5.6 DIQUAT (031)

RESIDUE AND ANALYTICAL ASPECTS

Diquat was first reviewed by the 1970 JMPR. The toxicology and residues aspects of diquat were reconsidered by the 2013 JMPR as part of the periodic review program. The 2013 JMPR established an ADI of 0–0.006 mg/kg bw and an ARfD of 0.8 mg/kg bw, and recommended a residue definition for compliance with the MRL and dietary risk assessment for plant and animal commodities of *diquat cation*, along with maximum residue levels in a number of plant and animal commodities.

Diquat was scheduled by the Forty-ninth Session of the CCPR (2017) for evaluation of additional residues data in pulses and cereals.

Methods of analysis

No new methods of analysis were submitted to the Meeting. In all trials presented to the Meeting, samples were analysed using a LC-MS/MS method (method number GRM012.03A), which was considered by the 2013 JMPR. Additional validation data in pulse matrices (chickpea, lentil, dry bean and dry pea seed) were generated for the current Meeting, since the previous validation data for this method did not include a high protein commodity. Acceptable recovery values were achieved in these matrices over a fortification range of 0.01–3.0 mg/kg.

Stability of residues in stored analytical samples

The Meeting received the final version of a storage stability study provided as an interim report to the 2013 JMPR, together with storage stability data generated concurrently with the cereal residue trials. The final version of the storage stability study confirmed the assessment of the 2013 JMPR, that residues of diquat are stable in a range of commodities (spinach, wheat grain, oilseed rape seed, lentil, whole orange, potato and wheat straw) over 24 months frozen storage. This data covers a sufficient time interval to support the proposition that residues of diquat will have remained stable for the storage times used in the trials presented to the Meeting.

Results of supervised residue trials on crops

The Meeting received supervised residue trial data for foliar application of diquat to beans, dry, chickpeas, lentils and peas, dry for pre-harvest desiccation, and for foliar application to barley, oats and wheat for weed control both early in the crop and immediately pre-harvest.

All rates discussed below are expressed in terms of g ai/ha of diquat cation.

Pulses

In the discussion of uses on the label from Canada below, the following applies concerning harvesting of pulses. There is no specific harvest interval on the label, however information on the label regarding harvesting states that ‘harvesting can normally commence within 4–10 days of desiccation’. The Meeting considered that 4 days represented the minimum interval likely to be used in practice, as sufficient time is required for effective desiccation or weed control.

Dry beans, Subgroup of

The critical GAP for beans (including white and red kidney beans, soya beans, adzuki beans and faba beans) in Canada is a single aerial application at 552 g ai/ha for pre-harvest desiccation.

Residue trials in beans, dry were conducted in Canada during the 2015 season and matching the Canadian GAP (1 application at 0.87–0.95× the maximum Canadian rate, and with sampling at a 4–5 day PHI). Residues observed in these trials are shown below (*in italics*) together with residues observed in data from JMPR 2013, from trials conducted in Germany in 1984 and the USA in 1994 matching the Canadian GAP.

Residues of diquat in beans, dry after treatment at GAP were (n = 24): *0.01*, *0.012*, *0.019*, < 0.02 (3), *0.040*, *0.044*, < 0.05 (8), 0.05, 0.08, 0.09, *0.15*, 0.15, *0.18* (*2*), and *0.35* mg/kg.

Similarly data was available in the 2013 JMPR for dry soya beans from trials conducted in France matching the Canadian GAP.

Residues of diquat in soya beans, dry after treatment at GAP were (n = 3): < 0.05, 0.06 and < 0.1 mg/kg.

The combined dataset in ranked order is (n = 27) were: 0.01, 0.012, 0.019, < 0.02 (3), 0.040, 0.044, < <u>0.05</u> (9), 0.05, 0.06, 0.08, 0.09, < 0.1, 0.15 (2), 0.18 (2) and 0.35 mg/kg.

The Meeting noted that several commodities in the subgroup of dry beans were covered by the Canadian GAP, and decided to estimate a maximum residue level for the subgroup. The Meeting estimated a maximum residue level of 0.4 mg/kg for diquat in the subgroup of Dry beans, together with a STMR of 0.05 mg/kg. The Meeting withdrew the previous recommendation of 0.2 and 0.3 mg/kg for beans (dry) and soya bean (dry), respectively.

