

Australian Government

Australian Pesticides and Veterinary Medicines Authority



Diquat

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Contents

Preface	1
About this document	1
Further information	1
Contact details	1
Introduction	2
Purpose of review	2
Product claims, use patterns and mode of action	3
Chemistry	5
Active constituent	5
Active constituent standards	6
Statutory considerations under the safety criteria – active constituents	7
Formulated products	8
Statutory considerations under the safety criteria – formulated products	8
Recommendations	13
Toxicology	14
Evaluation of toxicology	14
Biochemical aspects	14
Major toxicological mode(s) of action and key events	14
Acute toxicity	14
Acute toxicity in humans	15
Repeat dose toxicity	15
Genetic toxicology	16
Carcinogenicity	16
Reproduction studies	16
Development studies	17
Special studies	17
Health-based guidance values	19
Poisons scheduling	20
Recommendations	20
Worker health and safety	21
Worker exposure assessment	21
Ground-based and aerial application	22
Re-entry to treated areas	24

Recommended label changes	25
Signal headings	25
Restraints	25
First aid statements (all products)	26
Safety directions (all products)	26
Re-entry statements for diquat products	26
Re-entry statements for diquat and paraquat combination products	26
Residues and trade	27
Metabolism	27
Analytical methods and storage stability	27
Analytical methods	27
Stability of residues in stored analytical samples	28
Residue definition	28
Residues in foods	29
Cropping situations	29
Summary of diquat residues in submitted studies	30
Fruit crops	32
Vegetable crops	35
Cereals	43
Oilseeds	47
Sugarcane	51
Hops	51
Processed commodities	52
Use in aquatic areas	52
Residues in animal feeds	53
Animal feed derived from grasses (including cereals)	53
Animal feed derived from legumes	54
Animal feeds derived from oilseeds	54
Other animal feeds	55
Conclusion on residues in animal feeds	55
Animal transfer studies and animal commodity MRLs	55
Poultry	55
Ruminants	57
Required animal commodity MRLs	60
Crop rotation	60
Spray drift	61

Dietary risk assessment	61
Chronic dietary exposure assessment	61
Acute dietary exposure assessment	61
Residue related aspects of trade	61
Conclusions from the residues and trade assessment	65
Other uses that are no longer supported from a residues perspective	66
Winter cereals	67
Supported withholding periods	67
Aquatic areas	67
Spray drift	68
Trade	68
Required MRL changes	68
Consideration of proposed APVMA reconsideration outcomes for diquat	71
Hops (supported use: 0.28 kg ac/ha)	73
Lucerne (supported use: 0.088 kg ac/ha)	73
Oilseed poppies	74
Pasture renovation and establishment	74
Berries and other small fruit (except grapes)	74
Brassica vegetables: broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe-tsai)	75
Bulb vegetables: bulb onions	75
Fruiting vegetables other than cucurbits	75
Leafy vegetables	75
Legume vegetables	76
Root and tuber vegetables	76
Pre-emergent application to wheat and oats and as a cultivation aid for pastures and selected cereals, pu oilseeds	lses and 76
Animal commodities	77
Trade	77
Revised dietary exposure assessment	77
Chronic dietary exposure assessment	77
Acute dietary exposure assessment	78
Revised MRL changes	78
Environmental safety	81
Assessment scenarios Fate and behaviour in the environment	
Risks to non-target species	

Terrestrial vertebrates	89
Aquatic species	92
Bees	96
Other arthropod species	96
Soil organisms	97
Non-target terrestrial plants	98
Combination toxicity	98
Assessment scenarios	98
Effects on non-target species	99
Risks to non-target species	101
Recommendations	105
Spray drift	108
Storage and disposal	111
Storage	111
Disposal	111
Appendix A – Summary of assessment outcomes	113
Appendix B – Listing of environmental endpoints	122
Appendix C – Terrestrial vertebrate assessments	142
Appendix D – PBT and POP assessments	150
Persistence criterion	150
Bioaccumulation criterion	150
Toxicity criterion	151
Potential for long-range environmental transport	151
Conclusion	151
Acronyms and abbreviations	152
Glossary	155
References	159

List of tables

Table 1: Diquat product groups	3
Table 2: Nomenclature and structural formula of the active constituent diquat	5
Table 3: Key physicochemical properties of the active constituent diquat dibromide	6
Table 4: Current active constituent approvals for diquat dibromide	8
Table 5: Currently registered chemical products containing diquat	9
Table 6: Points of departure for human health risk assessment	19
Table 7: Acceptable daily intake for diquat	19
Table 8: Acute reference dose for diquat	20
Table 9: Assumptions used in modelling exposure for professional use of diquat	21
Table 10: Risk assessment outcomes for liquid diquat products	22
Table 11: Risk assessment outcomes for liquid paraquat plus diquat products	24
Table 12: Summary of use patterns, crop groups and residue studies submitted for assessment	30
Table 13: Recommended MRLs for animal feeds	55
Table 14: Calculation of poultry broiler dietary burden of diquat	56
Table 15: Calculation of poultry broiler dietary burden of diquat	57
Table 16: Calculation of beef cattle dietary burden of diquat	59
Table 17: Calculation of dairy cattle dietary burden of diquat	59
Table 18: International MRLs for Australian major export commodities (December 2023)	62
Table 19: Amendments to Table 1 of the MRL Standard	68
Table 20: Amendments to Table 4 of the MRL Standard	71
Table 21: Diquat uses supported by human health, environment, and residues and trade risk assessments	71
Table 22: Paraquat and diquat combination uses that are supported by human health, environment and residues and trade risk assessments	73
Table 23: Revised amendments to Table 1 of the MRL Standard	78
Table 24: Revised amendments to Table 4 of the MRL Standard	80
Table 25: Environmental risk assessment scenarios for diquat	81
Table 26: Key regulatory endpoints for environmental exposure assessment	84
Table 27: Toxicity endpoints for aquatic primary producers used in SSD analysis	87
Table 28: Post-emergent toxicity endpoints for dicots used in SSD analysis based on data from laboratory and field studies	88
Table 29: Regulatory acceptable levels for non-target species	88
Table 30: Summary of risk assessment outcomes for terrestrial vertebrates	90
Table 31: Assessment of risks to non-target aquatic species for aquatic use situations	93
Table 32: Soil exposure estimates	93
Table 33: Assessment of runoff risks to aquatic species for terrestrial use situations	94
Table 34: Screening level assessment of risks to bees	96

viii Diquat Review Technical Report

Table 35: Assessment of risks to other non-target arthropods	97
Table 36: Screening level assessment of risks to soil organisms (worst-case scenario)	98
Table 37: Diquat/paraquat combination products: environmental risk assessment scenarios	98
Table 38: Diquat/paraquat combination products – Predicted toxicity endpoints for non-target terrestrial plants (post- emergent exposure) used in SSD analysis	100
Table 39: Diquat/paraquat combination products: regulatory acceptable levels for non-target species	101
Table 40: Diquat/paraquat combination products: crop groups for terrestrial vertebrate assessment	103
Table 41: Diquat/paraquat combination products: acute risks to terrestrial vertebrates	103
Table 42: Summary of risk assessment outcomes for risks of combination products containing 115 g/L diquat and 13 g/L paraquat to terrestrial vertebrates	35 104
Table 43: Screening level assessment of risks of combination products containing 115 g/L diquat and 135 g/L paraque to bees	uat 104
Table 44: Assessment of risks to other non-target arthropods	105
Table 45: Supported uses of diquat from the viewpoint of environmental safety	105
Table 46: Uses of diquat not supported from the viewpoint of environmental safety	106
Table 47: Regulatory acceptable levels of diquat resulting from spray drift	108
Table 48: Regulatory acceptable levels of paraquat and diquat resulting from spray drift of chemical products co- formulated with both active constituents	108
Table 49: Diquat – buffer zones for boom sprayers	109
Table 50: Diquat – buffer zones for aircraft (metres; MEDIUM droplet size)	110
Table 51: Diquat/paraquat co-formulated product buffer zones for boom sprayers	110
Table 52: Risk assessment outcomes for products containing diquat	113
Table 53: Risk assessment outcomes for products containing paraquat and diquat	117
Table 54: Diquat – dissipation in animal food items	122
Table 55: Diquat – fate and behaviour in soil	122
Table 56: Diquat – fate and behaviour in water and sediment	124
Table 57: Diquat – fate and behaviour in air	126
Table 58: Diquat – monitoring data	126
Table 59: Diquat – effects on terrestrial vertebrates	127
Table 60: Diquat – laboratory studies on aquatic species	127
Table 61: Diquat – microcosm studies on aquatic species	129
Table 62: Diquat – effects on bees	129
Table 63: Diquat – effects on other non-target arthropods	130
Table 64: Diquat – laboratory studies on soil organisms	130
Table 65: Diquat – field studies on soil organisms	131
Table 66: Diquat – laboratory studies on non-target terrestrial plants	131
Table 67: Diquat – field studies on non-target terrestrial plants (post-emergent exposure)	133
Table 68: Diquat/paraquat combination products: short-term effects on terrestrial vertebrates	133
Table 69: Diquat/paraquat combination products: short-term effects on aquatic species	135

Table 70: Diquat/paraquat combination products: short-term effects on bees	137
Table 71: Diquat/paraquat combination products: effects on other terrestrial arthropods	138
Table 72: Diquat/paraquat combination products: short-term effects on soil organisms	139
Table 73: Diquat/paraquat combination products: effects on non-target terrestrial plants (post-emergent exposure)	139
Table 74: Seasonal exposure estimates for diquat in animal food items	142
Table 75: Acute risks of diquat to wild mammals (RAL 12 mg/kg bw)	144
Table 76: Acute risks of diquat to birds (RAL 7.0 mg/kg bw)	147

Preface

The Australian Pesticides and Veterinary Medicines Authority (APVMA) is the independent statutory authority with responsibility for the regulation of agricultural and veterinary chemicals in Australia. Its statutory powers are provided in the Agricultural and Veterinary Chemicals Code (the Agvet Code), which is scheduled to the *Agricultural and Veterinary Chemicals Code Act 1994*.

About this document

This Technical Report is intended to provide an overview of the assessments that have been conducted by the APVMA and of the specialist advice received from its advisory agencies. It has been deliberately presented in a manner that is likely to be informative to the widest possible audience, thereby encouraging public comment.

This document contains a summary of the assessment reports generated in the course of the chemical review of an active ingredient, including the registered product and approved labels. The document provides a summary of the APVMA's assessment, which may include details of:

- the toxicology of both the active constituent and product
- the residues and trade assessment
- occupational exposure aspects
- environmental fate, toxicity, potential exposure and hazard
- efficacy and target crop or animal safety.

Further information

Further information can be obtained via the contact details provided below. More details on the chemical review process can be found on the APVMA website: <u>apvma.gov.au</u>.

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Introduction

Diquat is a non-selective contact herbicide belonging to the bipyridinium class of compounds which also includes the herbicide paraquat. Diquat and paraquat have been registered for use in Australia since 1964. Both compounds share a similar mode of herbicidal action which involves the inhibition of photosynthesis (specifically photosystem I) thereby generating superoxide, leading to lipid peroxidation and membrane damage. Plants die rapidly after treatment and exposure to light.

Purpose of review

Diquat and the related bipyridinium herbicide paraquat were placed under reconsideration by the APVMA, then the National Registration Authority (NRA) in the third cycle of the Existing Chemicals Review Program, in a notice published in the NRA Gazette on 2 December 1997.

The reconsideration covers all aspects of the active constituent approval, product registration and label approval to evaluate whether the continuing use of diquat would:

- not be an undue hazard to the safety of people exposed to it during its handling or people using anything containing its residues
- not be likely to have an effect that is harmful to human beings
- not be likely to have an unintended effect that is harmful to animals, plants or things or to the environment
- not unduly prejudice trade or commerce between Australia and places outside Australia
- be effective in accordance with the instructions for its use.

The following aspects of active constituent approvals and product registrations for diquat have been assessed:

- Toxicology
- Worker health and safety
 - Risks arising from exposure during handling and application
 - Re-entry exposure risks
 - Determination of appropriate personal protective clothing requirements
- Residues and trade
 - Residues in treated produce arising from application in accordance with label instructions
 - Maximum residue limits (MRLs) to underpin the assessment of dietary and trade risk for all commodities on which diquat is used
 - Determination of dietary exposure resulting from the consumption of produce treated with diquat
- Environmental safety, including spray drift

The APVMA has also considered information pertaining to chemistry (impurities of toxicological concern).

Although paraquat and diquat are structurally related, their relative risk to human and environmental safety, and trade, have been assessed separately.

A summary of the combined risk assessment outcomes for each use pattern, and whether it is supported for continued approval, is presented in Appendix A.

Product claims, use patterns and mode of action

Diquat is an active constituent in 67 products registered for use in Australia by the APVMA¹. These products can be divided into 2 groups based on the presence of paraquat as a second active constituent, as indicated in Table 1. These 2 groups can be further divided based on the concentration of diquat and paraquat.

Table 1: Diquat product groups

Group	Active constituent(s)	Active constituent concentration
1 (20 products)	Diquat	200 g/L diquat
2 (39 products)	Paraquat/diquat	135 g/L paraquat; 115 g/L diquat

Diquat and diquat/paraquat combination products are registered for the control of broadleaf weeds in seed beds before sowing, and pre-harvesting operations of a number of crops as well as post-emergence inter-row weed control. Diquat products often include instructions for use as a tank-mix with paraquat or other herbicides to improve efficacy against particular weed species (e.g. capeweed) or provide residual activity (e.g. diuron used for control of annual grasses and broadleaf weeds in lucerne (*Medicago sativa*)) Diquat is also used to facilitate harvesting operations of a number of crops such as desiccating weeds, accelerating the drying of crops and reducing the moisture content of seeds. Diquat is also registered for use in aquatic situations for control of various aquatic weeds, particularly invasive species. A detailed list of use patterns considered in this assessment is provided in <u>Appendix A – Summary of assessment outcomes</u>.

This reconsideration has only considered the approved label uses of diquat. Current off label permits for use of diquat have not been assessed.

Diquat is a group 22² mode of action bipyridinium herbicide and is most commonly supplied as the dibromide salt. It is a non-selective contact herbicide and desiccant, absorbed by the foliage, with some translocation in the xylem. It accepts electrons from photosystem I (PS-I, electron diversion), resulting in interaction with the photosynthetic process to produce a hydroxyl radical and other reactive oxygen species that destroy unsaturated lipids and

¹ Note that 3 products registered after 28 February 2024 are not formally within scope of the registration and will be dealt with through separate regulatory actions.

² Mode of Action tables maintained by Croplife are available on the CropLife website (accessed May 2024).

chlorophyll. It is inactivated on contact with soil and not taken up by plant roots. Diquat is used to control weeds before planting, before or just after crop emergence, and directed spray between the rows of established crops.

