvest aid	Seed	7	0.09 0.08 (0.08)	PP901/0316
Lafayette IN USA 1987 Williams 82	1	0.56	153	Harvest aid	Seed	7	< 0.01 < 0.01 (< 0.01)	PP901/0316
Hollande MN USA 1987 NK 1346	1	0.56	187	Harvest aid	Seed	7	0.15 0.16 (0.16)	PP901/0316
Greenville MS USA 1987 Centennial	1	0.56	187	Harvest aid	Seed	7	0.02 < 0.01 (0.02)	PP901/0316
Oregon MO USA 1987 Asgrow 3127	1	0.56	219	Harvest aid	Seed	7	0.04 0.03 (0.04)	PP901/0316
Columbus OH USA 1987 Zane	1	0.56	281	Harvest aid	Seed	10	0.03 0.03 (0.03)	PP901/0316
Dallas Center IA USA 1987 Asgrow 2187	1	0.56	187	Harvest aid	Seed	7	0.03 0.02 (0.02)	PP901/0316

[a] Replicate field samples collected from the same plot, mean in brackets

Carrots

Six supervised trials on carrots were conducted in Germany during 1983–1984. An SG formulation of diquat and paraquat was applied two or three times at rates of 0.71 to 0.98 kg ai/ha. Applications were made inter-row for the control of weeds. An additional trial on carrots was conducted in Italy during 1993 where a single application of an SL formulation of diquat was made between the crop rows at 0.8 kg ai/ha. Samples were stored frozen for up to 256 days. Residues of diquat from the trials in Germany were analysed using method PPRAM 1A or PPRAM 1B and in the Italy trial using method RAM 005/01.

Table 46 Residues in carrots (directed inter-row application for weed control). Trials at Lüneburg Germany 1983, Freisbach Germany 1984 and Lombardo Italy 1993 used spray shields.

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Lüneburg Germany 1983 Caramba	2 (37)	0.75 0.75	2500 1250	14 days before harvest	Roots	0 4 9 14 22	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	PP901/0636
	2 (37)	0.75 0.75	2500 1250	14 days before harvest	Roots	0 4 9 14 22	< 0.02 < 0.02 < 0.02 < 0.02 < 0.02	
Steinfeld Germany 1983 Nantaise	2 (19)	0.75 0.75	3250 2350	9 days before harvest	Roots	0 4 9 14 21	< 0.02 < 0.02 < 0.02 0.02 < 0.02	PP901/0636
Büchen Germany 1984 Caramba	2 (21)	0.75 0.75	2500 2500	5–10 cm 30–35 cm	Roots	0 4 6 14 21	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	PP901/0630
Lüneburg Germany 1984 Lange Rote	3 (24 20)	0.75 0.75 0.75	2500 2500 2500	20 cm 30 cm 45 cm	Roots	0 4 9 14	0.01 0.01 0.01 0.02 c0.01	PP901/0630

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Freisbach Germany 1984 Tip Top	1	0.75	1200	40–45 cm	Roots	0 4 8 13 19	< 0.01 0.01 0.01 0.01 0.01	PP901/0630
Montanaso Lombardo Italy 1993 Nantese	1	0.80	500	PH	Roots	1 7 13 20	< 0.02 < 0.02 < 0.02 < 0.02	PP901/0285

Lüneburg Germany 1983 Caramba, appears to be one trial at same location, similar application dates

Potatoes

Sixteen supervised residue trials were conducted on potatoes in Europe during 2009 and 2010. An SL formulation of diquat was applied once at a rate of 1.0 kg ai/ha. A wide range of potato types was used in these trials from early-maturing to late-maturing varieties. Samples of potatoes were stored for a maximum of 8 months. Potato samples were analysed for residues of diquat using method GRM012.03A.

Table 47 Residues of diquat in potatoes following pre-harvest use.

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Bruck an der Leitha Austria 2009 Maxilla	1	1.0	300	BBCH 93	Tubers	0 3 8 10 15	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Reichersberg Austria 2009 Albatros	1	0.95	286	BBCH 47–48	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Chassenet France 2009 Mona Lisa	1	1.0	262	BBCH 48–49	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Chapelle de Guinchay France 2009 Charlotte	1	0.98	244	BBCH 47–48	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10276
Sutton Bridge Lincolnshire UK 2010 Maris Piper	1	1.0	209	BBCH 48–49	Tubers	10	0.01	A1412A_10295
Thelnetham Norfolk UK 2010 Melody	1	1.0	207	BBCH 48	Tubers	10	0.01	A1412A_10295
La Chapelle de Guinchay France 2010 Bintje	1	1.0	260	BBCH 46–48	Tubers	10	0.01	A1412A_10295
Rohrau Austria 2010 Pluto	1	1.1	321	BBCH 48	Tubers	10	0.02	A1412A_10295
Midi-Pyrénées France 2009 Spunta	1	0.96	241	BBCH 43–49	Tubers	0 3 7 10 14	< 0.01 0.02 [a] < 0.01 < 0.01 < 0.01	A1412A_10277
Nîmes France 2009 Mona Lisa	1	0.99	247	BBCH 48–55	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Azzano d'Ash Italy 2009 Marabel	1	0.96	288	BBCH 47	Tubers	0 3 7 11 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277
Villena Spain 2009 Desiree	1	1.0	280	BBCH 46–47	Tubers	0 3 7 10 14	< 0.01 < 0.01 < 0.01 < 0.01 < 0.01	A1412A_10277
Nîmes Languedoc-Roussillon France 2010 Mona Lisa	1	1.1	278	BBCH 48–49	Tubers	10	< 0.01	A1412A_10291
Ges Midi-Pyrénées France 2010 Agata	1	1.0	257	BBCH 91	Tubers	10	0.01	A1412A_10291
Cervesina Lombardy Italy 2010 Hermes	1	0.95	238	BBCH 91	Tubers	10	< 0.01	A1412A_10291
Albacete Spain 2010 Hermes	1	1.0	280	BBCH 48–49	Tubers	10	< 0.01	A1412A_10291

[a] Mean of two determinations on single sample (individual values not reported)

Eight supervised trials using diquat as a desiccant for potatoes were conducted in various locations in the US in 1994. Potato tubers were collected 7 days after the last application. Samples were maintained in freezers at –20 °C from 196 to 260 days prior to extraction. Diquat residues were determined using analytical method RAM 252/01.

Table 48 Residues in potatoes following pre-harvest desiccation use

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Russet Burbank	2 (5)	0.56 0.56	136 135	Mature Mature	Tubers	7	< 0.05	PP901/0286
Platteville CO USA 1994 Ranger	2 (5)	0.56 0.56	136 136	Mature Mature	Tubers	7	< 0.05	PP901/0286
Caldwell ID USA 1994 Shipody	2 (5)	0.56 0.56	185 185	Green beginning to go down Green	Tubers	7	< 0.05 0.06 (0.05)	PP901/0286
Presque Isle ME USA 1994 Atlantic	2 (6)	0.56 0.56	168 245	Tubers 5.1–7.0 cm Tubers 5.1–7.0 cm	Tubers	7	< 0.05	PP901/0286
Northwood ND USA 1994 Russet Burbank	2 (6)	0.56 0.56	187 93.5	Nearing crop maturity Nearing crop maturity	Tubers	7	< 0.05	PP901/0286
Waterloo NY USA 1994 Monona	2 (5)	0.56 0.56	180 263	Tubers 7.6–10.2 cm Tubers 7.6–10.2 cm	Tubers	6	0.07 0.05 (0.06)	PP901/0286
Ontario OR USA 1994 Russet Burbank	2 (5)	0.56 0.56	184 184	Mature Desiccated	Tubers	7	< 0.05	PP901/0286
Arlington WI USA 1994 Atlantic	2 (5)	0.56 0.56	152 152	Mature Mature	Tubers	7	< 0.05	PP901/0286

Rape seed

Sixteen supervised residue trials were conducted on oilseed rape in Europe during 2009 and 2010. A diquat SL formulation was applied once at a rate of 0.6 kg ai/ha. Samples of rape seed and plants were

stored for a maximum of 12 months. Samples were analysed for residues of diquat using method GRM012.03A.

Table 49 Residues in rape seed (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Burgenland Austria 2009 NK Petrol	1	0.63	314	BBCH 88	Seed	0 1 3 5 7	0.53 0.09 0.07 0.07 0.07	A1412A_10278 + Neo Wett
					Remaining plant	0 1 3 5 7	2.2 0.40 0.11 0.19 < 0.01	
Gemeinlebern Austria 2009 NK Petrol	1	0.65	323	BBCH 87–88	Seed	0 1 3 5 7	0.23 0.42 0.43 0.39 0.42	A1412A_10278 + Neo Wett
					Remaining plant	0 1 3 5 7	4.1 0.78 1.7 0.97 1.3	
La Chapelle de Guinchay France 2009 Hexagone	1	0.62	258	BBCH 87–89	Pods Pods Pods Seed Seed	0 1 3 5 7	31 8.1 2.8 0.10 0.05	A1412A_10278 + LI700
					Remaining plant	0 1 3 5 7	8.7 5.0 7.5 0.18 3.8	
Nancelle Burgundy France 2009 Exocet	1	0.62	256	BBCH 87–88	Pods Pods Pods Seed Seed	0 1 3 5 7	21 8.3 1.6 0.08 0.07	A1412A_10278 + LI700
					Remaining plant	0 1 3 5 7	8.6 3.5 1.2 1.6 1.1	
La Chapelle de Guinchay France 2010 PR44W29	1	0.62	620	BBCH 89	Seed	4	0.03	A1412A_10292 + LI700
Sôpte Vas Hungary 2010 Ontario	1	0.56	281	BBCH 88–89	Seed	5	0.02	A1412A_10292 + Silwet Top
Stowbridge Norfolk UK 2010 D06	1	0.61	205	BBCH 88–89	Seed	5	0.12	A1412A_10292 + Activator 90
Stetchworth Sufolk UK 2010 Castille	1	0.63	209	BBCH 88–89	Seed	5	0.05	A1412A_10292 + Activator 90
Albacete Spain 2009 Dante	1	0.60	288	BBCH 87–89	Seed Seed Seed Seed Seed	0 1 3 5 7	1.2 2.6 0.15 0.02 0.03	A1412A_10279 + Agral
					Remaining plant	0 1 3 5 7	17 8.1 4.7 3.1 2.5	

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Alessandria Piedmont Italy 2009 Makila	1	0.57	285	BBCH 89	Pods Pods Seed Seed Seed	0 1 3 5 8	14 7.1 0.56 0.38 0.21	A1412A_10279 + Etravon
					Remaining plant	0 1 3 5 8	6.5 3.2 3.0 1.8 1.2	
Savés Ger Haute-Garome France 2009 ES Anabal	1	0.58	243	BBCH 87–89	Pods Pods Pods Seed Seed	0 1 3 5 7	4.3 1.6 0.85 0.06 0.04	A1412A_10279 + LI700
				BBCH 87–89	Remaining plant	0 1 3 5 7	11 11 3.2 2.0 0.35	
Nîmes Languedoc-Roussillon France 2009 ES Acaba	1	0.58	192	BBCH 87–89	Pods Pods Pods Seed Seed	0 1 3 5 7	1.2 0.73 0.23 0.27 0.14	A1412A_10279 + LI700
				BBCH 87–89	Remaining plant	0 1 3 5 7	16 17 7.6 2.2 2.7	
Albacete Spain 2010 Grizzly	1	0.61	255	BBCH 82–83	Seed	5	0.33	A1412A_10293 + Agral
Nîmes Languedoc-Roussillon France 2010 ES Akaba	1	0.66	273	BBCH 83–87	Seed	4	0.45	A1412A_10293 + LI700
Gers Midi Pyrénées France 2010 ES Annibal	1	0.65	270	BBCH 87–89	Seed	5	0.22	A1412A_10293
Asti Piedmont Italy 2010 Pioneer PR4SD03	1	0.61	253	BBCH 95	Seed	5	0.44	A1412A_10293 + Etravon

Nine supervised residue trials were conducted on oilseed rape (Canola) during 2009 and 2010. In these trial an SL formulated was applied once at a rate of 0.56 kg ai/ha. Samples of rape seed were stored for a maximum of 26 months. Samples were analysed for residues of diquat using method GRM012.03A (modified).