Chickpeas

The critical GAP for chickpeas in Australia is a single application at 600 g ai/ha for pre-harvest crop desiccation, with a 2-day PHI. No trials were available with a 2-day PHI, and only two were available with a 1-day PHI.

The GAP for chickpeas in Canada is a single ground foliar spray application at 408 g ai/ha for pre-harvest desiccation.

Residue trials in chickpeas were conducted in Canada during the 2015 season and matching the Canadian GAP (1 application at 1.1-1.29× the maximum Canadian rate, and with sampling at a 4-5 day PHI).

Residues of diquat in chickpeas after treatment at GAP were (n = 9): 0.070, 0.10, 0.16, 0.18, <u>0.24</u>, 0.26, 0.32, 0.38, and 0.58 mg/kg.

The Meeting estimated a maximum residue level of 0.9 mg/kg, together with a STMR of 0.24 mg/kg, for diquat in chickpea (dry).

Subgroup – Dry peas (except chick-peas)

Lentils

The critical GAP for lentils in Australia is a single application at 600 g ai/ha for pre-harvest crop desiccation, with a 2-day PHI. No trials were available with a 2-day PHI, and only two were available with a 1-day PHI.

The GAP for lentils in Canada is a single aerial application at 552 g ai/ha for pre-harvest desiccation.

Residue trials in lentils were conducted in Canada during the 2015 season and matching the Canadian GAP (1 application at 0.85-0.91× the maximum Canadian rate, and with sampling at a 4-5 day PHI).

Residues of diquat in lentils after treatment at GAP were (n = 8): 0.052, 0.070, 0.10, 0.16, 0.18, 0.21, 0.33, and 0.57 mg/kg.

Peas, dry

The GAP for dry peas in Australia is a single application at 600 g ai/ha for pre-harvest crop desiccation, with a harvest withholding period not required.

The GAP for peas, dry in Canada is a single application at 552 g ai/ha for pre-harvest desiccation.

Residue trials in peas, dry were conducted in Canada during the 2015 season and matching Canadian GAP (1 application at 0.87–0.93× the maximum Canadian rate, and with sampling at a 4–5 day PHI). Residues observed in these trials are shown below (*in italics*) together with data from JMPR 2013, from trials conducted in Germany in 1984/5 and the UK in 1992, and the USA in 1994 matching the Canadian GAP.

The combined dataset is (n = 21): *0.014*, *0.020*, 0.03, *0.038*, 0.04, < 0.05 (3), 0.05 (4), *0.054*, 0.06 (2), *0.061*, 0.09, 0.10, 0.11, *0.13*, and 0.56 mg/kg.

The Meeting noted that data were available for lentils, and peas, dry and considered a maximum residue level for the subgroup of dry peas (except chickpeas). The Meeting noted that the median residues for the datasets for the two crops differed by less than 5-fold, and noted that the datasets were not statistically similar (Mann-Whitney). The Meeting therefore decided to estimate a maximum residue level for the subgroup of dry peas based on the lentil dataset.

The Meeting estimated a maximum residue level of 0.9 mg/kg, together with a STMR of 0.17 mg/kg, for diquat in the subgroup of dry peas (except chickpeas). The Meeting withdrew the previous recommendation of 0.3 mg/kg for peas (dry).

Cereals

In the discussion of uses on the label from Australia below, the following applies concerning harvesting of cereals after a single pre-harvest application. Where a harvest withholding period is stated as being not required when used as directed, the Meeting considered that at least 4 days would be required for effective weed and crop dry down. The Meeting considered that harvest at a minimum of 4 days was consistent with expected agricultural practice in Australia.

Barley

The GAP for barley in Australia is a single application at 600 g ai/ha made shortly before harvest for weed control. A harvest withholding period is stated as being not required when used as directed. Residue data were available at 2-4 day harvest intervals and at a 7-day harvest interval.

Residues of diquat cation in barley at 4 days after application were (n = 1): 0.15 mg/kg.

Considering that decline data were available for all trial sites, the Meeting noted that for several of the barley trial sites, the interpolated residue level at 4 days after application differed by less than ±25% from the measured level at 2 or 3 days after application.

Residues of diquat cation in barley approximating GAP were (n = 6): 0.15, 0.53, 1.1, 2.0 (2), and 2.1 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg for diquat in barley, together with a STMR of 1.55 mg/kg.