Chemistry

Active constituent

Diquat dibromide in its pure form is a colourless to yellow-coloured crystal with an earthy odour. Diquat dibromide is an extremely hygroscopic material and is commercially supplied as a technical concentrate (manufacturing concentrate) consisting of an aqueous solution with a typical concentration of 375–485 g/kg. It is very soluble in water (718 g/L at 20°C in pH 5.2, pH 7.2 and pH 9.2), with a slight solubility in methanol (25 g/L) and is practically insoluble in acetone, dichloromethane, ethyl acetate, hexane and toluene (< 0.1 g/L). Diquat is stable to hydrolysis under acidic, neutral and alkaline conditions. No significant decrease in concentration was observed at pH 5–7, with <10% loss of diquat at pH 7 after 30 days at 25°C. Diquat shows rapid photodegradation with only 15.8% parent compound remaining after 3 days irradiation. Photodegradation follows first-order kinetics with an estimated half-life of 31 hours. Further information about the identity and physicochemical properties of diquat are provided in Table 2 and Table 3. There are currently 12 active constituent approvals for diquat dibromide which are listed in Table 4.

Common name (ISO):	Diquat
IUPAC name:	1,1'-ethylene-2,2'-bipyridyldiylium (diquat) 1,1'-ethylene-2,2'-bipyridyldiylium dibromide (diquat dibromide)
CAS registry number:	2764-72-9 (diquat cation) 85-00-7 (diquat dibromide)
Molecular formula:	C12H12N2 (diquat) C12H12Br2N2 (diquat dibromide)
Molecular weight:	184.2 gmol-1 (diquat cation) 344.1 gmol-1 (diquat dibromide salt)
Structural formula:	$ \begin{array}{c} $

Table 2: Nomenclature and structural formula of the active constituent diquat

Appearance	Colourless to yellow crystals solid (pure active ingredient) Dark brown liquid (technical active ingredient)
Melting point	325°C (decomposes before melting)
Relative density	1.61 g/cm
Solubility in water (20°C)	718 g/L at 20°C
Organic solvent solubility (20°C)	Slightly soluble in alcohols and hydroxylic solvents.
	Desetially include in service service setuents
	Practically insoluble in non-polar organic solvents.
Octanol/water partition coefficient (Log Kow)	Log Kow = -4.60 at 20°C
Vapour pressure	<0.01 mPa at 25°C
Henry's law constant (calculated)	< 5 × 10 ⁻⁹ Pa.m ³ mol ⁻¹
Hydrolysis (DT ₅₀ ; 25°C)	DT_{50} at pH 7 in stimulated natural sunlight is 74 days.
	Hydrolytically stable in the dark condition at pH 4, pH 7 and pH at 50°C for 5 days.
Photolysis (DT ₅₀)	Aqueous photolysis (DT50) is 1.3 days.

Table 3: Key physicochemical properties of the active constituent diquat dibromide

Active constituent standards

The <u>Agricultural and Veterinary Chemicals Code (Agricultural Active Constituents) Standards 2022</u> (Agricultural Active Constituents Standards 2022) entry for diquat dibromide specifies a minimum purity of diquat dibromide of 940 g/kg on a dry weight basis, with maximum levels for 2 toxicologically significant impurities of 10 mg/kg for ethylene dibromide and 2.5 g/kg for free 2,2'-bipyridyl (0.25% w/w maximum of the diquat dibromide content).

The Food and Agriculture Organization of The United Nations (FAO) Specifications for Plant Protection Products (FAO Specification for Diquat: FAO, 2008) specification for diquat dibromide technical concentrate (manufacturing concentrate) is 377 g/kg or 467 g/L of diquat dibromide (calculated by multiplying the mass of diquat ion content by 1.87), with maximum levels for 3 toxicologically significant impurities, 10 mg/kg for ethylene dibromide, 0.75 g/kg for free 2,2'-bipyridyl and 1 mg/kg for total terpyridines.

The impurity ethylene dibromide is genotoxic and is a carcinogen while the relevant impurities of 2,2'-bipyridyl and total terpyridines have acute oral toxicity (FAO, 2008).

Figure 1: Structures of toxicologically significant impurities in diquat dibromide



Statutory considerations under the safety criteria - active constituents

Under section 5A of the Agvet Code, when determining whether an active constituent satisfies the safety criteria, the APVMA must (amongst other matters) have regard to:

- · the method by which the active constituent is or is proposed to be manufactured
- the extent to which the active constituent will contain impurities
- whether an analysis of the active constituent has been carried out and the results of any such analysis
- any other relevant matters.

The manufacturing processes of each source of diquat dibromide were assessed at the time of approval, along with batch analyses of the chemical composition, including the levels of impurities.

Diquat dibromide is manufactured using 2,2'-bipyridyl and 1,2-dibromoethane (ethylene dibromide) as starting materials. As both of these compounds are of toxicological significance, maximum limits have been specified in both the APVMA standard and in the FAO specification for diquat dibromide. Terpyridines, which are also of toxicological significance, can be formed as a byproduct during the manufacture of 2,2'-bipyridyl and can therefore be present in diquat dibromide technical concentrates.

Based on the information considered at the time of approval (particularly the manufacturing process information), other impurities of toxicological significance are not expected to be present in approved sources of diquat dibromide technical concentrate.

A limit for terpyridines is not currently included in the APVMA standard for diquat dibromide. Due to the toxicological hazard presented by levels of total terpyridines exceeding the limit prescribed by the FAO specification, the APVMA is not satisfied that diquat dibromide approvals which do not comply with the FAO specification meet the safety criteria. It is therefore proposed to revise the APVMA standard for diquat dibromide technical concentrate to harmonise with the FAO specification.

Based on the information provided and the assessments conducted at the time of approval, in respect of the chemistry-related matters in the section 5A safety criteria, the APVMA remains satisfied in respect to the manufacturing method for approved diquat dibromide active constituents.

In regard to the analyses of approved diquat dibromide actives and the extent to which they contain impurities, the APVMA is satisfied that the active constituent approvals 44219 and 88174 comply with the FAO specification and meet the safety criteria. The APVMA is not currently satisfied that the remaining diquat dibromide technical concentrate approvals listed in Table 4 meet the safety criteria, as holders of these approvals have not demonstrated that they comply with the FAO specification, including the limit for terpyridines.

To demonstrate that these approvals satisfy the safety criteria, holders would need to provide revised Declarations of Composition and batch analyses demonstrating compliance with the proposed new APVMA standard (and the FAO specification) for diquat dibromide.

Approval number	Approval holder
44219 (manufacturing concentrate)	Syngenta Australia Pty Ltd
56655 (manufacturing concentrate)	Halley International Enterprise (Australia) Pty Ltd
56808 (manufacturing concentrate)	Conquest Crop Protection Pty Ltd
58221 (manufacturing concentrate)	Sinon Australia Pty Limited
58386 (manufacturing concentrate)	ADAMA Australia Pty Limited
59111 (manufacturing concentrate)	Pacific Agriscience Pty Ltd
62650 (manufacturing concentrate)	Agrogill Chemicals Pty Ltd
64501 (manufacturing concentrate)	Sharda Worldwide Exports Pvt Ltd
67123 (manufacturing concentrate)	Titan Ag Pty Ltd
87160 (manufacturing concentrate)	Agrogill Chemicals Pty Ltd
88034 (manufacturing concentrate)	Foisen Scitech Co., Limited
88174 (manufacturing concentrate)	Foisen Scitech Co., Limited

Table 4: Current active constituent approvals for diquat dibromide

Formulated products

There are currently 20 registered products containing diquat as the only active constituent. In addition, 39 agricultural chemical products contain both diquat and paraquat as the active constituents. The products are listed in Table 5.

Statutory considerations under the safety criteria – formulated products

Under section 5A of the Agvet Code, when determining whether a chemical product satisfies the safety criteria, the APVMA must (amongst other matters) have regard to:

- how the product is formulated
- the composition and form of the constituents of the product
- any relevant particulars entered into the Register for the product.

And the APVMA may have regard to:

- the stability of the product
- specifications for containers for the product.

The APVMA has previously assessed the formulation details, constituent specifications, formulation type, manufacturing process (how the product is formulated), stability and containers of each proposed product prior to registration. Based on the information provided and assessed at the time of registration, the APVMA remains satisfied with respect to the chemistry related aspects of the safety criteria for products containing diquat dibromide as the active constituent in relation to how the product is formulated, the composition and form of the constituents of the products and product stability. Additional excipients and manufacturing impurities from the active constituent up to the levels declared in the declarations of composition are considered acceptable and do not present any additional toxicological concern.

The APVMA was satisfied at the time of registration that the containers for the products met the safety criteria and remains satisfied of that aspect.

All currently registered diquat products are soluble concentrates. The formulation type recorded in the register for all products should be soluble concentrate (SL).

Registration number	Product name	Holder	Active constituents	Product group
Products conta	aining diquat as diquat dib	romide		
46534	Reglone Non-Residual Herbicide	Syngenta Australia Pty Ltd	Diquat 200 g/L	1
58411	Imtrade Diquat 200 Non-Residual Herbicide	Imtrade Australia Pty Ltd	Diquat 200 g/L	1
58833	Conquest Sanction 200 Non-Residual Herbicide	Conquest Crop Protection Pty Ltd	Diquat 200 g/L	1
59332	Kenso Agcare Diquat 200 Herbicide	Kenso Corporation (M) Sdn. Bhd.	Diquat 200 g/L	1
60297	Dia-Kill 200 Herbicide	Sinon Australia Pty Limited	Diquat 200 g/L	1
63173	Accensi Diquat 200 Non-Residual Herbicide	Accensi Pty Ltd	Diquat 200 g/L	1
64177	Titan Diquat 200 Non-	Titan Ag Pty Ltd	Diquat 200 g/L	1

Table 5: Currently registered chemical products containing diquat

Registration number	Product name	Holder Active constituents		Product group		
	Residual Herbicide					
64311	Farmalinx Diquat 200 Herbicide	Farmalinx Pty Ltd	Diquat 200 g/L	1		
64889	Genfarm Diquat 200 Non-Residual Herbicide	Nutrien Ag Solutions Limited	Diquat 200 g/L	1		
65909	Rainbow Diquat 200 Non-Residual Herbicide	Shandong Rainbow International Co Ltd	Diquat 200 g/L	1		
66064	KDPC Desiquat Non- Residual Herbicide	KD Plant Care Pty Ltd	Diquat 200 g/L	1		
68432	Ozcrop Diquat 200 Herbicide	Oz Crop Pty Ltd	Diquat 200 g/L	1		
81984	AQ 200 Aquatic Herbicide	Aquatic Site Maintenance Pty Ltd	Diquat 200 g/L	1		
82741	Water Treats Aquatic Weed Killer	Clearwater Lakes And Ponds Pty Ltd	Diquat 200 g/L	1		
83557	Apparent Diquat 200 Herbicide	Titan Ag Pty Ltd	Diquat 200 g/L	1		
84436	4Farmers Diquat 200 Herbicide	4 Farmers Australia Pty Ltd	Diquat 200 g/L	1		
88533	Barmac Diquat 200 Herbicide	Amgrow Pty Ltd	Diquat 200 g/L	1		
88796	Foison Diquat 200SL Herbicide	Foison Scitech Co., Limited	Diquat 200 g/L	1		
89075	Agrevo Diquat 200SL Herbicide	Agrevo Australia Pty Ltd	Diquat 200 g/L	1		
90843	Slash 200 SL Herbicide	Asiatic Agricultural Industries Pte Ltd	Diquat 200 g/L	1		
92386	KELPIE DIQUAT 200SL Herbicide	SINOCHEM INTERNATIONAL AUSTRALIA PTY. LTD.	Diquat 200 g/L	1		
Soluble conce	ntrate (SL) formulation con	taining paraquat as paraqua	at dichloride and diquat as diquat o	libromide		
46516	Spray.Seed 250 Herbicide	Syngenta Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2		
58336	Halley Premier 250 Herbicide	Halley International Enterprise (Australia) Pty Ltd	Diquat 115g/L paraquat 135g/L	2		

Registration number	Product name	Holder Active constituents		Product group
58412	Imtrade Spraykill 250 Herbicide	Imtrade Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
58470	Conquest Scorcher 250 Herbicide	Conquest Crop Protection Pty Ltd	Diquat 115g/L paraquat 135g/L	2
58733	4Farmers Brown Out 250 Herbicide	4 Farmers Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
59098	Spray-Plant 250 Herbicide	Sipcam Pacific Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
59333	Kenso Agcare Speedy 250 Herbicide	Kenso Corporation (M) Sdn. Bhd.	Diquat 115g/L paraquat 135g/L	2
59878	Genfarm Di-Par 250 Herbicide	Nutrien Ag Solutions Limited	Diquat 115g/L paraquat 135g/L	2
60287	Combik 250 Herbicide	Sinon Australia Pty Limited	Diquat 115g/L paraquat 135g/L	2
61460	Alarm Herbicide	Sipcam Pacific Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
61860	Titan Eos Herbicide	Titan Ag Pty Ltd	Diquat 115g/L paraquat 135g/L	2
62495	Sanonda Paraquat/Diquat Herbicide	Sanonda (Australia) Pty Ltd	Diquat 115g/L paraquat 135g/L	2
62631	Accensi Paraquat/Diquat 250 Herbicide	Accensi Pty Ltd	Diquat 115g/L paraquat 135g/L	2
63274	Uni-Spray 250 Herbicide	UPL Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
63565	Ozcrop Blowout Herbicide	Oz Crop Pty Ltd	Diquat 115g/L paraquat 135g/L	2
64325	Farmalinx Paradat Herbicide	Farmalinx Pty Ltd	Diquat 115g/L paraquat 135g/L	2
64704	Fosterra Paraquat / Diquat Herbicide	Fosterra Pty Ltd	Diquat 115g/L paraquat 135g/L	2
64802	Kwicknock 250 Herbicide	Grow Choice Pty Limited	Diquat 115g/L paraquat 135g/L	2
65295	Rainbow Diqu-Para 250 Herbicide	Shandong Rainbow International Co Ltd	Diquat 115g/L paraquat 135g/L	2
65708	Pacific Diquat/Paraquat	Pacific Agriscience Pty	Diquat 115g/L paraquat 135g/L	2

Registration number	Product name	Holder	Active constituents	Product group
	250 Herbicide	Ltd		
66197	Unispray 250 Herbicide	UPL Australia Pty Ltd	Diquat 115g/L paraquat 135g/L	2
66327	AW Dismantle Herbicide	Agri West Pty Limited	Diquat 115g/L paraquat 135g/L	2
66788	Agro-Essence Paraquat+Diquat 250 Herbicide	Agro-Alliance (Australia) Pty Ltd	Diquat 115g/L paraquat 135g/L	2
67399	Easyfarm Paraquat- Diquat 250 Herbicide	Easyfarm Pty Ltd	Diquat 115g/L paraquat 135g/L	2
67627	Apparent Weedy Seedy 250 Herbicide	Titan Ag Pty Ltd	Diquat 115g/L paraquat 135g/L	2
67707	Smart Combination 250 Herbicide	Crop Smart Pty Ltd	Diquat 115g/L paraquat 135g/L	2
67891	Spalding Exocet 250 Herbicide	DGL Environmental Pty Ltd	Diquat 115g/L paraquat 135g/L	2
68075	Ezycrop Paraquat- Diquat 250 Herbicide	Ezycrop Pty Ltd	Diquat 115g/L paraquat 135g/L	2
68202	Novaguard Paraquat- Diquat 250 Herbicide	Novaguard Pty Ltd	Diquat 115g/L paraquat 135g/L	2
68280	Agro Burner 250 Herbicide	Agrogill Chemicals Pty Ltd	Diquat 115g/L paraquat 135g/L	2
68479	Agmate Paraquat & Diquat 250 SL Herbicide	Agcare Pty Ltd	Diquat 115g/L paraquat 135g/L	2
81790	Relyon Di-Par 250 SC Herbicide	Nutrien Ag Solutions Limited	Diquat 115g/L paraquat 135g/L	2
83169	Barmac Paraquat/Diquat 250 Herbicide	Amgrow Pty Ltd	Diquat 115g/L paraquat 135g/L	2
83923	Accensi Paraquat / Diquat Prime 250 Herbicide	Accensi Pty Ltd	Diquat 115g/L paraquat 135g/L	2
85112	Raystar Paraquat Diquat SL Herbicide	Raystar Cropprotection Pty Ltd	Diquat 115g/L paraquat 135g/L	2
89832	Genfarm Di-Par 250 SC Herbicide	Nutrien Ag Solutions Limited	Diquat 115g/L paraquat 135g/L	2

Registration number	Product name	Holder	Active constituents	Product group
89918	Trio Paraquat Diquat 250 SL Herbicide	CTS Chemicals Pty Ltd	Diquat 115g/L paraquat 135g/L	2
90172	Cropsure Squadron 250 Herbicide	Cropsure Pty Ltd	Diquat 115g/L paraquat 135g/L	2
91135	Agmerch Paraquat 135 & Diquat 115 Herbicide	Agmerch Pty Ltd	Diquat 115g/L paraquat 135g/L	2

Recommendations

The APVMA notes that the limits for impurities of toxicological concern in the FAO specification for diquat dibromide are lower than those in the Active Constituent Standard 2022 for free 2-2'bipyridyl and total terpyridines. The APVMA is proposing to amend the Active Constituent Standard to align with the FAO Specification.