Table 50 Residues in rape seed (pre-harvest desiccation)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) [a]	Reference
Sanford NC USA 2009 DK 1369	1	0.54	145	Seed formation	Seed	6	0.51 0.53 (0.52)	ASF886_50000 + Induce
Minot ND USA 2009 Liberty Link 8440	1	0.54	191	Podding	Seed	8	0.71 0.74 (0.72)	ASF886_50000 + Preference
Minot ND USA 2009 Roundup Ready DKL 30–42	1	0.56	200	Podding	Seed	8	0.48 0.49 (0.48)	ASF886_50000 + Preference
Prosser WA USA 2009 Rapier	1	0.53	231	Podding	Seed	8	0.05 0.07 (0.06)	ASF886_50000 + Ad-Wet 90
Moxee WA USA 2009 67007	1	0.52	203	seed	Seed	8	0.23 0.24 (0.24)	ASF886_50000 + 90 Plus

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg) [a]	Reference
Brookings SD USA 2009 Freedom 84501	1	0.53	192	60–70% seed turned brown	Seed	6	0.27 0.34 (0.30)	ASF886_50000 + Induce
Brookings SD USA 2009 Freedom 84501	1	0.53	191	60–70% seed turned brown	Seed	5 7 10 15	0.46 0.48 (0.47) 0.49 0.36 (0.42) 0.48 0.44 (0.46) 0.44 0.40 (0.42	ASF886_50000 + Induce
Aurora SD USA 2009 InVigor 8440	1	0.53	233	Ripening (60% ripened)	Seed	6	0.29 [b] 0.30 [b] (0.30)	ASF886_50000 + Induce
Kimberly ID USA 2009 Sunrise	1	0.53	246	Mature (70% brown)	Seed	6	0.78 0.86 (0.82)	ASF886_50000 + Activator 90

[a] Replicate field samples collected from the same plot, mean in brackets)

[b] Mean of duplicate analyses (individual results not reported)

Sunflowers

Ten trials on sunflowers were conducted in France using diquat as a desiccant or harvest aid. All treated plots received one application of diquat as an SL formulations at the rate of 0.6 kg ai/ha. Sunflower heads were collected 5 to 7 days after treatment and either shelled by hand or threshed by combine. Samples were stored frozen for 7 months prior to analysis. Sunflower seeds were fractioned into oil and cake components, analysing each component separately and calculating residues in the seed using weight ratios of oil to cake, which were roughly 40% to 60%, respectively. Residues of diquat from the 1993 and 1994 trials were analysed using methods RAM 005/01 and method RAM 252/01, respectively. Residues of diquat in the 2004 trials were analysed using RAM 252/02 and RAM 272/02.

Table 51 Residues of diquat in sunflower seed (pre-harvest desiccation) (residue levels reported for sunflower seeds were calculated from residues in oil and cake and the weight ratios of the components in each sample analysed)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Coulombs France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	6	0.15 [a,b] < 0.05 (66) 0.14 (34)	PP901/0424
Marchezais France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	7	0.11 [a,b] < 0.05 (65) 0.10 (35)	PP901/0424
Chambray Les Tours France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	7	0.11 [a, b] < 0.05 (58) 0.11 (42)	PP901/0424
Joue Les Tours France 1993 Eurosol	1	0.60	300	When bracts become dark	Seed Oil Cake	5	0.19 [a, b] < 0.05 (54) 0.22 (46)	PP901/0424
Marchezais France 1994 Eurosol	1	0.60		When bracts become dark	Seed Oil Cake	7	0.08 [a, b] < 0.05 0.06	PP901/0426
Coulombs France 1994 Eurosol	1	0.60		When bracts become dark	Seed Oil Cake	7	0.46 [a, b] < 0.05 0.46 c0.05	PP901/0426
Oyre France 1994 Albena	1	0.60		5.2–5.3 “Code Binoire Cetiom”	Seed Oil Cake	7	0.41 [a, b] < 0.05 0.39	PP901/0426

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Chatellerault France 1994 Santa Fe	1	0.60		5.2–5.3 "Code Binoire Cetiom"	Seed Oil Cake	7	0.54 [a, b] < 0.05 0.50 c0.05	PP901/0426
Monferran Saves France 2004 Melody	1	0.63	317	BBCH 85–87	Seed Oil Cake	7	0.06 [a] < 0.05 (32) 0.07 (68)	PP901/1769 +Agral
	1	0.57	283	BBCH 85–87	Seed Oil Cake	7	0.09 [a] < 0.05 (42) 0.12 (58)	+Agral
Correlles Beaujolais France 2004 All Star	1	0.57	287	BBCH 87–89	Seed Oil Cake	7	0.06 [a] < 0.05 (47) 0.07 (53)	PP901/1769 +Agral
Francheleins France 2004 Pegasol	1	0.62	312	BBCH 87–89	Seed Oil Cake	7	< 0.05 [a] < 0.05 (49) < 0.05 (51)	PP901/1769 +Agral
Brie France 2004 Aurasol	1	0.58	291	BBCH 87–88	Seed Oil Cake	7	0.10 [a] < 0.05 (43) 0.13 (57)	PP901/1769 +Agral
Taize France 2004 Dynamec	1	0.59	297	BBCH 87	Seed Oil Cake	7	0.07 [a] < 0.05 (40) 0.09 (60)	PP901/1769 +Agral

[a] Calculated residue from separate oil and meal determinations, values in brackets are percentage yield of oil and cake from seed

[b] Residues corrected for recovery

Coffee

Table 52 Residues of diquat in coffee (directed sprays for weed control)

Location, year variety	No	kg ai/ha	L/ha	GS	Sample [a]	PHI (d)	Diquat (mg/kg)	Reference
La Luisa, Costa Rica 1993 Catuai Rojo	3 (36 97)	0.15 0.15 0.15		160 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (36 97)	0.60 0.60 0.60		160 cm	Fruit	0 3	< 0.05 < 0.05	
La Margarita, Costa Rica 1992 Catuai Rojo	3 (34 30)	0.15 0.15 0.15		160 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (34 30)	0.60 0.60 0.60		160 cm	Fruit	0 3	< 0.05 < 0.05	
Juan Vinas, Costa Rica 1992 Caturra	3 (32 34)	0.15 0.15 0.15		170 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B
	3 (32 34)	0.60 0.60 0.60		170 cm	Fruit	0 3	< 0.05 < 0.05	
Retalhuleu Guatemala 1992 Caturra	3 (30 31)	0.15 0.15 0.15		200 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 31)	0.60 0.60 0.60		200 cm	Fruit	0 3	< 0.05 < 0.05	
Retalhuleu Guatemala 1992 Catimor 5269	3 (30 30)	0.15 0.15 0.15		300 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 30)	0.60 0.60 0.60		300 cm	Fruit	0 3	< 0.05 < 0.05	

Location, year variety	No	kg ai/ha	L/ha	GS	Sample [a]	PHI (d)	Diquat (mg/kg)	Reference
Quetzaltenango Guatemala 1992 Catuai	3 (30 30)	0.15 0.15 0.15		300 cm	Fruit	0 3	< 0.05 < 0.05	RJ1607B + Agral
	3 (30 30)	0.60 0.60 0.60		300 cm	Fruit	0 3	< 0.05 < 0.05	

[a] Coffee pods were pulped, fermented, the beans washed with water and dried.

Animal feed stuffs

Legume Animal Feeds

Diquat is used as a desiccant in the following crops and is applied shortly before harvest to dry the plants and facilitate harvest therefore, in addition to seeds, the derived animal feed commodities are straw and hay.

Dry beans-straw

Table 53 Residues of diquat in bean straw

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Visalia CA USA 1994 Greencrop	1	0.42	91	crop fully mature, pods drying	straw	4	9.4 9.0 (9.2)	PP901/0325
Ault CO USA 1994 Bill Z	1	0.42	93	crop mature	straw	4	6.2	PP901/0325
Jerome ID USA 1994 Pinto Vofi 196	1	0.42	76	crop mature	Straw	4	6.3	PP901/0325
Bridgeport MI USA 1994 Blackhawk	1	0.42	92	crop mature	Straw	4	7.8	PP901/0325
Hutchinson MN USA 1994 Montcalm	1	0.42	89	crop mature, pods yellow	Straw	4	5.5	PP901/0325
Madrid NE USA 1994 Vaccaro	1	0.42	93	crop mature	Straw	4	1.8	PP901/0325
Fabius NY USA 1994 Light Red Kidney	1	0.42	93	crop mature	Straw	4	9.8	PP901/0325
Northwood ND USA 1994 Norstar	1	0.42	94	crop near maturity, 70% defoliated	Straw	4	5.5	PP901/0325

Table 54 Residues in pea straw (haulm)

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquation (mg/kg)	Reference
Dorrington Lincolnshire UK 1990 Helka	1	0.53	300	PGRO/Knott 301-302	Haulm	5	3.6[a] c0.05	PP901/0319 +Agral
Warwickshire UK 1990 Princess	1	0.53	300	PGRO/Knott 301-303	Haulm	10	2.1[a]	PP901/0319 +Agral
Icklingham East Anglia UK 1990 Solara	1	0.53	300	PGRO/Knott 301-302	Haulm	8	3.6[a] c0.25	PP901/0319 +Agral
Dorrington Lincolnshire UK 1992 Baroness	1	0.26	200	PGRO/Knott 301-302	Haulm	4	8.3	PP901/0322 +Agral
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	14	
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	18	+Agal
Welton Cuff Lincolnshire UK 1992 Progreta	1	0.26	200	PGRO/Knott 301-302	Haulm	4	5.5	PP901/0322 +Agral

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquation (mg/kg)	Reference
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	12	
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	14	+Agal
Sandy Gate Lincolnshire UK 1992 Princess	1	0.26	200	PGRO/Knott 301-302	Haulm	4	9.4	PP901/0322 +Agral
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	25	
	1	0.53	200	PGRO/Knott 301-302	Haulm	4	20	+Agal

[a] Recovery residues corrected for residue measured in the corresponding unfortified control sample

Table 55 Soya bean forage

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Avignon France 1994 Goldor	1	0.60		Mature	Forage	4	10 (23 ppm)	PP901/0328
Blois France 1994 Maple Arrow	1	0.60		Mature	Forage	4	6.0 (9 ppm)	PP901/0328

ppm = dry weight basis

Though described in the report as fodder, the water content of the plant samples was around 50% (estimated, as the residues increased by 1.5–2.3 times on oven drying), corresponding to forage as defined in the OECD animal feedstuffs table (56% dry matter).

Table 56 Lentil fodder

Location, year variety	No	kg ai/ha	L/ha	GS	sample	PHI (d)	Diquat (mg/kg)	Reference
Portage La Prairie, Manitoba Canada 1993 Eston	1	0.55	200	Lower 1/3 pods brown, mid 1/3 yellow	Fodder	5 + 2	10 (14 ppm) c0.12	RJ1895B
	1	1.1	200	Lower 1/3 pods brown, mid 1/3 yellow	Fodder	5 + 2	14 (19 ppm) c0.12	
Saskatoon, Saskatchewan Canada 1993 Laird	1	0.55	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	20 (28 ppm) c0.22	
	1	1.1	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	53 (74 ppm) c0.22	
Saskatoon, Saskatchewan Canada 1993 Eston	1	0.55	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	39 (49 ppm) c0.07	
	1	1.1	199	Lower/mid 1/3 pods brown, upper 1/3 yellow	Fodder	6	74 (92 ppm) c0.07	

ppm = dry weight basis

Saskatoon site, same location, same application date, harvest date

FATE OF RESIDUES IN STORAGE AND PROCESSING

Data are available to demonstrate the stability of diquat under conditions more extreme than those encountered in commercial food processing. Residue analytical methods for diquat in crops extract diquat from crop matrices by reflux in aqueous acid. At these concentrations of acid used pHs are low (< 0) and reflux temperatures are above 100 °C. Under these conditions there was no evidence of

degradation with acceptable mean recovery efficiencies obtained for diquat. Diquat is hydrolytically stable under conditions of extreme acidity and elevated temperature that might be encountered in commercial food processes.

The effect of processing on the level of diquat-derived residues was also investigated for soya beans to oil and rape seed to oil.