Oats

The GAP for oats in Australia is an early application for weed control at 140 g ai/ha made between the 3-leaf and early tillering stage (BBCH 13–22) plus a pre-harvest weed control application at 600 g ai/ha shortly before harvest.

Residue trials generated in Australia for oats were provided to the Meeting but did not match GAP.

Rye and triticale

The GAP for winter cereals in Australia is a single application at 600 g ai/ha made shortly before harvest for weed control. A harvest withholding period is stated as being not required when used as directed.

The Meeting agreed to use the wheat data to estimate maximum residue levels for rye and triticale.

Considering that decline data were available for all trial sites, the Meeting noted that for several of the trial sites, the interpolated residue level at 4 days after application generally differed by less than ±25% from the measured level at 2 or 3 days after application.

Residues of diquat cation in wheat at 2–4 days after application (at trial sites where values consistent with those expected from use in accordance with GAP were obtained) were (n = 6): 0.28, 0.41, 0.45, 0.56, 0.57 and 0.78 mg/kg.

Based on the wheat data, the Meeting estimated maximum residue levels and STMRs of 1.5 mg/kg and 0.505 mg/kg respectively for rye and triticale.

Wheat

The GAP for wheat in Australia is an early application for weed control at 140 g ai/ha made between the 4-leaf and early tillering stage (BBCH 14–22) plus a pre-harvest weed control application at 600 g ai/ha shortly before harvest.

Residue trials generated in Australia for wheat were provided to the Meeting but did not match GAP.

Animal feeds

Barley forage

Residue data were available from the Australian cereal residue trials for barley forage. However, there is no relevant GAP in barley involving application at or before the forage stage.

Oat forage

The Australian GAP for application of diquat to oats at the forage stage is 1 × 140 g ai/ha application, with a 1-day grazing interval. Trials conducted in Australia in oats included forage sampling; however these trials did not match GAP.

Wheat forage

The Australian GAP for application of diquat to wheat at the forage stage is 1 × 140 g ai/ha application, with a 1-day grazing interval. Trials conducted in Australia in wheat included forage sampling; however these trials did not match GAP.

Barley, rye and triticale straw

The GAP for barley, rye and triticale straw in Australia is a single application at 600 g ai/ha made shortly before harvest for weed control.

Considering that decline data were available for all trial sites, the Meeting noted that for many of the trial sites, the interpolated residue level at 4 days after application differed by less than ±25% from the measured level at 2 or 3 days after application.

The Meeting considered that straws of cereal crops are not distinguished in trade and considered that data for barley, oat and wheat straw matching the GAPs for barley, rye and triticale could be combined for the purpose of obtaining more robust estimates for maximum residue levels.

Residues of diquat cation in barley straw at 2–4 days after application (at trial sites where values consistent with those expected from use in accordance with GAP were obtained) were (n = 5): 2.8, 6.2, 6.9, 23, and 26 mg/kg (on a dry weight basis). Residues of diquat cation in oat straw at 2–4 days after application (at trial sites where values consistent with those expected from use in accordance with GAP were obtained) were (n = 4): 0.27, 1.8, 2.8, and 3.1 mg/kg.

Residues of diquat cation in wheat straw at 2-4 days after application (at trial sites where values consistent with those expected from use in accordance with GAP were obtained) were (n = 8): 1.2, 2.0, 2.4, 2.8, 3.3, 4.3, 5.6 and 6.1 mg/kg.

The Meeting further noted that the median residues of the barley, oat and wheat data sets differed by < 5×, and that the datasets were statistically similar (Kruskal-Wallis), and agreed to combine them for the purpose of estimating maximum residue levels.

The combined data set is (n = 17): 0.27, 1.2, 1.8, 2.0, 2.4, 2.8 (3), 3.1, 3.3, 4.3, 5.6, 6.1, 6.2, 6.9, 23, and 26 mg/kg.

The Meeting estimated maximum residue levels of 40 mg/kg for diquat in barley straw and fodder (dry), rye straw and fodder (dry), and triticale straw and fodder (dry), together with median and highest residues of 3.1 and 26 mg/kg respectively.

Oat straw

The GAP for oat straw in Australia is an early application for weed control at 140 g ai/ha made between the 4-leaf and early tillering stage (BBCH 14–22) plus a pre-harvest weed control application at 600 g ai/ha shortly before harvest.

Residue trials generated in Australia for oats were provided to the Meeting but did not match GAP.