The recommendations of the chemistry assessment are that the APVMA:

- remains satisfied that the diquat dibromide active constituents (manufacturing concentrates) with the approval numbers 44219 and 88174 comply with the FAO Specification for diquat dibromide and continue to meet the safety criteria from a chemistry and manufacture perspective
- not be satisfied that the remaining active constituent approvals listed in Table 4 meet the safety criteria as the holders have not demonstrated that the active constituents do not contain the impurities of toxicological concern identified in the FAO Specification
- could be satisfied that all diquat dibromide active constituent approvals listed in Table 4 meet the safety criteria if the holders of those approvals provide an updated Declaration of Composition and the results of 5 batch analyses to demonstrate that they conform to the FAO Specification for Diquat to the APVMA
- be satisfied that continued registration of products containing diquat dibromide, listed in Table 5, would meet the safety criteria under section 5A of the Agvet Code from a chemistry and manufacture perspective.

Toxicology

A large toxicology database is available for diquat and was considered to be of sufficient breadth and quality for human health risk assessment purposes. The following is a summary of the conclusions of the mammalian toxicology and metabolism/toxicokinetics of diquat.

Evaluation of toxicology

Biochemical aspects

Diquat is rapidly, but poorly absorbed following oral dosing in the rat, with only 4–11% of an oral dose absorbed (Daniel & Gage, 1966). Following absorption, diquat is widely distributed, with highest concentrations in the kidneys; however, it is not extensively metabolised. The highest levels following oral absorption were present in the stomach and intestines reflecting their contents (Johnston et al, 1991). In rats, unchanged diquat was excreted in the faeces, with around 5% of administered dose excreted in the urine (Williams et al 1991) the majority of the administered dose is excreted in the faeces (up to 80%), with smaller amounts (10–20%) in the urine. Elimination of oral dosing was virtually complete by 168 h after dosing (Johnston et al, 1994(a,b)), with only 0.02% of the administered dose retained in tissues.

Percutaneous absorption of diquat in male rats resulted in maximum absorption of 3.4% (Brorby et al, 1988). Human skin or isolated epidermis showed lower levels of absorption (Scott et al 1991a & b) and was also proportional to the amount of diquat applied. The absorption rate for human, rat, rabbit, mouse and guinea pig skins was 0.058, 0.231, 0.333, 0.431 and 0.455 µg diquat cation/cm²/h, indicating that human skin was the least permeable of tested skin (Scott and Corrigan, 1989).

Major toxicological mode(s) of action and key events

Diquat mediates toxicity to mammals in 2 principal ways: direct irritation of mucous membranes, and intracellular redox cycling, which generates oxygen radicals that injure or kill cells in which they are formed.

Acute toxicity

The acute oral toxicity of diquat is moderate in rats and mice (lethal dose to 50% of sample (LD₅₀) from 120–231 mg/kg bw; Swan 1960, 1962; Duncan et al, 1985a; McCall and Robinson, 1990a), rabbits and guinea pigs (LD₅₀ approximately 100 mg/kg bw; Swan, 1960; Clark and Hurst, 1970). In dogs and monkeys the LD₅₀s were 100–200 mg/kg bw; Swan, 1960; Clark and Hurst, 1970). A range of clinical signs have been observed in laboratory animals following acute oral exposures including pupillary dilatation, difficulty in breathing, weight loss, piloerection, hypothermia, distended abdomen, upward curvature of the spine, staining around the mouth and nose, diarrhoea and incontinence.

In rats, the acute dermal toxicity of diquat is moderate ($LD_{50} > 420 \text{ mg/kg bw}$; McCall and Robinson, 1990b); however, there is high dermal toxicity in rabbits (50 mg/kg bw; Duncan, *et al.* 1985b). The acute inhalational toxicity in rats is high ($LC_{50} = 121 \text{ mg/m3}$, whole body exposure, 4-h; Bruce et al, 1985). Diquat manufacturing concentrate was a slight skin irritant (Robinson, 1998a) and a slight eye irritant ((Levy et al, 1979, Robinson, 1998(b)). While diquat dibromide was a moderate sensitiser (Rattray and Robinson, 1990), a diquat manufacturing concentration was negative for sensitisation (Thompson et al, 1985).

Acute toxicity in humans

Accidents resulting in human exposure to diquat have resulted in severe skin and eye damage, as well as corrosive damage to the mucosa following ingestion. Paralytic ileus can result in accumulation of fluid in the gut, leading to hypovolaemic shock. Nephrotoxicity, ranging from transient proteinuria to renal failure frequently occurs (Jones and Vale, 2000, Vanholder et al, 1981). Treatment with gastric lavage and the administration of activated charcoal, as well as supportive therapy, has been effective. Diquat is poorly absorbed through human skin, at around 0.3% (Feldmann & Maibach 1974).

Repeat dose toxicity

Ocular toxicity

Diquat causes cataracts in experimental animals on repeated administration. Although 8–16 weeks of continuous exposure was required in rats and dogs, cataract formation is the most sensitive indicator of medium- and longterm dietary exposure to diquat and is one of the toxicological effects upon which the original NOAEL of 0.2 mg/kg bw/d in rats was based. However, re-evaluation of this study has determined that there is no evidence of progression in rats at 15 ppm (equal to 0.6 mg/kg bw/d; Hodge, 1988; Hodge, 1989(a)), in contrast to effects at higher doses, and this is now considered to be the NOAEL for the study. The LOAELs for cataract formation were 3.6 mg/kg bw/d in rats and 2.5 mg/kg bw/d in dogs (Hopkins, 1990). Several chronic studies revealed time- and dose-dependency in the rate of onset, which was hastened by increasing doses. Interestingly, mice did not develop cataracts in 80-week and 2-year studies at doses up to approximately 50 mg/kg bw/d (Hodge, 1992(a,b)). Early studies demonstrated that diquat cataractogenesis was independent of ambient light and could not be ameliorated by dietary supplementation with ascorbic acid. It has subsequently been suggested that the reductive potential of diquat is involved in cataract formation. Injection of 300 nmol diquat into the eyes of rabbits results in enlargement and vacuolation of the posterior and anterior lens sutures within 1-3 days, separation of lens fibres within 3-4 days and complete opacity of the lens within 4-6 weeks after administration (Bhuyan and Bhuyan, 1994). These observations correlate with increased intra-ocular formation of oxy and hydroxyl radicals and H2O2, produced by the reaction of diquat free radical with O2. While the mechanisms underlying diquat cataractogenesis in laboratory species would also operate in humans, there has been no evidence that diquat has caused cataracts to develop in humans, even among occupationally exposed persons.

Renal toxicity

The kidney is the major route of excretion of diquat and is the organ in which the highest tissue residue levels of the chemical are found, and hence is vulnerable to cellular injury caused by superoxide anions generated from diquat by redox cycling. In primates and humans, the impairment and loss of renal function following acute poisoning with diquat has been well documented, as has the destruction and shedding of cells lining the renal tubule.

Renal toxicity has also been observed in repeat-dose studies with diquat, affecting mice, rats and dogs. Of these 3 species, the rat appears to be the most sensitive, developing renal impairment at and above 2.9 mg/kg bw/d during the second half of a 2-year study, although without any associated morphological abnormalities (Colley et

al, 1985). Rats fed 28 mg/kg bw/d diquat over 4 weeks displayed polyuria whereas those receiving 40 mg diquat/kg bw/d in a subchronic study showed an increased tendency to shed renal tubule cells into the urine (Horner, 1992(a)). At approximately 22 mg/kg bw/d, parental generation rats in a reproduction study had renal tubular dilatation and hypertrophy/hyperplasia of the collecting duct, whereas their offspring manifested a variety of lesions in the renal cortex, nephrons and papillae (Hodge, 1990). Urinary incontinence, renal tubule dilatation and tubular hyaline droplet formation occurred at and above 12 mg/kg bw/d in chronically exposed mice (Hodge, 1992(a,b). Renal enlargement, although not functional impairment, was seen in dogs at the termination of a 1-year dietary study in which they had been treated with diquat at 12.5 mg/kg bw/d (Hopkins, 1990).

Taken together, these results suggest that the kidney is able to withstand prolonged dietary exposure to diquat at doses equivalent to 10-20% of the LD₅₀.

Gastrointestinal tract toxicity

Consistent with its inflammatory and destructive effects on the gastrointestinal tract (GIT) epithelium subsequent to acute administration, diquat also causes similar lesions after repeated dosing. In developmental studies, stomach and intestinal inflammation and other abnormalities were found in some rabbit dams gavaged at 5 and 10 mg/kg bw/d. Short-term repeat-dose, subchronic and chronic studies in rats and dogs showed that these species are highly sensitive to irritant effects on the mouth, stomach and intestine when treated with diquat by dietary admixture. Indeed, the maximum dose was limited by ulceration and development of other lesions within the oral cavity. Even comparatively low concentrations of diquat in the feed caused macro- and microscopically detectable changes in intestinal morphology. A 1-year study by Hopkins (1990) recorded inflammation and hypertrophy of the intestine in dogs receiving 0.5 mg diquat/kg bw/d or more.

Genetic toxicology

Diquat has been assayed for genotoxicity in a wide variety of *in vitro* and *in vivo* test systems. Negative results have been obtained in assays for reverse mutation in bacteria (Callander, 1986(a,b)), recessive lethal mutation in insects (Benes and Sram, 1969), dominant lethal mutation in mice (Pasi et al ,1974; McGregor, 1974), clastogenic activity in mice (Sheldon et al, 1986) and rats (Anderson et al, 1978), and unscheduled DNA synthesis in rats (Trueman RW, 1987). Although diquat has caused forward mutation and clastogenicity in cultured mammalian cells, these effects were observed only in the presence of marked cytotoxicity, and so are not indicative of genotoxic activity *per se* (Richardson et al, 1986; Wildgoose et al, 1986).

Carcinogenicity

Long-term feeding studies in mice and rats revealed no evidence that diquat was carcinogenic (Colley, 1995; Hodge, 1992(a,b); Harling et al, 1997).

Reproduction studies

Diquat does not cause reproductive toxicity or foetal developmental malformations but is fetotoxic at maternally toxic doses. In adequate multi-generation rat studies, cataracts, oral cavity lesions and impeded food utilisation occurred in parental animals, consistent with effects noted in some repeat-dose and chronic studies (Griffiths et al, 1966; Fletcher et al, 1972; Hodge, 1990). These findings were accompanied by reduced litter size, pup bodyweight and bodyweight gain and functional and morphological evidence of injury to the urinary tract of pups. Cataracts did

not occur in pups. The lowest parental NOAEL was 1.4 mg/kg bw/d, while the NOAEL in pups was 7 mg/kg bw/d (Griffiths et al, 1966; Fletcher et al 1972).

Development studies

In developmental studies, the most sensitive species appears to be the mouse, in which NOAELs for foeto- and materno-toxicity were not established even at the lowest dose of 1 mg/kg bw/d (Palmer et al, 1978). By contrast, rats are more resistant, showing lowest NOAELs of 4 mg/kg bw/d for materno- and foeto-toxicity (Wickramaratne, 1989(a, b)). The lowest maternal and foetal NOAELs in rabbits were 1 and 3 mg/kg bw/d, respectively (Hodge, 1989(b)). In all 3 species, the most consistent toxic signs were depressed maternal bw gain, foetal viability and foetal growth, and delayed foetal ossification. Ocular injury was never observed in pups or foetuses.

Special studies

Neurotoxicity

In both humans and animals, diquat is capable of causing CNS effects at or near lethal doses. Rats given high doses orally or by injection show pupillary dilation, abolition of the light reflex, muscular twitching and convulsions. Intoxicated persons may display nervousness, disorientation and diminished reflexes. Persistent neurological symptoms have been observed following non-fatal diquat poisoning (Rudez et al. 1999), while grand mal seizures may occur in patients who do not survive. Coma is invariably present in fatal cases. These effects are thought to arise from injury to the brain, in which perivascular haemorrhage, tissue lysis and infarction of the pons are commonly found postmortem (Jones and Vale, 2000).

Modern acute and repeat-dose neurotoxicity studies with diquat in rats have been assessed (Horner, 1992(a,b)). There were no behavioural signs indicative of CNS impairment and no pathological features consistent with injury to the brain or peripheral nervous system, at even the highest doses.

There is no convincing evidence that diquat induces Parkinson's disease or any similar condition in humans or animals. Only a small (0.5%) proportion of an IV dose of diquat is taken up into the mouse brain, from which the chemical becomes rapidly depleted. A search of the available literature has not revealed any other reports associating diquat with Parkinson's disease in humans.

Human studies

The toxicity of diquat has been well characterised in humans, in part because of the considerable extent and duration of its use as a herbicide, and also because of incidents involving accidental or suicidal ingestion of diquat products.

In general, the symptoms of human exposure to toxicologically significant amounts of diquat are similar to those reported in acute and short-term studies in animals. Due to its irritancy to the skin and mucous membranes, inflammation and bleeding of the nasal mucosa have been observed in people handling crystalline diquat powder under laboratory conditions, and heavy inhalation exposure to diquat spray mist can cause irritation of the upper respiratory tract. Concentrated diquat products have been reported to delay the healing of superficial cuts on the hands of spray operators, and to cause discolouration, growth disturbances and shedding of finger or toenails.