As a measure for the transfer of residues into processed products, a processing factor was used, which is defined as

$$PF = \frac{\text{Total residue in processed product (mg/kg}^{-1})}{\text{Total residue in raw agricultural commodity (mg/kg}^{-1})}$$

A concentration of residues takes place when PF > 1.

Soya beans

One application of diquat was made to soya beans (*var* Asgrow 2187) at a rate of 2.8 kg ai/ha seven days before normal commercial harvest. At harvest, samples of treated and untreated seed were collected and transported frozen to the processing facility. The beans were dried in a forced-air oven to achieve the optimal moisture content for hull removal (10%). The conditioned beans were cracked and the hulls removed by aspiration. After hulling the kernels were pre-heated to 74 °C and flaked by rolling to a thickness of 0.2–0.3 mm. Flaked kernels were solvent extracted using hot (63 °C) hexane for six cycles (3 hours). After draining the solvent, the flakes were dried using warm air for a further 4 hours to produce solvent-extracted meal. The miscella (oil and hexane mixture) was separated by evaporation, during which the crude oil reaches 85 °C temperature. Crude oil was sampled and the hexane discarded. Crude oil was refined by mixing crude oil with sodium hydroxide for 90 minutes at 20–24 °C and 20 minutes at 63–67 °C. After allowing to settle for an hour at 60–65 °C, the oil was refrigerated for at least 12 hours before the refined oil was decanted and filtered. The fraction remaining is the soapstock. Refined oil and soapstock were sampled.

The balance study achieved overall diquat mass balances of 141 and 131% for oil production. Residues and processing factors are presented in Table 57.

Table 57 Diquat residues in soya beans and processed commodities (PP901/0442)

Trial	Sample	Residue (mg/kg)	PF
Iowa 1987 R010 Run 1	Soya bean (RAC) [a]	0.24	–
	Soya bean (RAC) [b]	0.25	–
	Hulls	0.65	2.6
	Solvent-extracted Meal	0.18	0.7
	Crude Oil	< 0.01	< 0.04
	Soapstock	0.02	0.1
	Refined Oil	< 0.01	< 0.04
Iowa 1987 R010 Run 2	Soya bean (RAC) [a]	0.25	n/a
	Soya bean (RAC) [b]	0.14	n/a
	Hulls	0.50	3.6
	Solvent-extracted Meal	0.14	1.0
	Crude Oil	< 0.01	< 0.07
	Soapstock	0.03	0.2
	Refined Oil	< 0.01	< 0.07

[a] Soya bean sample collected from the field

[b] Soya bean sample collected from the bulk samples prior to processing

Rape seed

A processing study was performed for rape seed. Two residue trials on rape were conducted in northern France and the United Kingdom during 2011. One application of diquat was made to rape at

a rate of 2.0 kg ai/ha five days before normal commercial harvest. Rape seed was processed into refined oil. Two balance and two follow-up design tests were conducted, one balance study and one follow-up study on seed from each field trial. The process was representative of commercial oilseed rape processing.

Seed with non-optimal moisture content was dried until the optimal moisture content for pressing (6–10%) was achieved. The conditioned seed was cleaned manually using a sieve to remove parts of coarse stalks and weed seeds to produce cleaned seed. The rape seed was crushed to break the testa (seed coat) and flakes sampled. A screw press was used to separate the seed into a liquid phase (crude oil) and a solid phase (press cake). If required (depending on the pressing qualities of the seed), a heated press head was used. Crude oil and press cake were sampled. The press cake for solvent extraction was transferred to a small technical extraction plant. The first extraction step used n-hexane circulated through the press cake for about 2 hours at approximately 60 °C. After the circulation time, the solvent-oil-mixture (miscella) was pumped into a distillation vessel and after distillation, the extracted oil and the distilled n-hexane was transferred back to the press cake for a second extraction step. Fresh n-hexane was added and a second extraction performed under the same conditions as the first extraction. A second distillation was conducted as above, after which the remaining solvent was removed from the oil by rotary evaporation at 80 °C. Solvent-extracted oil and solvent-extracted meal were sampled. Before refining, crude oil (from screw pressing) from each sample was mixed with the corresponding solvent-extracted oil. The combined oil was sampled and then filtered. Refining of the crude oil included hydration, desliming (degumming), neutralisation, washing, drying, bleaching, filtration and deodorization steps, after which the refined oil was sampled. On completion of processing, samples were frozen immediately and stored below -18 °C.

Two balance and two follow-up processing studies were conducted where oilseed rape plants were treated with diquat and the harvested seeds processed by industrial processes into rape-seed oil. The procedures used closely mimicked industrial oil production processes. Good mass balances of diquat were achieved. Residues in processed commodities were reduced from those in raw rape seed, with processing factors from 0.17 to 0.76 in solvent-extracted meal and < 0.01 to < 0.03 in refined oil. Residues in by-products were also reduced from those in raw rape seed, with processing factors of 0.23 and 0.82 in press cake, 0.63 and 0.61 in crude oil and < 0.01 and < 0.03 in solvent-extracted oil. Only in waste (course plant debris and weed seeds) did residues increase, to 20 and 41 mg/kg in the two studies.

Residues of diquat (ion) were measured using method GRM012.03A. From receipt at the analytical facility, except for sample preparation and the removal of a sub-sample for analysis, the samples were stored frozen at or below –18 °C. Samples were stored frozen for a maximum period of 223 days from sampling to analysis and residues in the processed products are deemed to be stable over the storage period.

The balance study achieved overall diquat mass balances of 141 and 131% for oil production. The residues and processing factors found in the processed samples are presented in Table 58.

Table 58 Diquat residues in oilseed rape and processed commodities with corresponding processing factors

Country Year Trial	Crop Part	Diquat residue (mg/kg)	PF
France 2011 SRFR11-004-37HR	Rape Seed (RAC)	0.70	–
	Cleaned Seed	0.11	0.16
	Waste	20	29
	Flakes	0.17	0.24
	Press Cake	0.16	0.23
	Crude Oil	0.44	0.63
	Solvent-extracted Oil	< 0.01	< 0.01
	Solvent-extracted Meal	0.12	0.17
	Combined Oil	0.15	0.21
	Hydration Watery Phase	0.03	0.04

Country Year Trial	Crop Part	Diquat residue (mg/kg)	PF
	Desliming Watery Phase	< 0.01	< 0.01
	Soapstock	< 0.01	< 0.01
	Washing Water	< 0.01	< 0.01
	Refined Oil	< 0.01	< 0.01
France 2011 SRFR11-004-37HR (Follow-up study)	Rape Seed (RAC)	1.05	–
	Solvent-extracted Meal	0.21	0.20
	Refined Oil	< 0.01	< 0.01
United Kingdom 2011 SRUK11-003-37HR	Rape Seed (RAC)	0.38	–
	Cleaned Seed	0.24	0.63
	Waste	41	108
	Flakes	0.37	0.97
	Press Cake	0.31	0.82
	Crude Oil	0.23	0.61
	Solvent-extracted Oil	< 0.01	< 0.03
	Solvent-extracted Meal	0.29	0.76
	Combined Oil	0.11	0.29
	Hydration Watery Phase	0.02	0.05
	Desliming Watery Phase	< 0.01	< 0.03
	Soapstock	< 0.01	< 0.03
	Washing Water	< 0.01	< 0.03
	Refined Oil	< 0.01	< 0.03
United Kingdom 2011 SRUK11-003-37HR (follow-up study)	Rape Seed (RAC)	0.31	–
	Solvent-extracted Meal	0.18	0.58
	Refined Oil	< 0.01	< 0.03

Sunflower

No formal processing studies have been carried out for sunflower seeds. However, in ten supervised trials where diquat was applied as a desiccant or harvest aid, oil was extracted from seeds and residues were determined in the separated oil and cake fractions. All residues of diquat in the oil were below the LOQ (< 0.05 mg/kg). Residues of diquat concentrated in sunflower cake by a mean factor of 1.2. Residues did not concentrate in the oil.

Table 59 Diquat residues in sunflower oil and cake following application as a desiccant in France

Trial	Diquat residues (mg/kg)			PF		Reference
	Seed [a]	Oil	Cake	Seed to oil	Seed to cake	
S.215.94	0.08	< 0.05	0.08	< 0.6	1.0	PP901/0426
S.216.94	0.46	< 0.05	0.60	< 0.1	1.3	
S.622.94	0.41	< 0.05	0.50	< 0.1	1.2	
S.623.94	0.54	< 0.05	0.64	< 0.1	1.2	
CEMS-2362A	0.06	< 0.05	0.07	< 0.8	1.2	PP901/1769
CEMS-2362B	0.09	< 0.05	0.12	< 0.6	1.3	
CEMS-2362C	0.06	< 0.05	0.07	< 0.8	1.2	
CEMS-2362D	< 0.05	< 0.05	< 0.05	< 1.0	1.0	
CEMS-2362E	0.10	< 0.05	0.13	< 0.5	1.3	
CEMS-2362F	0.07	< 0.05	0.09	< 0.7	1.3	

[a] Calculated from oil and cake residues

Livestock feeding studies

Dairy cow feeding study

The transfer of diquat residues from feed to tissues and milk of dairy cows was studied using incurred residues (Edwards *et al.*, 1976). A 2-hectare field of grass was sprayed with diquat at 4 kg ai/ha. The treated grass was harvested after 4 days of sunny, dry and warm weather and processed to grass nuts.

Levels of diquat in the grass nuts were 209 ppm after production and before study start and showed no decline in concentration during storage under ambient conditions.

Lactating cows (Friesian, 3 to 7 years, 394 to 559 kg, three per dose rate) were fed diets containing fresh grass and a mixture of treated (209 ppm diquat) and untreated grass. Mean daily feed consumption during the exposure period was 9.9 kg DM fresh grass and 8.8–9.1, 8.1–9.1, 9.0–9.1 and 5.3–7.6 kg grass nuts/cow for groups 1, 2, 3 and 4 respectively. Mean daily milk yield during the exposure period was 7 to 18 kg/cow/day. Based on mean daily feed consumption, the exposure was equivalent to 18, 50 and 84 ppm in the feed. Cows were milked twice daily and morning milk combined with milk from previous evening and three samples retained per week (Monday, Wednesday and Friday). Two cows per dose group were sacrificed after 30 days of dosing and samples of liver, kidney, fat and muscle (cardiac, pectoral and adductor) collected. The actual interval between last dosing and sacrifice was not reported. The remaining cow per dose group was fed untreated grass nuts and sacrificed after a further seven days.

Samples of feed and tissues were stored frozen for up to 4 weeks prior to analysis while milk samples were stored frozen for a maximum of 1 week. Feed samples (pelleted grass) were analysed for diquat using the analytical method PPRAM-5 to confirm the dose level of diquat in the feed. Milk samples were analysed for diquat using analytical method PPRAM-7 while samples of liver, kidney, fat and muscle were analysed for diquat using the analytical method TBM/3 (method adapted to determine diquat by monitoring the absorption at 379 nm).

There were no residues of diquat at or above the LOQ (0.001 mg/kg) in any of the milk samples from any of the dose groups, throughout the duration of the study. There were no residues of diquat at or above the LOQ (0.01 mg/kg) in any of the tissue samples (liver, kidney, fat and muscle) from any of the dose groups, throughout the duration of the study.

Table 60 Diquat residues in bovine milk and tissues

Matrix	18 ppm	50 ppm	84 ppm
Milk	< 0.001	< 0.001	< 0.001
Liver	< 0.01	< 0.01	< 0.01
Kidney	< 0.01	< 0.01	< 0.01
Fat	< 0.01	< 0.01	< 0.01
Muscle	< 0.01	< 0.01	< 0.01

Laying hen feeding study

A transfer study was conducted in White Leghorn chickens (1.70–1.82 kg bw, 28 weeks old) where laying hens were fed for 21 or 28 days on diets containing 1, 5 or 10 ppm diquat in the feed (Lai *et al.*, 1977). Each group were fed with basal feed treated with a known amount of diquat dibromide monohydrate. The dose level for each group was adjusted by mixing treated and untreated feed to obtain concentrations of diquat in feed on a dry weight basis of 1.0, 5.0 and 10 ppm. Mean daily food consumption during dosing period was 116–128 g/hen/day for the control group and 117–125, 112–141 and 109–140 g/hen/day for the 1, 5 and 10 ppm feed level groups respectively. The efficiency of egg production was not affected by the dosing with mean egg production during dosing period of 89–96% for the control group and 86–98%, 90–98% and 91–99% for the 1, 5 and 10 ppm feed level groups respectively. Eggs were collected daily and retained for analysis from days 1, 7, 14, 21, 28 and also day 35 (after a depuration period of 7 days). Eggs from each dose group were pooled for each day of sampling. Ten chickens from each group (excluding control Group 1) were sacrificed after 21 days and 28 days of treatment and after 7 days of depuration (study day 35). Samples of liver, muscle, heart, gizzard, skin and fat were collected from all sacrificed animals. The period of storage prior to analysis was not reported.