Wheat straw

The GAP for wheat straw in Australia is an early application for weed control at 140 g ai/ha made between the 4-leaf and early tillering stage (BBCH 14–22) plus a pre-harvest weed control application at 600 g ai/ha shortly before harvest.

Residue trials generated in Australia for wheat were provided to the Meeting but did not match GAP.

Fate of residues during processing

No processing studies were provided to this Meeting. The 2013 JMPR considered a processing study in soya bean, and this was used to estimate updated values for processed soya commodities based on the increased STMR covering soya bean RAC estimated by the Meeting.

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)	RAC MRL (mg/kg)	Processed commodity MRL
Soya bean	Hulls	2.6 3.6	3.1	0.05	0.155	0.4	1.24
	Meal	0.7 1.0	0.85		0.0425		-
	Oil	< 0.04 < 0.07	< 0.055		< 0.00275		-

Based on the estimated maximum residue level for the RAC of the dry beans subgroup, and the processing factor, the Meeting estimated a maximum residue level of 1.5 mg/kg for soya bean hulls (3.1 × 0.4 = 1.24, rounded up to nearest 'step').

Residues in animal commodities

Farm animal feeding studies

The 2013 JMPR 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 or 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.

The 2013 JMPR 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.

Livestock dietary burden

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 2016 edition of the FAO Manual, are presented in Annex 6 and summarised below.

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	4.0	1.33	17	6.3	29❶	18❸	1.27	1.27
Dairy cattle	6.7	3.0	18	7.2	29❷	14❹	2.25	0.95
Poultry Broiler	1.37	1.37	1.32	1.30	0.34	0.34	0.20	0.20
Poultry Layer	1.37	1.37	5.8❺	3.5❻	0.34	0.34	0.04	0.04

❶ Highest maximum beef or dairy cattle dietary burden suitable for maximum residue level estimates for mammalian meat

❷ Highest maximum dairy cattle dietary burden suitable for maximum residue level estimates for mammalian milk

❸ Highest mean beef or dairy cattle dietary burden suitable for STMR estimates for mammalian meat.

❹ Highest mean dairy cattle dietary burden suitable for STMR estimates for milk.

❺ Highest maximum poultry dietary burden suitable for maximum residue level estimates for poultry meat and eggs.

❻ Highest mean poultry dietary burden suitable for STMR estimates for poultry meat and eggs.

Animal commodity maximum residue levels

The Meeting noted that at the estimated maximum dietary burdens of 29 and 5.8 ppm for cattle and poultry respectively, no residues are expected in tissues, milk, or eggs. Slight increases in the dietary burdens over those calculated by the 2013 JMPR were noted for dairy cattle and poultry.

The Meeting considered that the recommendations of the 2013 JMPR for maximum residue levels at the LOQ (0.01(*) mg/kg; 0.001(*) mg/kg for milk), together with nil STMR and HR values, for mammalian and poultry meat and offal, milk, and eggs remained appropriate.

The Meeting estimated maximum residue levels of 0.01(*) mg/kg for mammalian and poultry fats, together with STMR and HR values of 0.

RECOMMENDATIONS

On the basis of the data obtained from supervised residue trials the Meeting concluded that the maximum residue levels listed in Annex 1 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): *Diquat ion*

The residue is not fat-soluble.

DIETARY RISK ASSESSMENT

Long-term dietary exposure

The ADI for diquat is 0–0.006 mg/kg bw. The International Estimated Daily Intakes (IEDIs) for diquat were estimated for the 17 GEMS/Food Consumption Cluster Diets using the STMR or STMR-P values estimated by the 2013 and 2018 JMPR. The results are shown in Annex 3 of the 2018 JMPR Report. The IEDIs ranged from 2–30% of the maximum ADI.

The Meeting concluded that long-term dietary exposure to residues of diquat from uses considered by the JMPR is unlikely to present a public health concern.

Acute dietary exposure

The ARfD for diquat is 0.8 mg/kg bw. The International Estimate of Short Term Intakes (IESTIs) for diquat were calculated for the food commodities and their processed commodities for which HRs/HR-Ps or STMRs/STMR-Ps were estimated by the present Meeting and for which consumption data were available. The results are shown in Annex 4 of the 2018 JMPR Report. The IESTIs varied from 0–7% of the ARfD for children and 0–10% for the general population.

The Meeting concluded that acute dietary exposure to residues of diquat from uses considered by the present Meeting is unlikely to present a public health concern.