Diquat poisoning is less common than paraquat poisoning, but the misuse of diquat has caused numerous human fatalities and cases requiring hospitalisation. The dark brown to black colour of concentrated diquat solutions has contributed to their being mistaken for soft drinks when decanted from the original container into soft drink bottles. Particularly in Japan and some developing countries, diquat and/or paraquat have been used as an agent of suicide. Since 1987, however, there has been a decline in most countries in the total numbers of suicidal deaths, although the mortality rate among persons who have swallowed diquat or paraquat remains high (Reigart & Roberts 1999). The estimated lowest lethal dose of diquat in humans is 6 g (approximately 85 mg/kg bw); clinical experience suggests that fatality will occur in one third of the cases after an ingested dose of 1–12 g, while intakes of 12 g or more are usually fatal (Jones & Vale, 2000).

Even though intestinal absorption of diquat is relatively slow, uptake into target organs and tissues occurs within 6–18 h. The early symptoms of ingested diquat poisoning arise from irritation to the oral and gastric mucosa. They include burning pain in the mouth, throat, chest and abdomen, intense nausea and vomiting and diarrhoea. Blood may appear in the vomitus or faeces. Intestinal paralysis may occur, with pooling of fluid in the gut. The kidney is both the principal organ of excretion and target organ, and renal injury is a prominent feature in cases of diquat poisoning, especially among patients who die. Proteinuria, haematuria and pyuria (excretion of pus) and elevated BUN may be observed, with possible progression to renal failure. Liver injury may also occur, seen as elevated serum ALP, AST, ALT and LDH activity, sometimes accompanied by jaundice. Some patients display signs of CNS toxicity including nervousness, irritability, restlessness, combativeness, disorientation, nonsensical statements and diminished reflexes. Neurological signs sometimes progress to coma, accompanied by tonic-clonic seizures. Brain stem infarction, particularly involving the pons, have been noted consistently in fatal cases. If the patient survives for several hours or days, circulatory function may fail due to dehydration. Hypotension and tachycardia can occur, with shock resulting in death. Toxic cardiomyopathy or a secondary infection such as bronchopneumonia may develop (Reigart & Roberts 1999; Jones & Vale 2000).

There is no antidote, and the single most effective treatment is to prevent absorption of diquat from the GIT by administration of bentonite, Fuller's earth or activated charcoal. While the use of intestinal lavage has been recommended, however its effectiveness is in doubt and it should not be performed later than 1 h post ingestion, due to the risk of inducing bleeding, perforation or scarring in the bowel if it has already suffered irritation, necrotic or other traumatic injury (Reigart & Roberts, 1999; Jones & Vale 2000). Maintenance of adequate urinary output with IV fluids is considered to be essential to correct dehydration and metabolic acidosis, accelerate diquat excretion and reduce the concentration of diquat within the renal tubule. However, iv infusion must cease if renal failure develops, in which case haemodialysis should be performed. Reigart and Roberts (1999) warn that haemodialysis is not effective in clearing diquat from the blood and tissues, probably because the bipyridyl herbicides have a large volume of distribution.

Health-based guidance values

Table 6: Points of departure for human health risk assessment

Study type		Key effect	Point of departure	Reference	
Repeat dose exposure					
Short term oral exposure	28 day oral (dietary) repeat dose; rat)	Decreased food consumption, serum chemistry changes, increased urinary volume and increased kidney weight	NOEL 200 ppm, equal to 17 mg/kg bw/day LOEL 350 ppm, equal to 30 mg/kg bw/day	Colley et al, 1981	
	13 week dietary repeat dose, rat (adult)	Reduced weight gain, food consumption and food utilisation. Cataracts developed from week 8 at 500 ppm (40 mg/kg bw/d)	NOAEL 100 ppm (8.9 mg/kg bw/day)	Hodge 1988b and 1989a	
	13 week dietary repeat	Ocular lesions and	NOAEL of 60ppm	Noakes, 2003	
	dose, rat (adult)	lens opacities evident at 300 ppm	(4.7 mg/kg bw/d)		
Long term oral exposure	2 year oral (dietary repeat dose; rat (adult)	Cataracts	NOEL – 15 ppm 0.58 mg/kg bw/day	Colley et al, 1985	
			LOEL – 75 ppm		
Reproduction and development					
Reproduction	Three-generation reproduction study; rat	Parents: cataracts, decreased bodyweight	Parental: NOAEL 125 ppm (6.9 mg/kg bw/day	Fletcher et al 1972, Griffiths et al, 1966	
		Offspring: decreased bodyweight	Offspring: NOAEL 6.9 mg/kg bw/day		

Based on the evaluation of the available toxicological database the APVMA proposes to amend the current APVMA acceptable daily intake from 0.002 mg/kg bw/day to 0.006 mg/kg bw/day, based on the re-evaluation of the 2 year rat dietary study. The acute reference dose (ARfD; shown in Table 7) for diquat will be retained.

Table 7: Acceptable daily intake for diquat

Chemical	ADI mg/kg bw/day	NOEL	Date	Study	Comments
Diquat ion	0.006	0.6	February 2024	2-year dietary rat study; a NOAEL of 0.6 mg/kg bw/d was based on lenticular cataract formation at the next higher dose	Acceptable margin of exposure ≥ 100

Chemical	ARfD mg/kg bw/day	NOEL	Date	Study	Comments
Diquat ion	0.8	75	February 2024	Acute neurotoxicity rat study: a NOAEL of 75 mg/kg bw was based on clinical signs, inappetence and reduced bodyweight gain at the next higher dose	

Table 8: Acute reference dose for diquat

Poisons scheduling

Diquat is currently in included in Schedule 7 of the Standard for the Uniform Scheduling of Medicines and Poisons (SUSMP) except when included in Schedule 6. Diquat is included in Schedule 6 in preparations containing 20% or less of diquat.

No changes to the current poisons scheduling are required.

Recommendations

The toxicological component of the Review Technical Report considered the hazards identified in acute, shortterm, chronic, reproduction and developmental toxicity studies, genotoxicity, carcinogenicity and neurotoxicity studies of diquat.

The diquat toxicology component of the Review Technical Report concluded that, provided conditions of registration and label instructions were followed:

- that the active constituents and registration of products containing diquat would not be an undue hazard to the safety of people exposed to it during its handling or people using anything containing its residues
- that the active constituents and registration of products containing diquat would not be likely to have an effect that is harmful to human beings
- the acceptable daily intake (ADI) for diquat should be established at 0.006 mg per kilogram body weight
 per day based on a no observed adverse effect level of 0.6 mg/kg bw/day in a 2-year rat dietary study,
 based on lenticular cataract formation at the next higher dose. The ADI incorporates a 100-fold
 uncertainty factor to account for inter- and intra-species variation in sensitivity
- the acute reference dose (ARfD) for diquat should remain at 0.8 mg of diquat per kg body weight based on a no observed adverse effect level of 75 mg per kilogram body weight in a rat acute neurotoxicity study. The ARfD incorporates a 100-fold uncertainty factor to account for inter- and intra-species variation in sensitivity
- that the scheduling for diquat in the Standard for the Uniform Scheduling of Medicines and Poisons remain unchanged.

Worker health and safety

The risks associated with the use of products containing diquat have been assessed in accordance with the <u>APVMA Human Health Risk Assessment Manual</u>, and a summary of the evaluation is presented.

Worker exposure assessment

This exposure assessment and risk characterisations includes professional workers who mix, load and apply diquat and combination products and professional workers who re-enter treated areas.

For exposure during mixing, loading and application, the current assessment has utilised the US EPA Office of Pesticide Programs Occupational Handler Exposure Calculator (US EPA 2020(a)). For exposure associated with re-entry into pesticide treated area, the current assessment has utilised the US EPA Occupational Pesticide Reentry Exposure Calculator (US EPA 2020(b)).

The following assumptions have been used in the exposure modelling (see Table 9).

Parameter	Value
Point of departure for risk assessment	0.282 mg/kg bw/day (based on NOAEL of 4.7 mg/kg bw/day and a 6% oral availability)
Acceptable margin of exposure (MOE)	100*
Body weight (adult)	80 kg
Body weight (child)	1 to 2 y: 11 kg
	2 to 3 y: 15 kg
Dermal absorption factor	3.3%
Inhalation absorption factor	100%
Small scale agriculture ground boom application	6 ha/day
Groundboom field application (most crops)	60 to 600 ha/day
Groundboom field application (cotton)	600 ha/day
Groundboom field application (broadacre uses)	600 ha/day
Backpack application (mixer, loader, applicator)	150 L dilute product/day
Manually pressurised hand wand application	150 L dilute product/day
Mechanically pressurised hand wand application	150 L dilute product/day

Table 9: Assumptions used in modelling exposure for professional use of diquat

* As a NOAEL from an animal study was used to estimate risks, an acceptable MOE \geq 100 was considered acceptable. This value is based on a 10-fold uncertainty factor (UF) for intra-species and 10-fold UF for inter-species differences.

The exposure assessments and risk characterisations for professional use of diquat also rely upon a further series of reasonable assumptions, notably that professional users:

- are trained in accurate mixing, loading and application methods
- are trained in, and are competent and experienced users of, personal protective equipment and relevant application techniques and equipment
- have a high level of compliance with label directions, including label-specified application rates and the use of personal protective equipment specified on product labels
- wear long-sleeved shirt, long pants, shoes and socks or an equivalent single layer of clothing when using diquat, in addition to any personal protective equipment specified on product labels.

Ground-based and aerial application

The outcomes for the exposure risk assessments for the professional use of diquat in agricultural situations using ground-based or aerial application equipment are set out in

Table 10. Modelling for ground-based application assumed that all steps in the use of diquat products are performed by a single operator (i.e. a single operator mixes, loads and applies the pesticide) and that there was only one type of use or activity performed per operator per day. Modelling for re-entry activities (8-hour days) assessed worker exposure via dermal exposure, as inhalation exposure under these circumstances were regarded as negligible. It is noted that the calculated re-entry intervals are not required when crops are treated at the bare soil or pre-emergent stage. Modelling for all scenarios assumes maximum currently approved use rates. The application rates supported by the environmental risk assessment are significantly lower than the maximum label rates considered in the assessment for the exposure to workers. Based on the maximum acceptable quantities which it would acceptable to be used by a worker per day, noted in

Table 10 and Table 11 below, the area that could be treated exceeds the area assumed in the modelling. Therefore, restrictions on the maximum quantity of active constituent that may be handled per day are not considered necessary.

Activity	Scale of use	Minimum acceptable Personal ³	Use acceptable
	assessed	Protective Equipment (PPE)	(Yes/No/Restricted)
Ground boom	Small scale	Open cab	Yes

Table 10: Risk assessment outcomes for liquid diquat products

³ Note that although mixer/loader exposure is acceptable with open mixing/loading with the specified PPE for certain uses of diquat products, closed mixing/loading is proposed for all uses to minimise the likelihood of decanting into unacceptable containers, which may lead to consequential accidental exposure.

Activity	Scale of use assessed	Minimum acceptable Personal ³ Protective Equipment (PPE)	Use acceptable (Yes/No/Restricted)	
application mix, load	agriculture	Single layer	Maximum acceptable handling	
and apply (a single operator mixes,	(up to 6 ha/day)	Gloves	rate of 56.0 kg of diquat per operator per day	
loads and applies)		PF10 respirator		
		Face shield or goggles when mixing or loading		
	Broad scale	Enclosed cab application	Yes	
	agriculture (up to 600 ha/day)	Closed mixing and loading (single layer of clothing, gloves, PF10 respirator, face shield or goggles when connecting, disconnecting or cleaning components of the mixing and loading system)	Maximum acceptable handling rate of 317.7 kg of diquat per operator per day	
Aerial application	Pilot exposure	Enclosed cab application	Yes	
	extrapolated from enclosed cab ground application		Maximum acceptable handling rate of 543.0 kg of diquat per operator per day	
Closed mixing and	Mixing and	Closed mixing and loading (Single	Yes	
loading for aerial application	loading only	layer of clothing, gloves, PF10 respirator, face shield or goggles when connecting, disconnecting or cleaning components of the mixing and loading system)	Maximum acceptable handling rate of 765.1 kg of diquat per operator per day	
Manually	150 L/day	Single layer	Yes	
pressurised hand wand application (a		Gloves	Maximum acceptable handling	
single operator		PF10 respirator	rate of ≤ 6.2 kg of diquat per operator per day	
applies)*		Face shield or goggles when mixing and loading		
Mechanically	150 L/day	Single layer	Yes	
pressurised hand wand application (a		Gloves	Maximum acceptable handling	
single operator		PF10 respirator	rate of ≤ 1.5 kg diquat per operator per day	
applies)*		Face shield or goggles when mixing and loading		

Activity	Scale of use	Minimum acceptable Personal Protective Equipment (PPE) ⁴	Use acceptable (Yes/No/Restricted)
Ground boom application mix, load and apply (a single operator mixes, loads and applies)	Small scale agriculture (up to 6 ha/day)	Open cab Single layer Gloves PF10 respirator Face shield or goggles	Yes Maximum acceptable handling rate of 56.0 kg of diquat per operator per day
-	Broad scale agriculture (up to 600 ha/day)	Enclosed cab application Closed mixing and loading (single layer of clothing, gloves, PF10 respirator, face shield or goggles when connecting, disconnecting or cleaning components of the mixing and loading system)	Yes Maximum acceptable handling rate of 317. kg of diquat per operator per day
Manually pressurised hand wand application (a single operator mixes, loads and applies)	150 L/day	Single layer Gloves PF10 respirator Face shield or goggles when mixing and loading	Yes Maximum acceptable handling rate of ≤ 6.2 kg of paraquat per operator per day
Mechanically pressurised hand wand application (a single operator mixes, loads and applies)	150 L/day	Single layer Gloves PF10 respirator Face shield or goggles when mixing and loading	Yes Maximum acceptable handling rate of ≤ 1.5 kg diquat per operator per day

Table 11: Risk assessment outcomes for liquid paraquat plus diquat products

Re-entry to treated areas

Based on the acute hazards associated with exposure to paraquat or diquat, treated areas should not be entered until the spray has dried, except in a closed cab.

At the maximum application rates on currently approved paraquat and diquat labels, entry into treated areas without gloves requires a re-entry period >30 days for ploughing, tilling, levelling, planting and mechanical

⁴ Note that although mixer/loader exposure is acceptable with open mixing/loading with the specified PPE for certain uses of diquat, and paraquat plus diquat combination products, closed mixing/loading is proposed for all uses to minimise the likelihood of decanting into unacceptable containers, which may lead to consequential accidental exposure.

harvesting and for 17 days for scouting, non-hand-set irrigation, and 22 days for irrigation (hand set). Entry into treated areas without gloves requires a 17 day re-entry period for paraquat + diquat products. However, the re-entry periods can be refined considering the significantly lower application rates that are supported by the environment risk assessment (below). The re-entry exposure resulting from uses of diquat formulations at up to 283 g diquat/ha or uses of combined paraquat/diquat formulations at up to 175 g paraquat + diquat/ha requires re-entry periods as follows.