No residues of diquat were detected (< 0.005 mg/kg) in any of the egg, fat, muscle, liver or heart samples. With the exception of a residue of 0.006 mg/kg at the highest treatment rate on day 21, no detectable residues (< 0.005 mg/kg) were found in any of the chicken skin samples. Residues in gizzard reached a maximum of 0.019 mg/kg at day 21 in the birds dosed at the equivalent of 10 ppm,

were 0.018 mg/kg at day 28, declined during depuration to < 0.005 mg/kg, though a residue of 0.006 mg/kg remained in the 5 ppm group.

Table 61 Summary of diquat residues (mg/kg) in hen egg and tissues at end of dosing (day 28) [a]

Matrix	1 ppm	5 ppm	10 ppm
Egg	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)
Liver	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)
Muscle	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)
Heart	< 0.01	< 0.01	< 0.01
Gizzard	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (0.011, 0.007)	0.02 [b] (0.015, 0.021)
Skin	< 0.01	< 0.01	< 0.01
Fat	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)	< 0.01 [b] (< 0.01, < 0.01)

[a] LOD = 0.005 mg/kg, LOQ = 0.01 mg/kg.

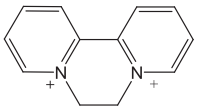
[b] Mean of duplicate determinations

APPRAISAL

Diquat is a non-selective contact herbicide with uses on many crops. Diquat has been evaluated several times by the JMPR with the initial evaluation in 1970 and the latest in 1994. Diquat was scheduled at the Forty-fourth Session of the CCPR (2012) for periodic re-evaluation of toxicology and residues by the 2013 JMPR.

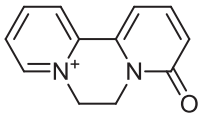
The Meeting received information on the metabolism of diquat in animals, on crops, methods of residue analysis, freezer storage stability, GAP information, supervised residue trials, fate of residue during storage and processing, and livestock feeding studies.

Diquat is 6,7-dihydrodipyrido[1,2-a:2',1'-c]pyrazinediium dibromide.

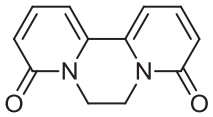


Metabolites referred to in the appraisal are addressed by their common names:

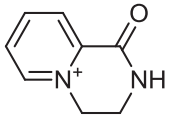
Diquat monopyridone



Diquat dipyridone



TOPPS



Animal metabolism

Metabolism of diquat in goats and hens involves formation of diquat dipyridone and diquat monopyridone. TRR are expressed in terms of diquat ion.

In a study where a lactating goat was orally treated once daily for 7 consecutive days with ring labelled [^{14}C]-diquat at a dose equivalent to 90 ppm in the feed, approximately 97% of the administered dose was recovered with the majority in the excreta (84% faeces, < 1% urine) or gastrointestinal tract (12%). The radioactivity in the tissues ranged from 0.003 in fat to 0.079 mg equiv/kg in kidney. TRR values in milk were up to 0.015 mg equiv/kg during the dosing period with

levels not reaching a plateau after seven days of dosing. Major components of the ^{14}C residues were unchanged diquat ion (liver 22% TRR), diquat dipyridone (kidney 29% TRR, liver 33% TRR, muscle 46% TRR, fat 20% TRR, milk 82% TRR) and diquat monopyridone (kidney 21% TRR, liver 13% TRR, muscle 13% TRR).

Laying hens were orally treated once daily in experiments where a single hen received a single dose at 4-5 ppm, five daily doses at 4–5 ppm or 14 doses daily doses at 0.4–0.5 ppm. By three days after administering the last dose the majority (> 94%) of the dose was recovered in the excreta. Radioactivity in tissues of hens dosed at 0.4-0.5 ppm ranged from 0.00010 mg equiv/kg in fat to 0.00045 mg equiv/kg in kidney. The ^{14}C levels in egg whites and yolks reached a plateau of 0.00003 and 0.00014 mg equiv/kg respectively by seven days of dosing. Yolk from day 9+10 eggs contained diquat ion (26% TRR), yolks from day 7 contained diquat monopyridone (85% TRR) and egg yolks from day 11 contained TOPPS (10% TRR).

In another study laying hens were each given daily doses of ^{14}C-ring labelled diquat by oral gavage for 4 days at the equivalent of 32 ppm in the diet. At sacrifice 18 hours after the last dose, radioactive residues in the muscle, fat and eggs were all < 0.01 mg equiv/kg. Levels of radioactivity in liver and kidney were 0.045 and 0.058 mg equiv/kg respectively with unchanged diquat (liver 48% TRR, kidney 12% TRR) and diquat monopyridone (liver 3.9% TRR, kidney 15% TRR) the main residue components. Minor components identified were TOPPS (liver 1.8% TRR, kidney 3.9% TRR) and diquat dipyridone (liver 3.1% TRR, kidney 6.6% TRR).

In an additional study laying hens fed a diet containing powdered grain harvested from barley plants treated with [^{14}C]-diquat, the dose was equivalent to 1 to 1.5 ppm in the feed for 11 consecutive days with hens sacrificed 4 hours or 7 days after the last exposure. The major components of the ^{14}C in the grain were diquat ion (17% TRR) and TOPPS (8.7% TRR). Most of the administered dose was recovered in the excreta (84–89%) with less than 0.1% recovered in eggs. Radioactive residues in egg white reached a plateau by day 5 of dosing with a maximum level of 0.0006 mg equiv/kg while egg yolk reached a plateau by day 8 with a maximum residue of 0.0039 mg equiv/kg. In tissues at sacrifice 4 hours after last exposure, ^{14}C residues were highest in kidney (0.014 mg equiv/kg) and much lower in muscle and fat at 0.0009 and 0.0022 mg equiv/kg respectively. Diquat ion was a minor component of the ^{14}C residues in egg yolk at 0.9% TRR with TOPPS and diquat monopyridone present at 3.5 and 3.0% TRR respectively.

Metabolism in laboratory animals (rat) was summarized and evaluated by the WHO panel of the JMPR in the present meeting. The metabolism of diquat in ruminants and laying hens is adequately understood. In both goats and hens diquat is oxidised to form diquat monopyridone and diquat dipyridone. TOPPS is found as a minor metabolite (< 10% TRR) in hens but was not detected in studies of the metabolism of diquat by goats or rats.

Plant metabolism

Diquat is used for two different situations:

Directed sprays for weed control (crop not intentionally treated)
Use as a crop desiccant to facilitate crop harvest (crop treated)

Plant metabolism studies were conducted with diquat to investigate these two situations.

Application prior to crop emergence

A single application of ^{14}C-diquat was made to soil into which tomato seeds had been sown prior to emergence. Residues in mature fruit and leaves harvested 112 days after application were < 0.001 and 0.002 mg equiv/kg respectively and were not analysed further.

Crop desiccation

The use of diquat as a pre-harvest desiccant was investigated in potato and rape following foliar spray application to the crop. Since the plants are senescent at the time of application or die quickly after application, metabolism is essentially stopped and translocation from the treated parts of the crops

into other plant parts such as seeds and roots is reduced. Following use as a crop desiccant, diquat ion was the major component of the ^{14}C residue in the skin and flesh of potato tubers accounting for more than 70% of TRR with no other individual component comprising more than 10% TRR. The major component in rape seed harvested from crops, following pre-harvest desiccation, was diquat ion at 48% TRR with smaller amounts of TOPPS (7.8% TRR) and diquat monopyridone (2.0% TRR).

The metabolism of diquat by plants is well understood. Following directed application to weeds using shielded sprayers there is minimal contact of the crop with diquat. A portion of the spray will reach the soil, but as described later, diquat is strongly absorbed by soil components such that it is largely unavailable for uptake by plant roots.

Following use as a pre-harvest desiccant, diquat ion is the major component of the ^{14}C residue in those parts exposed to direct sprays with TOPPS and diquat monopyridone present as minor components. Only low levels of radioactivity are found in plant parts such as potato tubers that are not directly exposed to the spray (< 0.05 mg equiv/kg).

Environmental fate

The Meeting received information on soil aerobic metabolism, soil photolysis and aqueous hydrolysis properties of [^{14}C]-diquat. Studies were also received on the behaviour of [^{14}C]-diquat in a rotational crop situation.

Diquat residues are persistent in soils, however residues in soil are strongly bound to soil components and not available for uptake by plants. As such, residues in soil should not contribute significantly to the residues in succeeding crops.

In soil incubation studies under aerobic conditions in the dark, diquat disappeared with a half-life that was > 290 days. In the absence of soil, diquat was rapidly and extensively degraded by soil micro-organisms normally found in soil pore water to give a small number of non-volatile degradation products (not identified) with mineralisation to CO_2. The DT50 for degradation in solutions of soil micro-organisms is rapid at < 1 week. Addition of clay to these solutions essentially stopped further degradation confirming that sorbed diquat is not available for biological degradation.

The degradation product TOPPS is also persistent in soils. Studies on the aerobic soil degradation of the diquat metabolite TOPPS estimated DT_{50} values for degradation of 28 to 757 days.

Soil photolysis has negligible effect on degradation. In a study with application of ^{14}C-diquat on the surface of a sterilised loam soil, the DT_{50}s for photolytic degradation on dry and wet soil were 237 and 37 days respectively.

In a study of aqueous photolysis the DT_{50} for degradation was 31 hours. The major degradation product was TOPPS with smaller amounts of diquat monopyridone and 1-hydroxy-3,4-dihydro-1H-pyrido[1,2-a]pyrazine-2-carboxylic acid formed.

In a confined rotational crop study with wheat, lettuce and carrot, a plot of sandy loam soil was treated with [^{14}C]-diquat at the equivalent of 1.1 kg ai/ha and crops sown 30, 120 and 365 days. At normal commercial harvest, crops grown in soil containing ^{14}C-diquat showed negligible uptake of radioactivity (TRR up to 0.02 mg equiv/kg). Residues above the LOD of 0.008 mg equiv/kg could have been due to contamination with adhering soil. Crops grown in rotation with diquat-treated crops are not expected to contain residues of diquat ion or diquat degradation products. Diquat residues in soil should contribute little to residue levels in rotational crops.

Methods of analysis

The Meeting received description and validation data for analytical methods for residue analysis of diquat in various plant and animal commodities. Early methods used in field trials generally involved extraction of residues by reflux with sulphuric acid with clean-up on cation exchange columns. Following reduction of diquat ion with alkaline dithionite or sodium borohydride, detection was initially achieved spectrophotometrically (350–450 nm). In more recent methods the diquat ion recovered from the cation exchange column is subjected to HPLC-UV or GC-NPD for quantitation. In

the case of animal commodities, trichloroacetic acid is sometimes used in place of sulphuric acid for the extraction step. LOQs were in the range 0.01 to 0.1 mg/kg.

The most recent advance in methods has been the use of LC-MS/MS which allows for the clean-up steps to be omitted with LOQs of 0.005 mg/kg for animal commodities, 0.006 mg/kg for potato and barley and 0.02 mg/kg for citrus.

The efficiency of the acid extraction step has been demonstrated during the metabolism studies where the majority of the total radioactive residue (TRR) was recovered in the acid extracts.

Multi-residue methods are currently not validated for diquat.

Stability of pesticide residues in stored analytical samples

The Meeting received information on the stability of diquat in samples of commodities from crops stored frozen.

Diquat is stable for at least 24 months in homogenised samples of spinach, wheat grain, wheat straw, rape seed, lentils, orange fruit and potato tubers fortified with diquat and stored frozen.