- Diquat: for scouting and non-hand-set irrigation: one day, for hand-set irrigation: 3 days, and for ploughing, tilling, levelling, planting and mechanical harvesting: 12 days.
- Combined paraquat/diquat: once spray has dried for all activities.

Recommended label changes

Signal headings

Diquat is currently in included in Schedule 7 of the Standard for the Uniform Scheduling of Medicines and Poisons (SUSMP) except when included in Schedule 6. Diquat is included in Schedule 6 in preparations containing 20% or less of diquat.

No change to the current signal heading is required.

Restraints

General restraints

- DO NOT remove contents except for immediate use.
- DO NOT apply by spraying equipment carried on the back of the users.
- DO NOT use open mixing/loading equipment. Closed mixing and loading must be used.
- DO NOT continue to use if eye irritation or bleeding from the nose occurs.

Restraints for specific uses

For broadacre boom spray applications:

• DO NOT apply using open cab equipment. Enclosed cab application MUST be used.

For small scale agriculture boom spray application (up to 6 ha per day):

• DO NOT apply using open cab equipment unless using a PF10 respirator.

For hand spray applications:

• DO NOT use hand wand sprays by spraying out of the window of a vehicle.

First aid statements (all products)

 If poisoning occurs, get to a doctor or hospital quickly. If sprayed on skin, wash thoroughly. If sprayed in mouth, rinse mouth with water. If in eyes, hold eyes open, flood with water for at least 15 minutes and see a doctor.

Safety directions (all products)

Very dangerous, particularly the concentrate. DO NOT swallow. The product, particularly the concentrate, can kill if swallowed, absorbed through the eyes or absorbed by skin contact. The liquid can cause burns particularly to the eyes. Will irritate the nose, throat and skin. When handling, DO NOT touch or rub eyes, nose or mouth with hand. Avoid contact with eyes and skin, open wounds and clothing. Protect eyes while using. If clothing becomes contaminated with product or with wet spray remove clothing immediately. DO NOT inhale spray mist. DO NOT allow children to play with containers or any equipment that is used. When connecting, disconnecting and cleaning equipment wear cotton overalls buttoned to the neck and wrist (or equivalent clothing) and a washable hat, impervious footwear, elbow-length chemical resistant gloves and a full face respirator with canister specified for paraquat/diquat OR half face-piece respirator with canister specified for paraquat/diquat OR half face-piece respirator with canister specified for goggles. When applying by low (manual pressurised) or high (mechanically pressurised) hand wand wear cotton overalls, over normal clothing, buttoned to the neck and wrist and a washable hat, impervious footwear and a full face piece respirator with a canister specified for paraquat/diquat. After use and before eating, drinking or smoking, wash hands, arms and face thoroughly with soap and water. After each days use wash gloves, face shield or goggles, respirator (and if rubber wash with detergent and warm water), clothing and footwear.

Re-entry statements for diquat products

DO NOT allow entry to treated areas until the spray has dried except in an enclosed cab. DO NOT allow entry
to the treated area for scouting and non-hand-set irrigation for one day, for hand-set irrigation for 3 days, and
for ploughing, tilling, levelling, planting, and mechanical harvesting for 12 days.

Re-entry statements for diquat and paraquat combination products

• DO NOT allow entry to treated areas until the spray has dried.

Residues and trade

This residues and trade assessment is completed as part of the diquat reconsideration to determine if the current registered uses of diquat are supported by residues data and continue to meet the statutory safety and trade criteria.

Metabolism

Metabolism studies conducted on plants, laboratory animals and food animals were considered.

Metabolism studies in tomatoes and maize (Slade, 1966), cereals (Leahey et al, 1973; Cavell, 1987; Heath and Leahey, 1989) potatoes (Smith, 1967) and oil seed rape (Leahey and Allard, 1971), as well as an irradiation study in aqueous solutions of glucose (Heath, 1992), demonstrate that diquat undergoes photodegradation on the plant surface rather than extensive metabolism in the plant. In the studies with tomatoes and maize, when the treated plants were maintained in darkness, no breakdown of diquat occurred; however, when they were exposed to sunlight there was very rapid loss of diquat and degradation continued when the plants were dead.

Diquat was the major component and the compound 1,2,3,4-tetrahydro-1-oxopyrido[1,2-a]-5-pyrazinium chloride (TOPPS) the most important single identified photoproduct. The compounds diquat monopyridone and diquat dipyridone were also formed in low levels (≤7.5% TRR). The major proportion of the residue on the treated crops parts consists of a complex mixture of unidentified photodegradation products bound to the natural plant constituents. This was likely to be the result of the photo-initiated generation of diquat free radicals which then react with the natural constituents. The degradation of diquat was dependent on light intensity and there is no evidence of translocation of the photoproducts and only limited translocation of diquat.

Studies conducted on the rat (Leahey, 1974), goat (Hemingway et al, 1973), lactating cow (Leahey et al, 1976; Hemingway et al, 1974) and laying hen (Leahey and Hemingway, 1973; Hughes and Leahey, 1975; French and Leahey, 1988) indicate that diquat is poorly absorbed after oral administration and is excreted largely unchanged, mostly in the faeces, with TOPPS and diquat monopyridone present in low amounts (≤10.5% TOPPS and <4% diquat monopyridone in goat faeces). Highest residues occurred in the liver and kidneys and consisted of low levels of diquat and diquat monopyridone. Traces of degradation products were present in milk and eggs at low levels (0.005 mg/kg), with the majority shown to be incorporated into natural constituents such as protein, fat and lactose.

Analytical methods and storage stability

Analytical methods

Twenty-seven reports of analytical method and validation studies were submitted. The analytical methods related to plants materials (Fujie, 1987(a); Earl and Boseley, 1989; Hogbin and Thorndycraft, 1992; Anderson, 1994(a,b); Reichert, 1996), animal tissues (Kennedy, 1986(a); Fujie, 1987(b); Earl, 1992(a); Earl, 1993(a); Anderson, 1996(a); Bolton, 1996), milk (Earl, 1992(b), water (Anderson, 1994(a)), oils (Anderson, 1995), soils (Coombe, 1994; Anderson and Boseley, 1995; Weber, 1995; James, 1996; Anderson and Boseley, 1997) and human plasma, serum and urine (Thomas and Woollen, 1994; Thomas 1995(a,b)).
The studies submitted included colorimetric, gas chromatographic and liquid chromatographic methods. One residues study of diquat in rice includes the method for measurement of TOPPS in rice grain and straw, otherwise all other methods submitted determine the parent compound only.

The limits of quantification (LOQs) of these methods ranged from 0.01 to 0.05 mg/kg for plant commodities, except for sunflower seed and rape seed for which the LOQ was up to 0.1 mg/kg and for rape seed cake, for which the LOQ was 0.5 mg/kg. For animal commodities, the LOQs ranged from 0.01 to 0.05 mg/kg for milk and 0.05 mg/kg for all other commodities.

Stability of residues in stored analytical samples

Data were presented of studies conducted on the stability of diquat residues during frozen storage in a wide range of commodities.

One study measured diquat residues in samples of wheat and barley grain stored at both ambient temperature and frozen at -18° C for a period of 6–8 months (Bullock, 1980). In another study diquat residues were measured periodically in coffee beans and bananas frozen at -18° C for up to 12 months (Coombe, 1995(a,b)). There was no significant decay measured over the test periods in both studies.

In a longer-term study, samples of carrot, cabbage and wheat grain were fortified with diquat then frozen (Fujie, 1988(a); Anderson, 1996(b)). Carrot and cabbage samples were analysed in triplicate at intervals over a period of 46 months and samples of wheat grain were analysed in triplicate at intervals over a period of 18 months. Diquat residues in all 3 crops were found to be stable under these conditions.

A further study conducted to assess the stability of diquat in samples of clover seed and hay, sorghum grain, soybeans, carrots, lettuce, potatoes, wheat grain and straw, and rice grain and straw which were stored for 6 months at –20°C (Earl and Muir, 1988; Langridge, 2013). For clover, sorghum and soybeans, field-incurred residues were present, and the stability was measured by re-analysis of replicate samples from the treated crops. For carrots, lettuce, wheat, rice and potatoes, untreated control samples were fortified. Diquat residues were found to be stable in the macerated crop matrices for a minimum of 6 months).

In another study, chaff from wheat harvested 7 days after treatment with C14-diquat and stored frozen for 5– 6 years was milled to a homogenous sample. On combustion, the total radioactive residue was measured as 157 mg/kg. This was compared to 168 mg/kg at the time of initial analysis (Bullock, 1980).

Residue definition

Due to little metabolism of diquat in plants and animals, diquat cation can be considered as the most appropriate residue definition for enforcement and risk assessment. This is consistent with the residue definition established overseas (see <u>Residue related aspects of trade</u>).

Residues in foods

The diquat product labels have broad crop groupings on the labels such as row crops, vegetables, market gardens and orchards. Diquat, by virtue of its use pattern groupings has historically lent itself to general commodity groupings in the MRL standard such as fruits and vegetables.

The current best practice is to approve label claims and establish MRLs based on the APVMA crop group guidance⁵ and Codex Alimentarius (Codex) commodity groups. Therefore, it is appropriate that the current MRLs for fruits and vegetables and use patterns on labels reflect the appropriate crop groups and be reconsidered separately as part of this review.

Cropping situations

There are 4 distinct diquat use patterns in cropping situations:

Crop establishment or pre-emergence weed control

Applications can be made pre-sowing or post-sowing pre-emergence. The maximum pre-sowing crop and pasture establishment use rate is 0.368 kg ac/ha. The maximum post-sowing pre-emergence use rate is 0.8 kg ac/ha and includes the broad categories of row crops, vegetables and market gardens, in addition to the specific crops asparagus and rice. The submitted residues data on a wide range of crops demonstrated pre-emergence applications generally do not produce detectable residues in the harvested commodity.

Crop post-emergence directed or shielded weed control

Applications can be made as inter-row shielded sprays to emerged row crops and vines or as a directed spray around the base of tree crops. The applications can occur at any stage of the crop growth cycle although they generally occur before the crop canopy closes over. The maximum rates are 0.8 kg ac/ha for row crops, vegetables and market gardens, 0.28 kg ac/ha for hops, and 0.368 kg ac/ha for potatoes. The maximum rate for applications around the base of tree crops or between vines is 0.368 kg ac/ha.

The submitted residues data demonstrated that shielded sprays at early crop post-emergence and directed sprays around the base of trees crops generally do not result in detectable residues. Where detectable residues did occur in fruit from tree crops, the sampled fruit had either fallen and was directly sprayed or was deliberately dropped onto the sprayed ground. For some vegetable crop groups, the available residue data does demonstrate a potential for low but finite levels of diquat residues following directed post emergent use (see <u>Vegetable crops</u>).

⁵ APVMA <u>crop group guidance</u>, available on APVMA website.

Crop or pasture post-emergence over the top weed control applications

Applications can be made over the top of plant and ratoon sugarcane and mature potato and cereal crops, the later 2 crops to assist digging and harvest. The maximum use rate is 0.23 kg ac/ha for sugarcane, 0.368 kg ac/ha for potatoes and 0.6 kg ac/ha for cereal crops. These applications to cereal crops are expected to result in detectable residues as the cereal head is exposed to the spray.

Diquat is also applied directly at rates of 0.276–0.368 kg ac/ha to lucerne, mixed pasture and grass pastures to assist in weed control for establishment and renovation, or to suppress kikuyu and paspalum pastures for oversowing of winter feed. These applications are expected to result in detectable residues in the plant material, which is routinely grazed, noting the grazing WHP is one day.

Pre-harvest desiccation applications

Applications to assist plant desiccation as well as weed control prior to harvest are expected to result in significant residues in the crop grains and remaining dried plant material that is cut or grazed for feed. The Australian use rate for cereal, oilseed, pulse and sugar cane crops is 0.6 kg ac/ha while for poppies, potatoes and sweet potatoes the rate is 0.8 kg ac/ha.

Summary of diquat residues in submitted studies

The submitted studies are categorised below according to their crop grouping and the related use pattern on the diquat labels. The submitted residues data was comprehensive for some crops and crop groups such as peas, beans, oilseeds, potatoes, and cereals; however, for other crop groups, there was less available data, or no available data.

Use pattern	Crop group	Submitted studies	
Orchards and vineyards (including bananas)	Pome	Apples	
Avocado, custard apple, lychee,	Stone	Peaches	
mango * Note: Berries other than grapes	Berries *	Grapes, strawberries, blueberries	
and pineapples will be considered against the row crop label claim	Assorted trop. and sub-trop. (edible peel)	Olives	
	Assorted trop. and sub-trop. (inedible peel)	Bananas	
	Citrus	None	
	Tree nuts	None	
Row crops, vegetables and market	Bulb vegetables	Onions	
gardens	Brassica vegetables	Broccoli, cabbage, Chinese cabbage, Brussels sprouts	

Table 12: Summary of use patterns, crop groups and residue studies submitted for assessment

Use pattern	Crop group	Submitted studies		
	Cucurbits	None		
	Fruiting vegetables, other than cucurbits	Tomatoes, capsicums		
	Herbs and spices	None		
	Leafy vegetables	Lettuce		
	Legume vegetables	Peas and beans		
Sweet potato Asparagus	Root and tuber vegetables	Potato, radish, turnip, sugar beet carrot		
	Stem and stalk vegetables	Celery		
Dry peas, dry beans, lentils, chickpeas, faba beans, lupins, mung beans, pigeon peas, soybean	Pulses	Peas, beans, lentils, field peas, soybeans		
Winter cereals	Cereal grains	Wheat, barley, oats		
Maize	-	Maize		
Sorghum	-	Sorghum		
Rice		Rice		
Sugarcane	Sugarcane	Sugarcane juice		
Linseed Poppies Canola Sunflower	Oilseeds	Cotton, linseed, peanuts, sesame, sunflower, rapeseed, poppies		
Hops	Hops	Hops		
Crop establishment	Pulses Cereal grains Oilseeds Pasture	See above		
Lucerne Pasture (grass and mixed) Legume seed crops	Pasture	Lucerne, clover, grass, forage and fodder of peas, beans, pulses and soybeans, fodder and forage of cereals		

Fruit crops

The current MRL for fruit crops, listed as 'Fruits' is LOQ (*0.05 mg/kg) includes all fruits on the labels from orchards (including bananas and vineyards), market gardens and row crops, and tropical fruits (avocado, custard apple, litchi and mango). In this assessment, separate MRLs for each of the codex groupings of fruits are proposed.

The following crops will be considered against the current label use pattern for orchards and vineyards (including bananas) claims: grapes, citrus, pome fruit, stone fruit, tree nuts, tropical fruit (edible peel), tropical fruit (inedible peel, except pineapple). Berries (other than grapes) and pineapples will be considered against the current label claim for row crops.

Pome fruit

The available diquat residue trials on pome fruit (apples) are summarised below. The maximum Australian use rate involves application around the base of trees at a rate of 0.368 kg ac/ha. Overseas trials were carried out using rates of 1.0–11.2 kg ac/ha, including one trial with 4.48 kg diquat dichloride/ha (Calderbank and Yuan, 1963; Anon., 1987). Single applications were made as sprays around the base of the tree, and in one trial applications were made directly to the bark of the tree in contravention of the current label instructions. Apples were harvested between 72 and 112 days after the application. In only one trial, at the rate of 6.7 kg ac/ha, were low finite residues (0.015 mg/kg) were detected in apples. In all other trials, residues were <LOQ. The LOQ was 0.01 mg/kg in all apple trials except for one which had a LOQ of 0.05 mg/kg. This data demonstrates that residues above the LOQ of 0.01 mg/kg should not occur in apples as a result of the current label use (0.368 kg ac/ha).