The periods of demonstrated stability cover the frozen storage intervals used in the residue studies.

Definition of the residue

In metabolism studies of diquat in goats and hens diquat ion was a significant component of the residue in hen (48% TRR liver; 12% TRR kidney) and goat (22% TRR liver; 4.3% TRR kidney) tissues. Other major components were diquat monopyridone (13% TRR liver; 13% muscle) and diquat dipyridone (33% TRR liver; 29% kidney; 20-46% muscle and fat; > 80% milk) with small amounts of TOPPS (1.8% liver; 3.9% kidney) formed in hens. Radioactivity in egg yolks comprised mostly diquat monopyridine (up to 85% TRR) and diquat ion (up to 26% TRR) with smaller amounts of TOPPS (up to 10%TRR).

The major components of the residue in livestock are diquat ion, diquat monopyridone and diquat dipyridone and should be considered for inclusion in the residue definition for compliance with MRLs and estimation of dietary intake in animal commodities. However, at realistic livestock exposures no residues of diquat ion, diquat monopyridone or diquat dipyridone are expected. Additionally, current analytical methods for tissues have only been validated for determination of residues of diquat. Noting the above, the Meeting considered diquat ion to be a suitable as a residue definition for compliance with MRLs and estimation of dietary intake for animal commodities.

The log P_{ow} for diquat is -4.6 suggesting diquat residues are not fat soluble. There was only a small difference in residue levels in muscle and fat confirming diquat ion does not preferentially partition into fat and that the residue should not be classed as fat soluble. The Meeting decided that residues of diquat are not fat soluble.

Diquat is used on crops for two different situations:

Directed sprays or pre-emergent application for weed control (crop not intentionally treated)
Use as a crop desiccant to facilitate crop harvest (crop treated)

No residues are expected in situations where crops are not directly sprayed (directed sprays for weed control, pre-emergent or pre-sowing applications). The conclusion is supported by the results of confined crop rotation studies where soil residues were not taken up by crops.

Following use as a crop desiccant, diquat ion was the major component of the residue in flesh and skins of potato tubers and in rape seeds accounting for more than 70% of TRR in potatoes and 48% TRR in rape seeds. TOPPS was also detected in rape seed but represented less than 10% of the TRR. In plants, the majority of diquat-related residues in crops are accounted for in the previous residue definition; diquat ion.

Based on the above the Meeting confirmed the previous residue definition for compliance with MRLs and estimation of dietary intake for plant commodities.

Definition of the residue for compliance with MRL and estimation of dietary intake (animal and plant commodities): *diquat ion*

The residue is not fat soluble.

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for diquat on citrus fruits, pome fruits, strawberries, banana, tomato, pulses, carrots, potatoes, rape, sunflower and coffee as well as for some animal feed commodities.

As no data were available for alfalfa fodder, barley, maize, oats, rice, sorghum and wheat the the Meeting agreed to withdraw previous recommendations for these commodities.

A range of uses for diquat involve the application to weeds growing under trees in a variety of countries. The Meeting noted the results of soil aerobic metabolism and confined rotational crop studies that show that diquat in soil is not available for plant uptake. As application to weeds growing under trees is not expected to result in residues in harvested commodities the Meeting decided to evaluate the use on tree crops together, using the data on the crops supplied as mutual support for recommendations for those commodities with approved use-patterns. Diquat is approved for weed control in citrus fruit (Brazil, Costa Rica, Dominican Republic), pome fruit (Slovakia), banana/plantain (Belize, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama), cashews (Dominican Republic), coffee (Belize, Brazil, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama), stone fruit (Slovakia) and also apple and other fruit trees (Canada, USA).

Tree crops (application to weeds)

Field trials involving citrus orchards where diquat was applied to weeds were conducted in Brazil and were available to the Meeting.

The GAP for citrus in Brazil is application directed to weeds at 0.5 kg ai/ha with a PHI of 14 days. In the trials matching this GAP diquat residues in ranked order were (n=3): < 0.01 (2), < 0.02 mg/kg. Residues in trials on citrus that utilized rates higher than permitted in Brazil were < 0.01 (2) mg/kg.

Field trials involving apples were conducted in Europe were made available to the Meeting. The GAP for apples in Slovakia is application directed to weeds at 1.0 kg ai/ha with a PHI not specified (unnecessary). In twelve trials matching this GAP and with PHIs ranging from 0 to 171 days residues were (n=12): < 0.01 (10), < 0.05 (2) mg/kg.

Diquat is permitted to be used for weed control in banana plantations in various countries of central America (Belize, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua, Panama) with an application rate of 0.6 kg ai/ha and no PHI required. In six trials from Costa Rica, Ecuador and Guatemala that matched GAP residues were < 0.05 mg/kg.

Diquat is approved in a range of Central and South American countries for weed control in coffee plantations including Belize, Brazil, Costa Rica, Dominican Republic, El Salvador, Guatemala, Nicaragua and Panama with maximum application rate of 0.5–0.6 kg ai/ha and a PHI typically 0 days. In trials from Costa Rica and Guatemala residues in coffee beans were < 0.05 (6) mg/kg.

The Meeting concluded that residues of diquat are not expected in harvested commodities from tree crops when application is to the weeds. The Meeting considered an LOQ of 0.02 mg/kg achievable and decided to estimate an STMR of 0 mg/kg, an HR of 0 mg/kg and a maximum residue level of 0.02 (*) mg/kg for citrus fruit, pome fruit, banana and coffee beans and to extrapolate the values to cashew apple (including cajou), cashew nuts and stone fruit.

Berries and other small fruit (application to weeds)

Strawberries

Trials were available from the UK. The GAP for strawberry in Sweden is a single application to weeds at 0.5 kg ai/ha before flowering or after harvest (use of spray shield) with no PHI required.

Residues in three trials from the UK at > 1.4 times the GAP of Sweden were: < 0.05 (3) mg/kg.

The Meeting utilized trials approximating the GAP of Sweden to estimate a maximum residue level for strawberries. Noting the exaggerated rates used in the three trials, the long interval between application and harvest and the requirement for a physical barrier when spraying, the Meeting estimated a maximum residue level of 0.05 * mg/kg, an STMR of 0 mg/kg and an HR of 0 mg/kg for strawberries.

Fruiting vegetables other than Cucurbits

Diquat is permitted to be used for weed control in row crops (includes tomatoes) in Spain with an application rate of 0.45 kg ai/ha and using spray protectors or shields, PHI 15 days.

Only one trial utilized a spray screen. The application rate was 2 times the GAP of Spain and residues were < 0.01 mg/kg. In another seven trials where the application rate was 2 times the maximum application rate of Spain and that did not use a spray shield the residues were also < 0.01 (7) mg/kg. The Meeting considered there is no expectation of residues above the LOQ for tomatoes and agreed to extrapolate the conclusion to fruiting vegetables other than cucurbits except sweet corn and fungi.

The Meeting estimated a maximum residue level of 0.01* mg/kg, an STMR of 0 mg/kg and an HR of 0 mg/kg for fruiting vegetables, other than cucurbits (except sweetcorn, fungi and mushrooms).

Pulses (pre-harvest desiccation)

Residue data from trials in common beans were made available from Germany and the USA for pre-harvest desiccation. The use pattern in Germany is 0.6 kg ai/ha with a PHI of 5 days. Analytical recoveries reported for trials from Germany on beans were low making the trials unsuitable for estimating maximum residue levels. The use pattern in Canada is for pre-harvest desiccation of beans at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In eight trials conducted in the USA approximating Canadian GAP residues were < 0.05 (8) mg/kg. The Meeting estimated an STMR of 0.05 mg/kg and a maximum residue level of 0.05* mg/kg for beans, dry replacing the previous recommendation of 0.2 mg/kg.

In Canada, diquat is permitted for pre-harvest desiccation of peas at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In five trials conducted in the USA approximating Canada GAP residues were: 0.05, 0.05, 0.09, 0.11 and 0.56 mg/kg. The Meeting considered five trials insufficient to estimate a maximum residue level for peas dry.

Pre-harvest desiccation sprays are permitted in Slovakia on peas at up to 0.8 kg ai/ha with a PHI of 6 days. In nine trials conducted in Europe, residues following a pre-harvest desiccation application at 0.6 kg ai/ha and after a 6 day PHI were: 0.03, 0.04, 0.04, 0.04, 0.05, 0.05, 0.06, 0.10, 0.15 mg/kg. The Meeting estimated an STMR of 0.05 mg/kg and a maximum residue level of 0.3 mg/kg for peas, dry confirming the previous recommendation.

In Canada, pre-harvest desiccation sprays are permitted in lentils at up to 0.41 kg ai/ha for ground application and 0.55 kg ai/ha for aerial application with a PHI of 4 days. In three trials conducted in USA with application at 0.42 kg ai/ha residues were < 0.05, 0.13 and 0.54 mg/kg at 4 days after application. The Meeting considered three trials insufficient to estimate a maximum residue level for diquat in lentils and withdrew its previous recommendation of 0.2 mg/kg.

In Canada, pre-harvest desiccation sprays are permitted in soya beans at up to 0.56 kg ai/ha with a PHI of 4 days. In seven trials conducted in USA at 0.56 kg ai/ha residues were < 0.01, 0.02, 0.03, 0.03, 0.04, 0.09, 0.16 mg/kg in samples harvested 7 to 10 days after application. The Meeting noted there was little decline in residues between 4 and 10 days and decided to use the data to estimate an STMR of 0.03 mg/kg and a maximum residue level of 0.3 mg/kg for soya beans (dry) replacing its previous recommendation of 0.2 mg/kg.

Carrots (directed application for weed control)

In Spain diquat is approved for general weed control in row crops including carrots (GAP: 0.45 kg ai/ha using spray protectors, PHI 15 days). In three trials in Germany and Italy that used spray shields and with application rates that were two times GAP of Spain residues were: 0.01, < 0.02, < 0.02 mg/kg.

The Meeting considered three trials insufficient to estimate a maximum residue level for carrots.

Potato (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of potato crops in various countries. Pre-harvest desiccation use-patterns approved in various countries include Austria (GAP: 0.5 kg ai/ha, PHI 10 days), Brazil (GAP 0.5 kg ai/ha, PHI 7 days), Canada (GAP 2×0.84 kg ai/ha, PHI 0 days), Germany (GAP: 1 kg ai/ha, PHI 10 days), the Netherlands (GAP: 0.8 kg ai/ha, max 2 sprays and 1 kg ai/ha per crop, PHI 0 days), Spain (GAP: 0.8 kg ai/ha, PHI 15 days), the UK (GAP: 1.0 kg ai/ha, max 2 sprays and 1 kg ai/ha per crop, PHI 0 days or 14 days if storing potatoes) and the USA (GAP:0.56 kg ai/ha, PHI 7 days).

In trials in Europe approximating the GAP of the UK residues were: < 0.01 (10), 0.01, 0.01, 0.01, 0.01, 0.02, 0.02 mg/kg.

In trials conducted according to the GAP of USA residues were: < 0.05 (6), 0.06, 0.06 mg/kg.

Using the residue data from the USA, the Meeting estimated an STMR of 0.05 mg/kg, an HR of 0.06 mg/kg and a maximum residue level of 0.1 mg/kg for potato replacing the previous recommendation of 0.05 mg/kg.

Rape seed, (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of oilseed rape in Austria (GAP: 0.6 kg ai/ha, PHI 5 days), Canada (GAP: 0.41 kg ai/ha, PHI 14 days), Germany (GAP: 0.6 kg ai/ha, PHI 5 days), the UK (GAP: 0.6 kg ai/ha, PHI 7-10 days) and the USA (GAP: 0.56 kg ai/ha, PHI 7 days).

Residues in rape seeds from trials conducted in Europe approximating German GAP were (n=12): 0.02, 0.03, 0.03, 0.05, 0.06, 0.07, 0.08, 0.10, 0.12, 0.22, 0.27, 0.33, 0.38, 0.42, 0.44, 0.45 mg/kg.

In trials approximating GAP in the USA total residues in rape seeds were (n=9): 0.06, 0.24, 0.30, 0.30, 0.46, 0.48, 0.52, 0.72, 0.82 mg/kg.

The Meeting considered the trials from the USA would lead to the higher maximum residue level and estimated an STMR of 0.49 mg/kg and a maximum residue level of 1.5 mg/kg for rape seed replacing its previous recommendation of 2 mg/kg.

Sunflower seed (pre-harvest desiccation)

Diquat is approved for pre-harvest desiccation of sunflowers in Canada (GAP: 0.41 kg ai/ha, PHI 15 days) and Slovakia (GAP: 0.6 kg ai/ha, PHI 6 days). Residues in trials from France approximating Slovakian GAP were (n=13): < 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.11, 0.15, 0.19, 0.41, 0.46, 0.54 mg/kg.

The Meeting estimated an STMR of 0.11 mg/kg and a maximum residue level of 0.9 mg/kg for sunflower seed replacing its previous recommendation of 1 mg/kg.

Animal feeds

Pea fodder (pre-harvest desiccation)

Residue levels occurring in pea straw were evaluated. In four trials conducted in the UK approximating GAPs in Austria (0.6 kg ai/ha, PHI 5 days) and France (0.6 kg ai/ha, PHI 4 days) residues in pea straw were 3.6, 14, 18, 25 mg/kg all on an as received basis. The Meeting estimated median and highest residues of 16 and 25 mg/kg on an as received basis for residues of diquat in pea straw.

The Meeting estimated a median residue of 16 mg/kg, a highest residue of 25 mg/kg (both on an as received basis) and a maximum residue level of 50 mg/kg for pea fodder (on a dry weight basis).

The Meeting received two trials conducted in France that measured residues in soya bean forage. The meeting considered two trials insufficient to make recommends for soya bean forage.

Fate of residues during processing

The Meeting received information on the fate of incurred residues of diquat during the processing of soya bean, oilseed rape/canola and sunflower seeds. Studies of the hydrolysis of diquat under a range of conditions showed diquat is stable.

Summary of selected processing factors for diquat

Raw commodity	Processed commodity	Individual PF	Best estimate PF	$STMR_{RAC}$ (mg/kg)	$STMR_{RAC}$ × PF (mg/kg)
Soya bean	Hulls	2.6 3.6	3.1	0.03	0.093
	Meal	0.7 1.0	0.85		0.0255
	Oil	< 0.04 < 0.07	< 0.055		< 0.00165
Rape/canola	Meal	0.17 0.20 0.58 0.76	0.39	0.49	0.19
	Oil	< 0.01 < 0.01 < 0.03 < 0.03	< 0.02		< 0.0098
Sunflower seed	Oil	< 0.1 < 0.1 < 0.1 < 0.5 < 0.6 < 0.6 < 0.7 < 0.8 < 0.8 <1	< 0.6	0.11	< 0.066
	Cake	1 1 1.2 1.2 1.2 1.2 1.3 1.3 1.3 1.3	1.2		0.132

Residues are not expected in oils obtained from treated crops.

Residues in animal commodities

Farm animal feeding studies

The Meeting received information on the residue levels arising in tissues and milk when dairy cows were fed a diet containing incurred residues of diquat at dietary levels of 18, 50 and 84 ppm for 30 consecutive days. There were no residues of diquat at or above the LOQ (0.001 mg/kg) in any of the milk samples from any of the dose groups, throughout the duration of the study. There were no residues of diquat at or above the LOQ (0.01 mg/kg) in any of the tissue samples (liver, kidney, fat and muscle) from any of the dose groups.

The Meeting also received information on the residue levels arising in tissues and eggs, when laying hens were fed a diet containing diquat at total dietary levels of 1, 5 and 10 ppm diquat for 21 or 28 consecutive days. No residues of diquat above the LOQ (< 0.01 mg/kg) were found in any of the egg, fat, muscle, skin, liver or heart samples.

Animal commodity maximum residue levels

Dietary burden calculations for beef cattle and dairy cattle and poultry are provided below. The dietary burdens were estimated using the OECD diets listed in Appendix IX of the 2009 edition of the FAO Manual.

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

	US-Canada		EU		Australia		Japan	
	max	mean	Max	Mean	max	Mean	max	Mean
Beef cattle	0.12	0.09	7.3	4.7	28 [a]	18 [c]	0.09	0.09
Dairy cattle	2.9	1.9	8.7	5.6	20 [b]	13 [d]	0.09	0.09
Poultry Broiler	0.06	0.06	0.11	0.10	0.08	0.08	0.04	0.04
Poultry Layer	0.06	0.06	2.9 [e]	1.9 [f g]	0.08	0.08	0.05	0.05

[a] Highest maximum beef or dairy cattle dietary burden suitable for MRL estimates for mammalian meat

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

[c] Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

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

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

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

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

Animal commodity maximum residue levels

The Meeting concluded that at the maximum estimated dietary burdens for cattle of 28 ppm and 2.9 ppm for poultry no residues are expected in tissues, milk and eggs.

The Meeting estimated HR and STMR values of 0 for milk, muscle, edible offal and fat. The Meeting estimated the following maximum residue levels: milk 0.001* mg/kg; meat (mammalian except marine mammals) 0.01* mg/kg and edible offal 0.01* mg/kg to replace its previous recommendations of: milk 0.01 mg/kg; meat (mammalian except marine mammals) 0.05 mg/kg and edible offal 0.05 mg/kg.

For poultry no residues are expected. The Meeting estimated the following maximum residue levels for poultry commodities: poultry meat 0.01* mg/kg; poultry edible offal 0.01* mg/kg and eggs 0.01* mg/kg to replace its previous recommendations of: eggs 0.05 mg/kg; poultry meat 0.05 mg/kg and poultry edible offal 0.05 mg/kg.

The Meeting estimated the following STMR values: poultry meat 0 mg/kg; poultry fat 0 mg/kg; poultry edible offal 0 mg/kg and eggs 0 mg/kg.

RECOMMENDATIONS

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

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

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

The residue is not fat soluble.

Table of recommendations

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
AL 1020	Alfalfa fodder	W	100		

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
FI 0327	Banana	0.02*		0	0
GC 0640	Barley	W	5		
VD 0071	Beans (dry)	0.05	0.2	0.05	
FT 2352	Cajou (pseudofruit)	0.02 *		0	0
FT 0292	Cashew apple	0.02 *		0	0
TN 0292	Cashew nut	0.02 *		0	0
FC 0001	Citrus fruits	0.02 *		0	0
SB 0716	Coffee beans	0.02 *		0	
MO 0105	Edible offal (mammalian)	0.01*	0.05	0	0
PE 0112	Eggs	0.01*	0.05	0	0
VO 0050	Fruiting vegetables, other than cucurbits (except sweetcorn, fungi and mushrooms)	0.01*		0	0
VD 0533	Lentil (dry)	W	0.2		
GC 0645	Maize	W	0.05		
MM 0095	Meat (from mammals other than marine mammals)	0.01*	0.05	0	0
ML 0106	Milks	0.001*	0.01	0	0
GC 0647	Oats	W	2		
VD 0072	Peas (dry)	0.3	0.2	0.05	
AL 0072	Pea fodder	50		16	25
FP 0009	Pome fruits	0.02*		0	0
VR 0589	Potato	0.1	0.05	0.05	0.06
PM 0110	Poultry meat	0.01*	0.05	0	0
PO 0111	Poultry, Edible offal of	0.01*	0.05	0	0
SO 0495	Rape seed	1.5	2	0.49	
GC 0349	Rice	W	10		
CM 0649	Rice, Husked	W	1		
CM 1205	Rice, Polished	W	0.2		
GC 0651	Sorghum	W	2		
VD 4521	Soya bean (dry)	0.3	0.2	0.03	
FS 0012	Stone fruits	0.02*		0	0
FB 0275	Strawberry	0.05 *		0	0
SO 0702	Sunflower seed	0.9	1	0.11	
OC 0172	Vegetable oils, Crude	W	0.05		
	Vegetables (except as otherwise listed)	W	0.05		
GC 0654	Wheat	W	2		

Commodity		Recommended MRL (mg/kg)		STMR or STMR-P (mg/kg)	HR, HR-P, highest residue (mg/kg)
CCN	Name	New	Previous		
CM 0654	Wheat bran, Unprocessed	W	2		
CF 1211	Wheat flour	W	0.5		
CF 1212	Wheat wholemeal	W	2		

Table of recommendations

Commodity		STMR or STMR-P (mg/kg)	HR-P or highest residue (mg/kg)
CCN	Name		
	Rape seed meal	0.19	
OR 0495	Rape seed oil, edible	0.0098	
	Sunflower seed cake/meal	0.132	
OR 0702	Sunflower seed oil, edible	0.066	
	Soya bean hulls	0.093	
	Soya bean meal	0.0255	
OR 0541	Soya bean oil, refined	0.00165	

DIETARY RISK ASSESSMENT

Long-term intake

The WHO Panel of the 2013 JMPR established an Acceptable Daily Intake (ADI) of 0–0.006 mg/kg bw for diquat.

The evaluation of diquat resulted in recommendations for MRLs and STMR values for 30 raw and processed commodities. Where data on consumption were available for the listed food commodities, dietary intakes were calculated for the 13 GEMS/Food Consumption Cluster Diets. The results are shown in Annex 3 of the 2013 JMPR Report.

The IEDIs in the thirteen Cluster Diets, based on the estimated STMRs were 0–4% of the maximum ADI (0.006 mg/kg bw). The Meeting concluded that the long-term intake of residues of diquat from uses that have been considered by the JMPR is unlikely to present a public health concern.

Short-term intake

The WHO Panel of the 2013 JMPR established an Acute Reference Dose (ARfD) of 0.8 mg/kg bw for diquat. The IESTIs represented 0% of the ARfD of 0.8 mg/kg bw.

The Meeting concluded that the short-term intake of residues of diquat resulting from uses that have been considered by the JMPR is unlikely to present a public health concern.

REFERENCES

Code	Author	Year	Title
PP901/0589	Anderson L	1994	The Determination of Residues of Paraquat and Diquat in Crops - A Second Derivative Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RAM 252/01. GLP, Unpublished. Syngenta File No PP901/0589
PP901/0328	Anderson L, Barnaud C	1995	Diquat: Residue Levels in Soyabean from Trials Carried out in France During 1994. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1934B. GLP, Unpublished. Syngenta File No PP901/0328
PP901/0522	Anderson L, Earl M	1996	Diquat: Residues in Soil Following Desiccation of Crops with Reglone (Final Report).Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ2167B.GLP, Unpublished. Syngenta File No PP901/0522
PP148/0350	Anderson L.	1995	The Determination of Residues of Paraquat and Diquat in Crops - A Second Derivative Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RAM 252/02. GLP, Unpublished. Syngenta File No PP148/0350
PP901/0226	Anderson L., Boseley A.	1995	The Determination of Residues of Paraquat and Diquat in Crops and Soil - a High Performance Liquid Chromatographic Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RAM 272/01. GLP, Unpublished. Syngenta File No PP901/0226
PP901/0225	Anderson L., Boseley A.	1997	The Determination of Residues of Paraquat and Diquat in Crops and Soil - A High Performance Liquid Chromatographic Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RAM 272/02. Not GLP, Unpublished. Syngenta File No PP901/0225
PP901/0689	Anderson L., Boseley A.	1995a	Paraquat and Diquat: Validation of an HPLC Analytical Method for the Determination of the Residues in Crops and Soil. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ2013B. GLP, Unpublished. Syngenta File No PP901/0689
PP901/0285	Anderson L., Lant M.	1994	Diquat: Residue Levels in Carrots, Lettuce and Onions from Trials carried out in Italy during 1993. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1730B. GLP, Unpublished. Syngenta File No PP901/0285
PP901/0424	Anderson L., Lant M., Renard C.	1995	Diquat: Residue Levels in Sunflowers from Trials Carried Out in France During 1993. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1734B. GLP, Unpublished. Syngenta File No PP901/0424
PP901/0426	Anderson L., Renard C.	1995	Diquat: Residue Levels in Sunflowers from Trials Carried out in France during 1994. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1904B. GLP, Unpublished. Syngenta File No PP901/0426
PP148/0910	Anon	1972	Determination of Residues of Paraquat in Crops - Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 001. Not GLP, Unpublished. Syngenta File No PP148/0910
PP148/0972	Anon	1972a	Determination of Residues of Paraquat in Crops - Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 001. Not GLP, Unpublished. Syngenta File No PP148/0972
PP901/0230	Anon	1972b	Determination of Residues of Diquat in Crops and Animal Tissues - spectrophotometric method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 005. Not GLP, Unpublished. Syngenta File No PP901/0230
PP901/0594	Anon	1970	Analysis of Diquat Residues – Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RM-5. Not GLP, Unpublished. Syngenta File No PP901/0594
PP901/1005	Anon	1972	Determination of Residues of Diquat in Milk and Water - Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 007. Not GLP, Unpublished. Syngenta File No PP901/1005
PP901/0478	Anon	1976	The Colorimetric Determination of Paraquat in Biological Samples, Tested Biochemical Method: TBM/3. ICI Industrial Hygiene Research Laboratories, Jealott's Hill Research Centre, Bracknell, Berkshire, RG42 6EY, UK. Appended to Syngenta file No. PP901/0478.