The available diquat residues data supports continued use in pome fruit orchards. The recommended entry into the MRL Standard for pome fruit is:

FP 0009 Pome fruits

*0.01 mg/kg

As the use is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for pome fruit.

Stone fruit

The available diquat residue trials on stone fruit (peaches) are summarised below. The maximum Australian use rate involves application around the base of trees at a rate of 0.368 kg ac/ha. No detectable residues were found in peach flesh harvested 28 or 52 days after 5 applications at rates of 0.39 to 0.9 kg ac/ha in 2 overseas trials (Swaine, 1981(a)). The LOQ was 0.01 mg/kg. This data demonstrates that residues above the LOQ (0.01 mg/kg) should not occur in peaches as a result of current rate (0.368 g ac/ha). While it is noted that only 2 peach trials are available for the stone fruit crop group, diquat residues data, which demonstrates that residues above the LOQ should not occur in other tree fruit crops, is supportive of this use in stone fruit.

The available diquat residues data supports continued use in stone fruit orchards. The recommended entry into the MRL Standard for stone fruit is:

As the use is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for stone fruit.

Berries and other small fruit

The available diquat residue trials on berries and other small fruit (grapes, strawberries, blueberries) are summarised below. The maximum Australian use rate to grapes involves application between the vines at 0.368 kg ac/ha. Seventeen overseas trials were conducted on grapes (Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; Kennedy, 1988(a); Anderson et al., 1994(a); Dick et al., 1995(a)), with detectable residues occurring in 2 trials where sampling occurred 2 days after application of 0.8 kg ac/ha (0.02, 0.016 mg/kg) and in the 4 trials where 3 applications of 1 kg ac/ha were made, and samples of dropped fruit (dropped 3–12 hours after the last application) were taken 14 days after the last application (0.03, 0.05, 0.06, 0.03 mg/kg). These rates are higher than the current Australian maximum use rate and the collection of fallen grapes is not normal practice. LOQs ranged from 0.01 to 0.05 mg/kg.

The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include berries and other small fruit, except for grapes (covered by the vineyard use). The use is pre-emergence or by shielded spray post emergence. No detectable residues of diquat were found in strawberry trials in and a blueberry trial with application rates of 0.4 to 1.4 kg ac/ha. LOQs were 0.01 to 0.05 mg/kg (Calderbank and McKenna 1964; Anon. 1981). In 3 additional strawberry trials summarised by the 2013 Joint FAO/WHO Meeting on Pesticide Residues (JMPR) residues were <0.05 mg/kg at 47–50 days after an inter-row directed spray at 0.85–0.92 kg ac/ha.

The available diquat residues data supports continued use in grapes (vineyards) and other members of the berries and other small fruit crop group. The recommended entry into the MRL Standard for berries and small fruits, including grapes, is as follows noting the LOQ is many of the grape and strawberry trials was 0.05 mg/kg:

FB 0018 Berries and other small fruits

*0.05 mg/kg

As the use is targeting inter-row weeds and not the crop, a harvest withholding period statement of 'Not Required when used as directed' is supported for berries and other small fruit.

Tropical and sub-tropical fruit with edible peel

The available diquat residue trials on tropical and sub-tropical fruit with edible peel (olives) are summarised below. The maximum Australian use rate involves application around the base of trees at a rate of 0.368 kg ac/ha. In 4 overseas olive trials single applications of rates from 0.24 to 0.78 kg ac/ha were made 6–17 days prior to sampling at either the ripening stage or maturity (Kennedy, 1987(a); Massey, 1987(a); Dick et al.,1995(b)). In 2 trials, ripening olives were sampled directly from the canopy and the whole fruit and extracted oil contained no detectable residues of diquat (LOQ 0.1 mg/kg for fruit, 0.05 mg/kg for oil). In the remaining 2 trials mature fruit lying on the ground at the time of treatment of 0.4 kg ac/ha, and collected 6–7 days later, contained diquat residues of 0.31 and 1.5 mg/kg. Collection of sprayed fruit would not be considered good agricultural practice. This data demonstrates that residues above the LOQ (0.1 mg/kg) should not occur in olives as a result of current rate (0.368 kg ac/ha). While it is noted that only 4 olive trials are available for the tropical fruit with edible peel crop group, diquat residues data which demonstrates that residues above the LOQ should not occur in other tree fruit crops is supportive of this use in tropical fruit with edible peel.

The available diquat residues data supports continued use in assorted tropical and sub-tropical fruits – edible peel. The recommended entries into the MRL Standard for are as follows noting that olives for oil production (SO 0305) will not be covered by the tropical fruit with edible peel group MRL:

•	FP 0026	Assorted tropical and sub-tropical fruits – edible peel	*0.1 mg/kg
•	S0 0305	Olives for oil production	*0.1 mg/kg

As the use is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for assorted tropical and sub-tropical fruits – edible peel.

Tropical and sub-tropical fruit with inedible peel

The available diquat residue trials on tropical and sub-tropical fruit with inedible peel (bananas) are summarised below. The maximum Australian use rate in orchards (which covers all tropical fruit with inedible peel, except pineapples) involves application around the base of trees at a rate of 0.368 kg ac/ha for the general use in orchards. There is a specific use on avocado, custard apple, lychee and mango at 27.6 g ai/100 L applied to ground cover beneath the trees. A second spray 14 days later may be required.

In 8 overseas trials on bananas 3 applications 28–33 days apart were made around the base of mature banana plants at rates of 0.15 to 0.6 kg ac/ha (Earl, 1993(b); Earl, 1994). Residues of diquat were not detected in bananas sampled immediately after the last application (LOQ 0.02 mg/kg). This data demonstrates that residues above the LOQ should not occur in banana as a result of current rate (0.368 kg ac/ha or 27.6 g ai/100 L). While it is noted that only banana trials are available for the tropical fruit with inedible peel crop group, diquat residues data, which demonstrates that residues above the LOQ should not occur in other tree fruit crops, is supportive of this use in tropical fruit with inedible peel, except for pineapple.

Residue data for diquat on pineapples have not been provided for the review and are not available in the JMPR evaluations. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops which may include pineapples. The use is pre-emergence or by shielded spray post emergence. The available banana data (0.15 to 0.6 kg ac/ha) did not address the application rate of 0.8 kg ai/ka and it is noted that crop physiology and agronomy for pineapple differs to bananas and other members of the tropical fruit with inedible peel crop group. As discussed in the risk assessment for <u>Vegetable crops</u> Vegetable crops, there is a potential for residues to occur in crops following the current label use for row crops. It is therefore not appropriate to support the continued use of diquat on pineapples without specific residue data as a robust assessment of the potential for residues in pineapples cannot be performed.

The available diquat residues data supports continued use in tropical fruit with inedible peel, which was covered by the label claim for orchards and the specific use for avocados, custard apples, litchis and mangoes (2 application, 14 days apart at 27.6 ai/100L). Continued use in pineapples, which was covered by the row crop label claim is not supported due to a lack or residues data. The recommended entry into the MRL Standard for is:

• FP 0030 Assorted tropical and sub-tropical fruits – inedible peel {except Pineapple} *0.02 mg/kg

As the use on tropical fruit with inedible peel (except pineapples) is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for assorted tropical and sub-tropical fruits – edible peel.

Citrus

The general use on orchards may include citrus. The maximum Australian use rate involves application around the base of trees at a rate of 0.368 kg ac/ha. No residues data for citrus has been submitted but owing to the nature of the use pattern (around the base of trees) and given the weight of evidence for other tree crops, diquat residues in citrus fruit at commercial maturity above the LOQ are not expected.

The available diquat residues data for other tree crops supports continued use in citrus orchards. The recommended entry into the MRL Standard for citrus fruit is:

• FP 0001 Citrus fruits

*0.05 mg/kg

As the use is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for citrus fruit.

Tree nuts

Some diquat product labels contain specific uses in hazelnuts, pistachios and walnuts and general use on orchards may also include tree nuts. The maximum Australian use rate involves application around the base of trees at a rate of 0.368 kg ac/ha. No residues data for tree nuts has been submitted but owing to the nature of the use pattern (to the base of tress) and given the weight of evidence for other tree crops, diquat residues in tree nuts at commercial maturity above the LOQ is not expected. For this reason the MRL of *0.05 mg/kg for diquat on tree nuts will remain in place.

As the use is directed to weeds and not the trees, a harvest withholding period statement of 'Not Required when used as directed' is supported for tree nuts.

Vegetable crops

The current MRL for vegetables [except potato and pulses] is *0.05 mg/kg. The general vegetable MRL will be broken down to separate MRLs for the various codex classifications of vegetables.

The following crop groups will be considered against the current row crop, vegetables and market garden label claims: brassica vegetables, bulb vegetables, fruiting vegetables (cucurbits), fruiting vegetables (other than cucurbits), leafy vegetables, legume vegetables, root and tuber vegetables, stalk and stem vegetables and herbs and spices.

Bulb vegetables

The available diquat residue trials on bulb vegetables (bulb onions) are summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens which may include bulb vegetables. The use is pre-emergence or by shielded spray post emergence. Detectable residues of diquat were measured in 6 suitable overseas trials in bulb onions (Calderbank and McKenna, 1964; Anon., 1972; Edwards, 1977; Kennedy, 1984(a); Massey, 1987(b); Anderson and Lant, 1994(a); Anon., no date(a)). In one trial residues of 0.10 and 0.03 mg/kg were measured in samples taken 6–7 days after the last of 3 applications of 0.8 kg ac/ha. In another trial residues were found of 0.05, 0.04, 0.03 and 0.02 mg/kg in samples taken 15 days after single applications of 0.56–1.12 kg ac/ha. One trial had residues of 0.08 and 0.14 mg/kg 11 days after applications of 1.2 and

0.2 mg/kg

2.4 kg ac/ha, respectively. Another had residues of 0.06 mg/kg in the unbrushed onion when sampled immediately after an application of 0.3 kg ac/ha. Detectable residues of diquat were measured in 2 additional trials with residue up to 0.02 mg/kg in samples taken from zero to 14 days after an application of 0.9 kg ac/ha and residues up to 0.04 mg/kg in samples taken from zero to 21 days after the last of 3 applications of 0.75 kg ac/ha.

The highest residues reported in bulb onions, which was relevant to the Australian use rate of 0.8 kg ac/ha, was 0.10 mg/kg after 3 applications of 0.8 kg ac/ha and an MRL at 0.2 mg/kg is considered appropriate for bulb onions. It is noted that the available onion trials addressed the bulb only, and residues data for green onions (or the leaves of onions) is not available. The representative crops for the bulb vegetable crop group are bulb onions (from the bulb onion subgroup) and spring onion (from the green onion subgroup)⁶. The residue potential from the post emergent shielded spray use may be higher for green onions than bulb onions as the edible commodity for green onions is above ground.

The available diquat residues data supports continued use in the bulb onion subgroup, which includes bulb onions, shallots and garlic (among others). In the absence of residues data for spring onion or other members of the green onion subgroup, continued use in members of the green onion subgroup is not supported noting that finite residues may be expected and a robust assessment of the potential for residues in green onions cannot be performed without specific residues data.

The recommended entry into the MRL Standard for bulb onions is:

VA 2031 Bulb onions

Although the high residue (HR) was observed at 6–7 days after application at 0.8 kg ac/ha (1x), a 'Not required when used as directed' withholding period is considered suitable for shielded spray application post emergence, noting also that lower residues were observed immediately after application and that an MRL has been recommended to cover the observed HR.

Brassica vegetables

The available diquat residue trials on brassica vegetables (broccoli, cabbage, Chinese cabbage, cauliflower and Brussels sprouts) are summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens which may include brassica vegetables. The use is pre-emergence or by shielded spray post emergence.

Overseas trials were conducted on broccoli and cauliflower, which are members of the flowerhead brassica subgroup as well as cabbage and Chinese cabbage which are members of the head brassica subgroup. A single

⁶ Crop group 009, Bulb vegetables, available on the APVMA website.

trial on Brussels sprouts was provided however that trial was considered to be unreliable. The representative crops for brassica vegetable crop group⁷ are broccoli or cauliflower, head cabbage and Brussels sprouts.

In the trials conducted on broccoli, cauliflower, cabbage and Chinese cabbage, one to 3 applications were made at rates of 0.5 to 2.2 kg ac/ha. Samples were collected 7–50 days after the last application. Residues of diquat were not detected in any of these trials (LOQ 0.01 to 0.02 mg/kg)(McKenna, 1966; Edwards, 1977).

The available diquat residues data supports continued use in the specific brassica vegetables for which there is suitable residues data, namely broccoli, cauliflower, cabbage and Chinese cabbage. In the absence of residues data for Brussels sprouts, which is a representative crop, use in Brussels sprouts or the entire brassica vegetable crop group is not supported due to a lack of relevant residues data (for Brussels sprouts). The recommended entries into the MRL Standard for Brassica vegetables are:

•	VB 0400	Broccoli	*0.02 mg/kg
•	VB 0041	Cabbages, head	*0.02 mg/kg
•	VB 0404	Cauliflower	*0.02 mg/kg
•	VB 0467	Chinese cabbage (type Pe-tsai)	*0.02 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for broccoli, cauliflower, cabbage and Chinese cabbage.

Fruiting vegetables (other than cucurbits)

The available diquat residue trials on fruiting vegetables, other than cucurbits (tomatoes, capsicums) are summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include fruiting vegetables. The use is pre-emergence or by shielded spray post emergence. In the single overseas capsicum (sweet pepper) trial residues of diquat were not detected in the whole fruit when applied once at 2.2 kg ac/ha and sampled 22 days later (LOQ 0.05 mg/kg; McKenna, 1966). In 2 overseas tomato trials, residues were not detected in whole fruit of tomatoes when applied one or 3 times at 0.6 kg ac/ha and sampled 6–7 days later, nor were residues detected when diquat was applied in overhead irrigation water at 0.1 ppm (LOQ 0.01 mg/kg; McKenna 1966). The 2013 JMPR considered additional residue data for tomatoes involving inter-row directed sprays for weed control (preharvest interval (PHI) 15 days) and concluded there is no expectation of residues above the LOQ (0.01 mg/kg; Edwards MJ, (1977).

The available diquat residues data supports continued use in fruiting vegetables (other than cucurbits) noting that residues data is available for the 2 representative crops of tomatoes and peppers. The recommended entry into

⁷ Crop group 010: Brassica (cole or cabbage) vegetables, Head cabbages, Flowerhead cabbages, available on the APVMA website.

the MRL Standard for Fruiting vegetables, other than cucurbits is as follows noting that the predominant LOQ in the available trials was 0.01 mg/kg:

• VO 0050 Fruiting vegetables, other than cucurbits *0.01 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for fruiting vegetables, other than cucurbits.