Code	Author	Year	Title
	Aramendia, M.A.; Borau, V.; Lafont, F.; Marinas, A.; Marinas, J.M.; Moreno, J.M.; Porras, J.M.; Urbano, F.J.	2006	Determination of diquat and paraquat in olive oil by ion-pair liquid chromatography-electrospray ionization mass spectrometry (MRM). Food Chemistry 97: 181-188.
ASF886_50000	Arsenovic M.	2011	Diquat - Magnitude of the Residue on Canola. Syngenta, IR-4 Project, North Brunswick, USA. IR-4 Project, North Brunswick, USA, 10091. GLP, Unpublished. Syngenta File No ASF886_50000
PP901/1438	Atkinson S.	2003	Method Verification of Diquat in Whole Potatoes. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-2044. GLP, Unpublished. Syngenta File No PP901/1438
	Calderbank A., Yuen S.H.	1966	An improved method for determining residues of diquat. Analyst, 91: 625-629.
	Chichila TM, Gilvydis DM.	1993	Determination of paraquat and diquat in low-moisture food crops using silica column cleanup and liquid chromatography with UV detection. J AOAC Int. 76:1323-1328.
	Chichila TM, Walters SM.	1991	Liquid chromatographic determination of paraquat and diquat in crops using a silica column with aqueous ionic mobile phase. J Assoc Off Anal Chem. 74:961-967.
PP148/0014	Cole J., Laws I., Stevens J., Riley D., Wilkinson W.	1986	Diquat: Long-term High-rate Trial, Frensham, UK. Crop & Soil data for the period 8 - 14 years after treatment. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0481B. Not GLP, Unpublished. Syngenta File No PP148/0014
PP901/0345	Coombe N, Hughes A, Roberts S	1999	Diquat: Residue Levels in Apples from Trials Carried out in the UK during 1998. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, CEMR-850. GLP, Unpublished. Syngenta File No PP901/0345
PP901/0671	Coombe N.	1994	Validation of Zeneca Agrochemicals SOP Residue Analytical Methods for the Analysis of Diquat and Paraquat Residues in Crops. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-322. GLP, Unpublished. Syngenta File No PP901/0671
PP148/3146	Crook S., Gardinal P.	2006	Paraquat and Diquat - Residue Method for the Determination of Paraquat Dichloride (PP148) as Paraquat Cation and Diquat Dibromide (PP901) as Diquat Cation in Crop Matrices. Final Determination by LC-MS/MS. Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, GRM 012.03A. Not GLP, Unpublished. Syngenta File No PP148/3146
PP901/0306	Culoto B, de Mallmann RJ	1982	General Report Diquat (Reglone 2) Peas For Splitting or Protein Peas. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RIC3385. Not GLP, Unpublished. Syngenta File No PP901/0306
A1412A_10298	Derz K.	2012	Diquat: Metabolism in Tomato. Syngenta. Fraunhofer Institute, Schmallenberg, Germany, SYN-005/7-08/A. GLP, Unpublished. Syngenta File No A1412A_10298
A1412A_10304	Derz K.	2012a	Diquat: Metabolism in Potato. Syngenta. Fraunhofer Institute, Schmallenberg, Germany, SYN-005/7-08/B. GLP, Unpublished. Syngenta File No A1412A_10304
A1412A_10305	Derz K.	2012b	Diquat: Metabolism in Oil Seed Rape. Syngenta. Fraunhofer Institute, Schmallenberg, Germany, SYN-005/7-08/C. GLP, Unpublished. Syngenta File No A1412A_10305
PP901/1604	Devine H.	2004	Diquat: Soil Residue Survey in The Netherlands. Syngenta. CEMAS, North Ascot, United Kingdom, CEMR-2409. GLP, Unpublished. Syngenta File No PP901/1604
ASF378/0002	Devine H.	2001	Method Validation of Paraquat and Diquat in Crops (RAM 272/02). Syngenta CEMAS, North Ascot, United Kingdom, CEMR-1481. GLP, Unpublished. Syngenta File No ASF378/0002

Code	Author	Year	Title
PP901/1769	Devine H.	2004a	Diquat (PP901): Residue Study in or on Sunflowers in Southern France. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-2362. GLP, Unpublished. Syngenta File No PP901/1769
RJ1895B	Dick JP, Taylor PS, Moons B	1995	Diquat: Residue levels in lentils from trials carried out in Canada during 1993. Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell Berkshire UK. Report RJ1895B. Unpublished.
PP901_10824	Dixon K.	2012	[14C]-Diquat - Rate and Route of Degradation under Aerobic Laboratory Conditions, in Four Soils at 20°C. Syngenta. Covance Laboratories Limited, Harrogate, UK, 8217420. GLP, Unpublished. Syngenta File No PP901_10824
PP901_10825	Dixon K.	2012a	[14C]-Diquat - Rate and Route of Degradation Under Anaerobic Laboratory Conditions, at 20°C. Syngenta Covance Laboratories Limited, Harrogate, UK, 8217422. GLP, Unpublished. Syngenta File No PP901_10825
PP901_10823	Dixon K., Alderman D.	2012	[14C]Diquat: Hydrolytic Stability. Syngenta Covance Laboratories Limited, Harrogate, UK, 8217421. GLP, Unpublished. Syngenta File No PP901_10823
CGA130327_10007	Dixon K., Dove R.	2012	R32245 - Rate of Degradation of [14C]-R32245, a Soil Metabolite, under Aerobic Laboratory Conditions, in Four Soils, at 20°C. Syngenta Covance Laboratories Limited, Harrogate, UK, 8246977. GLP, Unpublished. Syngenta File No CGA130327_10007
PP901_10832	Dixon K., Gilbert J.	2012	[14C]-Diquat - Soil Surface Photolysis in Moist and Dry Layers. Syngenta Covance Laboratories Limited, Harrogate, UK, 8217423. GLP, Unpublished. Syngenta File No PP901_10832
PP901/0318	Dodsworth C	1990	Residue Levels of Diquat in Lentils. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, CRR114. GLP, Unpublished. Syngenta File No PP901/0318
PP148/0017	Dyson J, Chapman P	1995	Diquat: Long/Term High/Rate Trial. Frensham UK 1971-1991. Fate of soil residues. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, TMJ3431B. Not GLP, Unpublished. Syngenta File No PP148/0017
PP901/0436	Earl M	1994	Diquat: Residue Levels in Coffee from Trials Carried out in Costa Rica and Guatemala During 1992/93. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1607B. GLP, Unpublished. Syngenta File No PP901/0436
PP901/0240	Earl M, Boseley AD	1989	Diquat: Method Validation Data for Residue Methods (PPRAM) 5A and 6A. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. ICI Agrochemicals, Bracknell, Berkshire, United Kingdom, M4895B. GLP, Unpublished. Syngenta File No PP901/0240
PP901/0359	Earl M.	1994	Diquat: Residue Levels in Bananas from Trials Carried Out in Costa Rica and Guatemala During 1992. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. , RJ1534B 92JH180 CEMS-198. GLP, Unpublished. Syngenta File No PP901/0359
PP901/0358	Earl M.	1993	Diquat: Residue Levels in Bananas From Trials Carried out in Ecuador During 1992/93. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1487B 92JH187 CEMS-199. GLP, Unpublished. Syngenta File No PP901/0358
PP901/0319	Earl M.	1991	Diquat: Residues in Peas from Trials carried out in the United Kingdom during 1990. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M5373B. GLP, Unpublished. Syngenta File No PP901/0319
PP901/0322	Earl M., Hall G.	1994	Diquat: Residue Levels in Peas from Trials Carried Out in the United Kingdom During 1992. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ1502B. GLP, Unpublished. Syngenta File No PP901/0322
PP901/0478	Edwards M, HaywardG, Ward R, Iswaran T	1972	Diquat: Residue and Toxicology Trials with Cows Fed Treated Grass. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2653A. Not GLP, Unpublished. Syngenta File No PP901/0478
PP901/2096	Eversfield S.	2007	Independent Laboratory Validation of a Method (GRM012.03A) for the Determination of Diquat in Lettuce and Sunflower Seed. Syngenta. CEMAS, North Ascot, United Kingdom, CEMR-3531. GLP, Unpublished. Syngenta File No PP901/2096

Code	Author	Year	Title
PP901/2097	Eversfield S.	2007a	Independent Laboratory Validation of a Method (GRM012.02A) for the Determination of Diquat in Milk, Liver and Eggs. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-3530. GLP, Unpublished. Syngenta File No PP901/2097
A1412A_10251	Francisco E., Capellari A.	2003	Reglone: Magnitude de Residuos de Diquat em Citrus - Brazil, 2003. Syngenta. Syngenta Proteção de Cultivos Ltd.a, São Paulo, Brazil, M03011. GLP, Unpublished. Syngenta File No A1412A_10251
PP901/0470	French D., Leahey J.	1988	Diquat: Quantification and Characterisation of Radioactive Residue in Hen Tissues and Eggs. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0622B. GLP, Unpublished. Syngenta File No PP901/0470 (includes addendum)
PP901/0470 addendum	Fujie G.	1988	Addendum to "Diquat - Quantification and Characterisation of Radioactive Residues in Hen Tissues and Eggs" (ICI Project No. PP901AA01). Chevron Chemical, Richmond, USA. Chevron Chemical, Richmond, USA, R010/ICIVAL. GLP, Unpublished. Syngenta File No: Included in PP901/0470
PP901/0868	Fujie G.	1987	Validation Of Residue Analytical Method RM/5B-1 For Diquat In Animal Tissues. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R-10RM5B1MV. GLP, Unpublished. Syngenta File No PP901/0868
PP901/0316	Fujie G.	1988a	Magnitude of Diquat Cation Residues in Soybeans. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R010/SOYBEAN. GLP, Unpublished. Syngenta File No PP901/0316
PP901/0238	Fujie GH	1987	Validation of Residue analytical Method RM-5C for Diquat in Crops. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R-10RM5CMV. GLP, Unpublished. Syngenta File No PP901/0238
PP901/0442	Fujie GH	1988	Effect of Processing on Diquat Cation Residues in Soybeans. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R010/SOYPROC. GLP, Unpublished. Syngenta File No PP901/0442
PP148/3147	Gardinal P.	2006	Paraquat and Diquat - Validation of Analytical Method GRM012.03A for the Determination of Residues in Crop Matrices (Sunflower Seed, Sunflower Oil, Lettuce, Cereal Grain, Orange, Hop and Cabbage). Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T010449-05-REG. GLP, Unpublished. Syngenta File No PP148/3147
PP148/3005	Gardinal P.	2006a	Paraquat and Diquat - Validation of Analytical Method GRM012.02A for the Determination of Residues in Animal Matrices (Cow Milk, Muscle, Liver, Kidney, Fat, Blood, and Hens Eggs). Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, T010451-05-REG. GLP, Unpublished. Syngenta File No PP148/3005
PP148/3006	Gardinal P., Crook S.	2006	Paraquat and Diquat - Residue Method for the Determination of Paraquat Dichloride (PP148) as Paraquat Cation and Diquat Dibromide (PP901) as Diquat Cation in Animal Matrices. Final Determination by LC-MS/MS. Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, GRM 012.02A. Not GLP, Unpublished. Syngenta File No PP148/3006
PP148/0576	Gowman MA, Riley D, Newby SE	1980	Paraquat and Diquat: Long-term High-rate Trial Frensham UK, 2. Persistence and Movement in Soil and Glasshouse Bioassays. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0014B. Not GLP, Unpublished. Syngenta File No PP148/0576
PP901/0461	Hughes H., Leahey J.	1975	Diquat: Residues Resulting in the Eggs and Tissues of Hens Dosed with 14C-Diquat Desiccated Barley Grain. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2581B. Not GLP, Unpublished. Syngenta File No PP901/0461
PP901/0244	James W	1996	Paraquat and Diquat: Validation of a Method for the Determination of Residues in Crops and Soil. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Restec Laboratories Ltd., Birlingham, United Kingdom, ZEN 0396. GLP, Unpublished. Syngenta File No PP901/0244
PP901/0349	Jones S.	2000	Diquat: Residue Levels in Apples from Trials carried out in the UK during 1999. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, CEMR-1101. GLP, Unpublished. Syngenta File No PP901/0349

Code	Author	Year	Title
PP901/0636	Kennedy S H	1984	Paraquat/Diquat: Residues on Vegetables from Trials carried out during 1983 in West Germany. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M3720B. GLP, Unpublished. Syngenta File No PP901/0636
PP901/0312	Kennedy S.	1986	Diquat: Residues in Fodder Beans From Trials Carried Out During 1984 and 1985 in West Germany. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4170B. GLP, Unpublished. Syngenta File No PP901/0312
PP901/0311	Kennedy S.	1985	Diquat: Residues in Fodder Peas From Trials Carried Out During 1984 and 1985 in West Germany. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4137B. GLP, Unpublished. Syngenta File No PP901/0311
PP148/0349	Kennedy SH	1986	The Determination of Residues of Paraquat in Crops - a Spectrophotometric Method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 001B. GLP, Unpublished. Syngenta File No PP148/0349
	Kolberg DI, Mack D, Anastassiades M, Hetmanski MT, Fussell RJ, Meijer T, Mol HG.	2012	Development and independent laboratory validation of a simple method for the determination of paraquat and diquat in potato, cereals and pulses. Anal Bioanal Chem. 404:2465-2474.
PP901/1321	Kuet S, Laverty B, Pinheiro S, Bauer MP	2001a	Exploratory Study on Microbial Degradation. Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, TM4642B. Not GLP, Unpublished. Syngenta File No PP901/1321
PP901/0741	Kuet S, Pinheiro S	2001	Diquat: Rate of Intrinsic Biodegradability. Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, RJ3205B. GLP, Unpublished. Syngenta File No PP901/0741
PP901/1244	Kuet S., Pinheiro S., Morrow A., Mason G.	2001b	Diquat : Comparative Rate of Intrinsic Biodegradability with 2,4-D. Syngenta - Jealott's Hill International, Bracknell, Berkshire, United Kingdom, TM4668B. Not GLP, Unpublished. Syngenta File No PP901/1244
PP901/0479	Lai JC, Slagowski JL, Leary JB	1977	D4.2/06:RIC1718:RPT:Diquat - Chicken Feeding Study. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RIC1718. Not GLP, Unpublished. Syngenta File No PP901/0479
A1412A_10282	Langridge G	2011	Diquat: Residue Study on Tomatoes in Southern France, Spain and Italy in 2009. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4415-REG. GLP, Unpublished. Syngenta File No A1412A_10282
A1412A_10276	Langridge G	2011a	Diquat: Residue Study on Potatoes in Northern France and Austria in 2009. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4411. GLP, Unpublished. Syngenta File No A1412A_10276
A1412A_10277	Langridge G	2011b	Diquat: Residue Study on Potatoes in Southern France, Spain and Italy in 2009. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4412. GLP, Unpublished. Syngenta File No A1412A_10277
A1412A_10278	Langridge G	2011c	Diquat: Residue Study on Oilseed Rape in Northern France and Austria in 2009. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4413. GLP, Unpublished. Syngenta File No A1412A_10278
A1412A_10279	Langridge G	2011d	Diquat: Residue Study on Oilseed Rape in Southern France, Spain and Italy in 2009. Syngenta - Jealott's Hill, Bracknell, United Kingdom. CEMAS, North Ascot, United Kingdom, CEMR-4414. GLP, Unpublished. Syngenta File No A1412A_10279
PP901_10854	Langridge G.	2012	Diquat dibromide: Frozen Storage Stability of Diquat Cation in Spinach, Wheat Grain, Oilseed Rape Seed, Lentil, Orange, Potato and Wheat Straw. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4964-INT. GLP, Unpublished. Syngenta File No PP901_10854
A1412A_10290	Langridge G.	2011	Diquat: Residue Study on Apples in Northern France, Austria and Hungary in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4622. GLP, Unpublished. Syngenta File No A1412A_10290

Code	Author	Year	Title
A1412A_10294	Langridge G.	2011a	Diquat: Residue Study on Apples in Southern France, Italy and Spain in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4623. GLP, Unpublished. Syngenta File No A1412A_10294
A1412A_10296	Langridge G.	2011b	Diquat: Residue Study on Tomatoes in Southern France, Spain and Italy in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4661. GLP, Unpublished. Syngenta File No A1412A_10296
A1412A_10295	Langridge G.	2011c	Diquat: Residue Study on Potatoes in Northern France, Austria and the United Kingdom in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4671. GLP, Unpublished. Syngenta File No A1412A_10295
A1412A_10291	Langridge G.	2011d	Diquat: Residue Study on Potatoes in Southern France, Spain and Italy in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4672. GLP, Unpublished. Syngenta File No A1412A_10291
A1412A_10292	Langridge G.	2011e	Diquat: Residue Study on Oilseed Rape in Northern France, Hungary and the United Kingdom in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4659. GLP, Unpublished. Syngenta File No A1412A_10292
A1412A_10293	Langridge G.	2011f	Diquat: Residue Study on Oilseed Rape in Southern France, Spain and Italy in 2010. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4660. GLP, Unpublished. Syngenta File No A1412A_10293
A1412A_10312	Langridge G.	2012a	Diquat: Residue Study on Oilseed Rape and Processed Products in Northern France and the United Kingdom in 2011. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-4975-REG. GLP, Unpublished. Syngenta File No A1412A_10312
PP901/0220	Laws I, Kennedy SH	1986	The determination of Residues of Diquat in Crops - a spectrophotometric method. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, PPRAM 005A. Not GLP, Unpublished. Syngenta File No PP901/0220
PP901/0464	Leahey J.	1973	Diquat: A Study of the Metabolism and Residues in Hens and their Eggs. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, AR2438B. Not GLP, Unpublished. Syngenta File No PP901/0464
432113	Leary J., Slagowski J.	1970	Analysis of Diquat Residues - Method RM-5, Analysis of Diquat Residues - Method RM-5-5, Analysis of Diquat Residues in Water - Method RM-5W-1. Syngenta Crop Protection, Inc., Greensboro, USA. Chevron Chemical, Richmond, USA, 8613239 A. Not GLP, Unpublished. Syngenta File No 432113
PP901/0451	Lee S.	1989	Diquat Confined Accumulation Study on Rotational Crops. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, MEF-0026. GLP, Unpublished. Syngenta File No PP901/0451
PP901/0310	Massenot F., Culoto B.	1985	Recherche De Residus De Diquat Dans Des Graines De Soja. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, R 2-FP. Not GLP, Unpublished. Syngenta File No PP901/0310
PP901/0630	Massey J	1987	Paraquat/Diquat: Residues in Carrots from Trials Carried Out in West Germany During 1984. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4417B. GLP, Unpublished. Syngenta File No PP901/0630
PP901/0315	Massey J.	1987	Diquat: Residues in Peas from Trials Carried out in Denmark During 1986. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, M4459B. GLP, Unpublished. Syngenta File No PP901/0315
PP901/1977	Mônego J.	2006	Rate of Degradation of (14C) -Diquat in Brazilian soil. Syngenta Proteção de Cultivos Ltd.a, São Paulo, Brazil. Bioensaios Análises e Consultoria Ambiental S/C Ltd.a., Viamão - RS, Brazil, 1469-BS-181-04. GLP, Unpublished. Syngenta File No PP901/1977
PP901/0724	Nagra B., Kingdom N.	2001	Diquat and Paraquat: Residue Levels in Protected Strawberries from Trials conducted in the UK during 2000. Syngenta CEMAS, North Ascot, United Kingdom, CEMR-1301. GLP, Unpublished. Syngenta File No PP901/0724
PP901/1892	Oliver R., Webb J.	2005	Diquat: Sterilised Natural Water Photolysis under Laboratory Conditions. Syngenta. Syngenta - Jealott's Hill, Bracknell, United Kingdom, RJ3568B 03JH029. GLP, Unpublished. Syngenta File No PP901/1892
PCP7639	Operhemmer D.	1982	Residues of diquat in lentils Canada 1982. Report PCP7639

Code	Author	Year	Title
CGA130327_10009	Patterson D.	2012	Diquat - Calculation of Kinetic Endpoints for the Soil Photodegradation Product TOPPS from Laboratory Study Data according to FOCUS Kinetics Guidelines. Syngenta - Jealott's Hill, Bracknell, United Kingdom, RAJ0920B. Not GLP, Unpublished. Syngenta File No CGA130327_10009
PP901/0742	Reichet N	1996	Determination of Diquat & Paraquat in Potato, Pea Seed, Bean Seed & Soil Validation of the Methods RAM 252/01 & RAM 253/01. Syngenta Crop Protection AG, Basel, Switzerland. Institut Fresenius, Taunusstein, Germany, IF-94/21111-00. GLP, Unpublished. Syngenta File No PP901/0742
PP901/0876	Ricketts D.	1997	Diquat- Microbial Degration. Zeneca Agrochemicals, Jealott's Hill, United Kingdom. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RIC3794. GLP, Unpublished. Syngenta File No PP901/0876
PP901/0325	Roper EM	1995	Diquat: Magnitude of the Residues of Diquat in Dry Beans From Trials Conducted in the USA During 1994 (WRC-95-058). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-033B. GLP, Unpublished. Syngenta File No PP901/0325
PP901/0324	Roper EM	1995a	Diquat: Magnitude of the Residues of Diquat on Dry Peas From Trials Conducted in the USA During 1994 (WRC-95-071). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-046B. GLP, Unpublished. Syngenta File No PP901/0324
PP901/0323	Roper EM	1995b	Diquat: Magnitude of the Residues on Lentils From Trials Conducted in the USA During 1994 (WRC-95-063). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-038B. GLP, Unpublished. Syngenta File No PP901/0323
PP901/0286	Roper EM	1995c	DIQUAT: Magnitude of the Residues of Diquat on Potatoes From Trials Conducted in the USA During 1994 (WRC-95-053). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RR 95-029B. GLP, Unpublished. Syngenta File No PP901/0286
A1412A_10320	Suchek E., Kamienski V.	1989	Residual analysis of Diquat in samples of citrus (oranges) Certificate 39510-A. Syngenta, 39510-A. Not GLP, Unpublished. Syngenta File No A1412A_10320
A1412A_10321	Suchek E., Kamienski V.	1989a	Residual analysis of Diquat in samples of citrus (oranges) Certificate 39533-A. Syngenta 39533-A. Not GLP, Unpublished. Syngenta File No A1412A_10321
	Tadeo JL, Sánchez-Brunete C, Pérez RA, Fernández MD	2000	Analysis of herbicide residues in cereals, fruits and vegetables. Journal of Chromatography A 882:175–191
PP901_10848	Wicksted G., Lowrie C.	2012	Diquat: Metabolism in the Lactating Goat. Syngenta. Charles River Laboratories, Edinburgh, United Kingdom, 33144. GLP, Unpublished. Syngenta File No PP901_10848
PP148/0662	Wilkinson W.	1980	Paraquat and Diquat: Long-term High-rate Trial, Frensham, UK.1. Management of site, effects on crops and weeds and residues in crops. Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0013B. Not GLP, Unpublished. Syngenta File No PP148/0662
PP901/0024	Wollerton C.	1987	Physico-chemical data file (pure diquat dibromide). Zeneca Agrochemicals, Jealott's Hill, United Kingdom, RJ0582B. Not GLP, Unpublished. Syngenta File No PP901/0024
	Worobey BL.	1993	Liquid chromatographic method for determination of diquat and paraquat herbicides in potatoes: collaborative study. J AOAC Int. 76:881-887.