Leafy vegetables

The available diquat residue trials on lettuce are summarised below. Relevant data for radish leaves are also summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens which may include leafy vegetables. The use is pre-emergence or by shielded spray post emergence.

A number of overseas trials conducted on head lettuce or leaf lettuce were provided (McKenna, 1966; Edwards, 1977; Kennedy, 1984(a); Massey, 1987(c); Anderson and Lant, 1994(a)). In trials that involved one to 2 applications at rates approximate to the Australian rate (0.7–1 kg ac/ha), residues were 0.01 (2), <0.02, 0.07, 0.13, 0.23 and 0.91 mg/kg at a zero day PHI. In the same trials, residues were <0.01, 0.01, <0.02 (2), 0.03, 0.05 and 0.07 mg/kg at a 7–10 day PHI. It is noted that the post-emergence treatments in the trials did not involve shielded sprayer and therefore represent a worst case.

Residues in radish leaves at zero days after the last of 4 applications at 0.6 kg ac/ha were 0.03 mg/kg, and <0.01 mg/kg at 8 days after the last of 3 applications at the same rate (Calderbank and Yuan 1963).

While a HR of 0.91 mg/kg was observed in lettuce at a zero day PHI, that sampling time is not relevant to preemergent application, and it is considered that post-emergent shielded spray applications would not be made close to harvest and crops should not be directly contacted with diquat spray under normal agronomic practice. The samples lettuce and radish leaf samples collected 7–10 days after application are considered to represent the realistic worse case residue potential. The OECD MRL calculator recommends an MRL of 0.15 mg/kg based on the 7–10 day data. A MRL at 0.2 mg/kg is considered to be appropriate leafy vegetables noting that one relevant trial is from radish leaves (from the brassica leafy vegetable subgroup⁸).

The available diquat residues data supports continued use in leafy vegetables. The recommended entry into the MRL Standard for leafy vegetables is:

VL 0053 Leafy vegetables
0.2 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for leafy vegetables.

⁸ <u>Crop group 13: Leafy vegetables (including Brassica leafy vegetables)</u>, available on the APVMA website.

Legume vegetables

The available diquat residue trials on legume vegetables (peas and beans) are summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include legume vegetables. The use is pre-emergence or by shielded spray post emergence. Overseas trials for peas and beans have been provided (Anon., no date(b); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1972; Edwards, 1977; Anon., 1980(a); Culoto and de Mallmann, 1982; Swaine, 1983(a); Culoto, 1985(a); Kennedy, 1986(b); Massey, 1987(d); Anon., 1987; Earl, 1991(a); Earl and Hall, 1994; Roper, 1995(a,b); Roper, 1996). It was not always clear from the submitted trial information whether the peas and beans were harvested when succulent (legume vegetables), or dried (pulses) but given that the use on legume vegetables pre-emergence or by shielded spray post emergence, the pre-emergent trials on peas and beans are considered relevant.

For 8 overseas trials where a pre-emergence or post-emergence application was made to peas, no detectable residues of diquat were found in the pea seed, pods or stalks/vines (LOQ 0.05–0.1 mg/kg). Rates in these trials ranged from 0.14 to 1.12 kg ac/ha. In one trial with a pre-emergence application of 1.7 kg ac/ha residues of 0.06 mg/kg were measured but that residue would scale to below the LOQ of 0.05 mg/kg when corrected for the Australian application rate (0.8 mg/kg). In one trial on snap beans residues of diquat were not detected after an application of 2.24 kg ac/ha (LOQ 0.05 mg/kg). Samples were taken 22 days after application and although not stated, snap beans are routinely harvested green, therefore this trial represents the Australian use pattern of weed control for legume vegetables (when corrected for rate). Based on this data, the pre-emergence and post-emergence (shielded sprayer) use pattern where the maximum Australian rate is 0.8 kg ac/ha is not likely to result in detectable residues in peas and beans at commercial maturity.

The available diquat residues data supports continued use in legume vegetables. The recommended entry into the MRL Standard for legume vegetables is:

VP 0060 Legume vegetables

*0.05 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for legume vegetables.

Root and tuber vegetables

The available diquat residue trials on root and tuber vegetables (potato, radish, turnip, sugar beet and carrot) are summarised below. The maximum Australian label rate for potatoes is 0.368 kg ac/ha for post-emergence and preharvest weed control and 0.8 kg ac/ha for pre-harvest desiccation. The withholding period is 7 days for the preharvest desiccation application. Another use allows application to potatoes at 368 g ac/ha at 3–7 days before digging, while there is a pre-harvest desiccation use on sweet potatoes which allows application at 800 g ac/ha with a 14 day withholding period. Other root and tuber vegetables are covered by the general row crop and market garden pre-emergent or post emergent shielded spray application use at 0.8 kg ac/ha.

Twelve reports were submitted containing results of residues trials from Australia and overseas on potatoes (Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Swaine, 1982(a); Kennedy, 1984(a); Kennedy, 1987(b); Earl and Anderson, 1989(a); Earl, 1991(b,c); Anderson and Earl, 1993; Earl et al.,1993; Roper, 1995(c)). The majority of the trials were pre-harvest desiccation applications, although several pre- and post-emergence weed control application trials were also submitted. Residues in the pre-harvest

desiccation trials were mainly below 0.02 mg/kg, although in one study mean residues of 0.06, 0.17 and 0.26 mg/kg occurred in tubers after an application of 0.84, 1.1 and 2.2 kg ac/ha, respectively. When scaled for the application rate of 0.8 kg ac/ha, the HR is 0.12 mg/kg. Residues of diquat in more recent reports were in the range <0.01 to 0.07 mg/kg in tubers sampled 4–44 days after 1–3 applications of 0.2 to 1.0 kg ac/ha, with most below the LOQ (0.01, 0.02 or 0.05 mg/kg).

The 2013 JMPR considered additional 16 European trials for a pre-harvest use on potatoes (residues ranging from <0.01–0.02 mg/kg, 0–15 days after treatment at approx. 1 kg ac/ha) along with data from the USA (that have been submitted for this review). The JMPR recommended an MRL of 0.1 mg/kg for diquat on potatoes for an approved use (good agricultural practice or GAP) similar to that registered in Australia (GAP from the USA: 0.56 kg ac/ha, PHI 7 days).

While no residues data is available for sweet potato, sweet potato and potato are both members of the same subgroup (Subgroup 016B, Tuberous and corm vegetables⁹) and therefore extrapolation from potato data to sweet potato is possible.

An MRL of 0.2 mg/kg is recommended for diquat on VR 0508 Sweet potatoes at the same level as the current MRL for VR 0589 Potatoes, which also remains appropriate, to cover the pre-harvest desiccation uses on these crops with 14 and 7 day withholding periods respectively. It is noted that a recommendation of the paraquat review for products containing paraquat and diquat for use on potatoes '3 to 7 days before digging and after tops have died down' was that application should occur '4–5 weeks before digging'. However, there are standalone diquat products that can be used on potatoes at up to 0.8 kg ac/ha 7 days before harvest.

Three reports were submitted that contain summary information of trials conducted on radish, turnip and sugar beet in Canada, Japan, Italy and the UK during the period 1962–75 (Calderbank and Yuan, 1963; McKenna, 1966; Edwards, 1977). Two trials on radish in Japan were pre-emergence weed control applications, the sugar beet trials were pre-harvest desiccation applications and the trials on radish and turnip in Canada were probably also pre-harvest desiccation applications, based on the PHI, however the use pattern was not stated in the report. No Australian trials were submitted.

No detectable residues of diquat occurred in tubers sampled zero to 96 days after one to 4 applications of rate from 0.4 to 4.4 kg ac/ha.

There were 13 overseas carrot trials conducted as pre-emergence and post-emergence weed control (Anon., no date(a); McKenna, 1966; Edwards, 1977; Kennedy, 1984(a); Anderson and Lant,1994(a): Massey, 1987(e)). Residues of diquat in these trials were generally <0.02 mg/kg, with a maximum of 0.07 mg/kg recorded in samples taken 14 days after an application of 1.0 kg ac/ha (1.25× the maximum label rate). The maximum residue recorded after application at 0.8 kg ac/ha (1× the maximum label rate) was 0.04 mg/kg in the same trial (14 day PHI). In another trial, residues were all <0.02 mg/kg in samples taken one, 7, 13 and 20 days after an inter-row weed control application of 0.8 kg a.i/ha. The PHI in all these trials ranged from one to 123 days and the shorter intervals

⁹ Crop group 016: Root and tuber vegetables, available on the APVMA website.

would not reflect typical agronomic practice where application as a pre-emergence weed control is earlier in the crop growth cycle, or via shielded sprayer later in the growing cycle.

Diquat residues in other root and tuber vegetables after pre-emergent or post emergent shielded spray application will be covered by an MRL recommended at 0.1 mg/kg in conjunction with a 'Not required when used as directed' harvest withholding period (the sugar beet MRL at 0.1 mg/kg will be deleted). This group MRL will cover the HR of 0.07 mg/kg observed in carrots after a pre-emergence application.

The supported/recommended MRLs are:

•	VR 0589 Potato	0.2 mg/kg
•	VR 0075 Root and tuber vegetables {except Potato; Sweet potato}	0.1 mg/kg
•	VR 0508 Sweet potato	0.2 mg/kg

Stem and stalk vegetables

The available diquat residue trials on stalk and stem vegetables (celery) are summarised below. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include stalk and stem vegetables. The use is pre-emergence or by shielded spray post emergence. There is also a specific use on asparagus prior to spear emergence at 0.28 kg ac/ha.

A single trial on celery was submitted and no relevant data was available in the JMPR evaluations (McKenna RH, 1966). No detectable residues occurred in celery stalks sampled 36 days after a single application of 2.22 kg ac/ha. However, the LOQ for the method was not reported and the trial is not considered to be reliable. The representative crops for the stalk and stem vegetable crop group¹⁰ are celery, asparagus and artichoke globe.

It is not appropriate to support the continued use of diquat on stalk and stem vegetables (including the specific asparagus use) without specific and reliable residue data for the representative crops as residue data for other vegetable crops have indicated a potential for finite residues from the current use in row crops and market gardens for some crop groups. Without residues data for stalk and stem crops such as celery, asparagus and artichoke globe (the representative crops) a robust assessment of the potential for residues in stalk and stem vegetables cannot be performed and these uses are not supported.

Cucurbits

Residue data for diquat on cucurbits have not been provided for the review and are not available in the JMPR evaluations. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include cucurbits. The use is pre-emergence or by shielded spray post emergence. However, it is not appropriate to support the continued use of diquat on cucurbits without specific residue data as residue data for

¹⁰ Crop group 017: Stalk and stem vegetables, available on the APVMA website.

other vegetable crops have indicated a potential for finite residues from the current use in row crops and market gardens for some crop groups. Without residues data for cucurbit crops such as rock melon (cantaloupe), cucumber and zucchini (the representative crops) a robust assessment of the potential for residues in cucurbits cannot be performed and these uses are not supported.

Herbs and spices

Residue data for diquat on herbs and spices have not been provided for the review and are not available in the JMPR evaluations. The maximum Australian label rate is up to 0.8 kg ac/ha for row crops and market gardens, which may include herbs and spices. The use is pre-emergence or by shielded spray post emergence. However, it is not appropriate to support the continued use of diquat on herbs and spices without specific residue data as residue data for other crops including leafy vegetables have indicated a potential for finite residues from the current use in row crops and market gardens for some crop groups. Without residues data for herb and spice crops, a robust assessment of the potential for residues in the herb and spice crop groups cannot be performed and these uses are not supported.

Pulses

The available diquat residue trials on pulses (lentils, field peas, soybean) are summarised below. Additional data for peas and beans, including dried, are also summarised below.

The maximum Australian label rate for pre-harvest desiccation of a range of pulse crops is 0.6 kg ac/ha. The specified pulse crops for the pre-harvest desiccation use are dry beans, dry peas, lentils, chickpeas, faba beans, lupins, mung beans, pigeon peas and soya beans. The current Australian MRL for Pulses is 1 mg/kg and the label withholding period range from nil (0 days) to 4 days, depending on the pulse crop.

Detectable residues generally occurred in the seeds, pods, or stalks/vines (haulm) from trials where the application of diquat occurred as a pre-harvest desiccant. Application rates in these trials ranged from 0.265 to 1.54 kg ac/ha (McKenna, 1966; Anon., 1972; Anderson, 1990; Dodsworth, 1990; Dick et al., 1995(c,d); Roper, 1995(d); Roper, 1996). However, in 5 trials conducted no detectable residues occurred in pea seed sampled 5–17 days after one or 2 applications of 0.6 kg ac/ha (Dick et al., 1995(c)). Similarly, in another 3 trials no detectable residues occurred in pea seed sampled 4 days after one application of 0.265 or 0.530 kg ac/ha.

In another 6 trials dry peas sampled 4 days after one application of 0.42 kg ac/ha (0.7× the current rate), residues of 0.05, 0.05, 0.09, 0.11, 0.40 and 0.56 mg/kg were observed (Roper, 1995(c); Roper, 1996). This last result was the HR obtained in pea seed from all the trials submitted and is calculated to be 0.8 mg/kg when scaled for the Australian application rate (0.6 kg ac/ha). In trials where the application was at the Australian maximum label rate for pre-harvest desiccation treatments of 0.6 kg ac/ha, diquat residues ranged from <0.02 to 0.10 mg/kg. The shortest PHI in these trials was zero days, where sampling occurred immediately after application (Anderson, 1990).

In dried beans, residues of diquat were not detected (LOQ of 0.02–0.05 mg/kg) in 75 determinations made in samples of seed taken 3–12 days (pre-harvest desiccation) or 55–123 days (pre- and post-emergence) after a single application in the range of 0.14 to 1.12 kg ac/ha. In other samples, finite residues were however observed in dried beans with concentrations ranging from 0.03 to 0.66 mg/kg (32 determinations) after an application in the range of 0.3 to 1.0 kg ac/ha.

No Australian trials for other pulses were submitted; however, overseas trials were available for lentils and soya beans. In all the trials, single applications of diquat were made as a pre-harvest desiccation treatment. In trials on lentils at rates approximating the Australian maximum use rate of 0.6 kg ac/ha, 8 sites had applications of 0.55 kg ac/ha from zero to 7 days prior to harvest. No detectable residues (LOQ of 0.05 mg/kg) were found in seed at 4 sites, and at the remaining sites residues of 0.07, 0.36 and 1.1 mg/kg were found in seed sampled immediately after application (zero day PHI) and residues of 0.04, 0.07 and 0.28 mg/kg were found in seed sampled 7 days after application (Dodsworth, 1990). In soya bean trials the range of residues from applications made approximating the Australian maximum rate of 0.6 kg ac/ha, excluding the days zero to 2 samples, was <0.01–0.16 mg/kg (rates of 0.56 to 0.8 kg ac/ha and PHI of 5–10 days). At zero days residues in seed were 0.62–0.63 mg/kg after application at 0.6 kg ac/ha or up to 0.91 mg/kg in the same trials after application at 0.8 kg ac/ha (Calderbank and McKenna, 1964; Anon., 1972; Swaine, 1982(b); Massenot and Culoto, 1985; Kennedy, 1986(c); Fujie, 1988(b); Anderson and Barnaud, 1995).

Additional Canadian studies on pulses were considered in 2018 by the Joint FAO/WHO Meeting on Pesticide Residues (JMPR, 2018) and have been provided in full for this review. Residues in beans dry after treatment at the Canadian GAP (0.55 kg ac/ha for pre-harvest desiccation, sampling 4–5 day PHI) were 0.01, 0.012, 0.019, 0.040, 0.044, 0.15, 0.18 (2) and 0.35 mg/kg. Residues in chickpeas after treatment at the Canadian GAP (0.41 kg ac/ha for pre-harvest desiccation, 4–5 day PHI) were 0.070, 0.10, 0.16, 0.18, 0.24, 0.26, 0.32, 0.38 and 0.58 mg/kg. Residues in lentils after treatment at the Canadian GAP (0.55 kg ac/ha for pre-harvest desiccation, 4–5 day PHI) were 0.052, 0.070, 0.10, 0.16, 0.18, 0.21, 0.33 and 0.57 mg/kg. Residues in dry peas after treatment at the Canadian GAP (0.55 kg ac/ha for pre-harvest desiccation, 4–5 day PHI) were 0.014, 0.020, 0.038, 0.054, 0.061 and 0.13 mg/kg.

The available diquat residues data supports continued use in pulses. There is a plethora of diquat residues data available relevant to the currently registered uses on pulses and the HR associated with the desiccation use (with a 4 day PHI) was 0.8 mg/kg in dried peas (scaled for the Australian rate). The supported MRL is:

VD 0070 Pulses

1 mg/kg

A 'Not required when used as directed' withholding period would be suitable for the shielded spray under the general vegetable use. The supported harvest withholding period for pre-harvest desiccation of all pulse crops with this use is 4 days to reflect the time required for effective desiccation or weed control and the sampling period in the more recent pulse trials.

Cereals

Winter cereals

The Australian winter cereal maximum use rate is 0.6 kg ac/ha for pre-harvest weed control. The withholding period is 'Not required when used as directed'. Current labels do not specify individual winter cereals for this use pattern. The current Australian MRLs are Wheat, Rye and Triticale at 2 mg/kg, and Barley and Oats at 5 mg/kg, which are the crops which will be considered here as MRLs were not previously established for other cereal crops which may be considered as a 'winter cereal'. The 2018 JMPR considered pre-harvest cereal use patterns with withholding periods of 'Not required when used as directed' and concluded that at least 4 days after treatment would be required for effective weed control and crop dry down.

The submitted residues data for winter cereals was described mostly as pre-harvest desiccation applications (Barrett et al., no date; Calderbank A and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1969; Anon., 1970(a); Anon., 1972; Ward, 1978; Anon., 1980(b); Swaine, 1982(d,e); Swaine, 1983(b); Kennedy, 1984(b); Kennedy, 1986(d); Laws et al, 1987; Fujie, 1988(c); Culoto, 1977; Benet and Massenot, 1993; Anderson et al, 1994(b); Anderson and Dack, 1994; Anderson and Lant, 1994(b); Anderson and Bonfanti, 1995; Anderson et al, 1995(a); Anon., 1996). The Australian winter cereal use pattern is a weed control application of diquat when the plants are fully mature. These 2 use patterns differ very little in timing and from a residues perspective are indistinguishable.

Residues in wheat grain at levels greater than the current Australian MRL of 2 mg/kg (up to 2.3 mg/kg) occurred in 2 trials 3–4 days after applications of 0.8 and 0.84 kg ac/ha (1.3–1.4× the maximum rate) and 4 times in trials after an application of 0.6 kg ac/ha (up to 2.67 mg/kg at zero day PHI). The zero day PHI samples, however, were harvested immediately after application, which is not considered to be typical agronomic practice. At the next sampling point in those trials addressing the rate of 0.6 kg ac/ha of 4 days after application, residues had declined to between 0.17 and 0.56 mg/kg. In other trials diquat residues were in the range of <0.05 to 0.40 mg/kg in samples of grain harvested 8 days after an application of 0.6 kg ac/ha.

Additional Australian trials on wheat were considered by the 2018 JMPR and have been provided in full for this review. Residues of diquat in wheat grain at 2–4 days after application at approximately 0.6 kg ac/ha were 0.20, 0.28, 0.41, 0.45, 0.56, 0.57, 0.63 and 0.78 mg/kg. The OECD MRL Calculator recommends an MRL of 1.5 mg/kg (STMR = 0.51 mg/kg, n = 8) based on this dataset.

The current MRL of 2 mg/kg for diquat on wheat remains appropriate. Similarly, the MRLs for diquat on rye and triticale (which are in the same crop subgroup as wheat in the APVMA crop group guidelines¹¹) should also remain at 2 mg/kg.

Diquat residues in barley grain tended to be higher than those in wheat. In a trial conducted at the Australian maximum use rate (0.6 kg ac/ha) had 3 Day zero results of 5.1, 5.12 and 5.7 mg/kg; however, by the next sampling at Day 4 residues had all declined to 1.5 mg/kg or less. In trials carried out more recently, one application of 0.8–0.944 kg ac/ha was applied and grain sampled one, 3 and 4 days later. Diquat residues ranged from 0.98 to 3.6 mg/kg. At 4 days residues in these more recent trials were 0.98, 1.1, 1.5 and 1.8 mg/kg.

Additional Australian trials on barley were considered by the 2018 JMPR and have been provided in full for this review. Residues of diquat in barley grain at 2–4 days after application at approximately 0.6 kg ac/ha were 0.15, 0.49, 0.53, 1.1, 2.0, 2.0 and 2.1 mg/kg.

The combined dataset based on the more recent trials and those evaluated by the 2018 JMPR is 0.15, 0.49, 0.53, 0.98, 1.1, 1.1, 1.5, 1.8, 2.0, 2.0 and 2.1 mg/kg. The OECD MRL Calculator recommends an MRL of 4 mg/kg

¹¹ <u>Crop group 020: Cereal grains</u>, available on the APVMA website.

(STMR = 1.1 mg/kg, n = 11). The current MRL of 5 mg/kg for diquat on barley remains appropriate noting it is equal to the Codex MRL, which was supported by JMPR in 2019.

In 2 of the more recent oat trials where one application was made at 0.8 kg ac/ha and grain sampled one, 3 and 4 days later, diquat residues ranged from 0.75 to 2.1 mg/kg. At 4 days residues were 0.75 and 0.90 mg/kg in these trials. Additional Australian data for diquat on oats were considered by the 2018 JMPR and have been provided for this review. Residues of diquat in oat grain at 2–4 days after application at approximately 0.6 kg ac/ha were 0.26, 0.41, 0.41 and 0.46 mg/kg.

The combined dataset for oats based on the more recent trials and those evaluated by the 2018 JMPR is 0.26, 0.41, 0.41, 0.46, 0.75 and 0.90 mg/kg. The OECD MRL Calculator recommends an MRL of 2 mg/kg (STMR = 0.44 mg/kg, n = 6). The current MRL for diquat on oats at 5 mg/kg should be replaced with an MRL at 2 mg/kg.

The supported MRLs are:

•	GC 0640	Barley	5 mg/kg
•	GC 0647	Oats	2 mg/kg
•	GC 0650	Rye	2 mg/kg
•	GC 0653	Triticale	2 mg/kg
•	GC 0654	Wheat	2 mg/kg

The current withholding period for winter cereals is nil. This should be replaced with a withholding period of 4 days to account for the period required for effective weed and crop dry down and the above MRL recommendations which were based on a 4 day PHI. Labels with the winter cereal use pattern should specify the crops as barley, oats, rye, triticale and wheat. The broad term of winter cereals should be removed from product labels as it does not align with the APVMA crop group guidance and replaced with specific claims for barley, oats, rye, triticale and wheat.

Alternative use pattern for wheat and oats

For wheat and oats there is an alternative use pattern that allows application at 140 g ac/ha between the 4 leaf stage (for wheat) or 3 leaf stage (for oats) up to early tillering. In Australian wheat trials considered by the JMPR (2018) and provided in full for this review, residues in wheat grain after 2 applications at approximately 140 g ac/ha with the first at BBCH 24–29 and the second at BBCH 24–52 were 0.04, 0.14, 0.22, 0.26, 0.28, 0.29, 0.30 and 0.34 mg/kg. Similarly for oat grain with the first application at BBCH 24 and the second at BBCH 24–45 residues were 0.13, 0.13, 0.19 and 0.21 mg/kg. (end of tillering = BBCH 29; for wheat the HR was observed when the last application was at BBCH 26, for oats the HR was observed when the last application was at BBCH 26, for oats for the pre-harvest use will cover the residues expected for this alternative over the top use. The MRLs should also be sufficient to cover crops treated for pre-harvest weed control as well as by this alternative use pattern.

The MRLs recommended above will also cover crop establishment uses for wheat, barley, oats, rye and triticale.

Sorghum and millet

The Australian maximum label rate for use on sorghum is 0.6 kg ac/ha for pre-harvest desiccation. There is also a use at crop establishment at 368 g ac/ha for sorghum and millet. The current Australian MRL for Sorghum is 2 mg/kg, there is no MRL currently established that would cover millet.

Pre-harvest desiccation trials on sorghum were submitted (Anon., 1969; 1970). No Australian trials were submitted.

Diquat residues in sorghum grain were <0.05 to 16.1 mg/kg after pre-harvest applications (PHI zero to 30 days) in the range 0.2 to 1.2 kg ac/ha, although only 6 of the 146 results recorded were greater than 2 mg/kg. The HR was at a 15 day PHI. The lack of reported trial information in these sorghum studies presents difficulties in obtaining field related explanations for the high results, or to have confidence in the results.

The available data for sorghum suggests that the current MRL of 2 mg/kg may not be appropriate. Is not possible to recommend a suitable MRL for diquat on sorghum at this time, given the lack of details for the trials with residues above the MRL. The pre-harvest desiccation use of diquat on sorghum is not supported but may be suitable for a phase out period.

At the end of the phase out period, the sorghum MRL should be replaced with an MRL at *0.05 mg/kg to cover use at crop establishment, noting the results of the pre-emergent trials on rice and maize where residues were <0.05 mg/kg. Similarly, an MRL of *0.05 mg/kg is also supported for GC 0646 Millet for the crop establishment use. The supported withholding period for this use is 'Not required when used as directed'.

Maize

The Australian maximum use rate on maize 0.368 kg ac/ha for pre-emergence weed control. The current Australian MRL for maize is 0.1 mg/kg.

Pre- and post-emergence weed control and pre-harvest desiccation trials on maize were submitted (Kennedy, 1986(d); Anderson and Bonfanti, 1995; Anderson and Lant, 1994(b)). No Australian trials were submitted.

Four overseas trials involved application at 0.28–1.12 kg ac/ha with samples collected at 68–149 days after application. Diquat residues in maize were <LOQ (0.05 mg/kg) in these trials when applications were made as preemergence and post-emergence weed control applications. The current MRL for diquat on maize at 0.1 mg/kg will be replaced with an MRL at *0.05 mg/kg.

The recommended MRL is:

• GC 0645 Maize

*0.05 mg/kg

The recommended withholding period for this crop establishment use is 'Not required when used as directed'.

Rice

The Australian maximum use rate on rice is 368 g ac/ha pre-emergence or 600 g ac/ha for preharvest desiccation. The current Australian MRLs are rice at 5 mg/kg and rice polished at 1 mg/kg.

Two trials were conducted in Australia, with additional trials conducted in Brazil, Japan and Italy (Kennedy, 1986(e); Laws et al, 1987; Anderson et al, 1995(b)). The treatments in the submitted trials on rice were as pre- and post-emergence weed control and pre-harvest desiccation applications. Only the pre-emergence weed control trial (where residues were <0.05 mg/kg) and the pre-harvest desiccation trials are consistent with Australian GAP.

For the pre-harvest desiccation trials residues in whole grain were in the range <0.05 to 13 mg/kg after applications of 0.22 to 1.5 kg ac/ha and a PHI of 5–37 days. In pre-harvest desiccation trials where application rates were at the Australian maximum rate of 0.6 kg ac/ha, residues (mg/kg) were 0.90, 5.2, 0.88 – 3.0, $\bar{x} = 2.1$ (n=5), 1.3, and 1.3–3.6, $\bar{x} = 2.1$ (n=4). Residues in husked grain from pre-harvest desiccation applications were in the range <0.05 to 1.5 mg/kg after applications in the range of 0.28 to 1.0 kg ac/ha, although the HR of 1.5 mg/kg was present after a lower application rate of 0.3 kg ac/ha.

The available data for rice suggests that the current MRLs of 5 mg/kg for rice and 1 mg/kg for polished rice may not be appropriate for the pre-harvest desiccation use. Is not possible to recommend a suitable MRL for diquat on rice for the pre-harvest desiccation use at this time, given the lack of details for the trials with residues above the MRL. It is noted that finite MRLs for rice have not been established overseas except for a brown rice MRL in Japan at 0.03 mg/kg. The pre-harvest desiccation use of diquat on rice is no longer supported but may be suitable for a phase out period.

In 2 pre-emergent trials, residues in rice at harvest were <0.05 mg/kg after an application at 0.464 kg ac/ha at 5 days prior to sowing. This pre-emergent use pattern for rice therefore can be supported from a residues perspective.

At the end of the phase out period the rice and polished rice MRLs should be replaced with an MRL at *0.05 mg/kg for rice to cover the pre-emergent use pattern.

Oilseeds

The available diquat residue trials on oilseeds (cotton, rapeseed, sunflower, linseed and poppies) are summarised below.

Cotton

The maximum Australian use rate on cotton is for a pre-harvest application at 0.6 kg ac/ha when 85% of the bolls are open with a withholding period of 'Not required when used as directed'. There is also a use at crop establishment at 368 g ac/ha.

A summary of a single trial on cotton was submitted (Calderbank and Yuan, 1963). The PHI was not stated but the applications were as pre-harvest desiccation treatments. Residues were <LOQ (not stated) after a single application of 0.64 kg ac/ha, similar to the Australian maximum use rate. Detectable residues occurred at higher rates (0.84–1.68 kg ac/ha). The current Australian MRL is Oilseeds at 5 mg/kg. A single residue trial lacking details on methods and PHI is not sufficient for a robust assessment of the residues potential and does not support a use

on a major export commodity such as cotton given also the late application timing. It is noted that the 1994 JMPR indicated no new residue data for cotton were available and data submitted to the 1972 JMPR were not resubmitted. The 1994 JMPR withdrew the previous MRL recommendation for cotton seed.

The continued pre-harvest use of diquat on cotton is not supported due to a lack of relevant residues data for cotton seed but may be suitable for a phase out period. At the end of the phase out period an MRL of *0.05 mg/kg will be established for to support the alternative use at crop establishment as data for other crops (rice, maize and peanuts) has indicated residues are not expected at harvest for this use. The appropriate withholding period for this supported crop establishment use in cotton is 'Not required when used as directed'.

The recommended MRL for diquat use at cotton crop establishment is:

SO 0691 Cotton seed

Peanuts

The use on peanuts is at crop establishment at 368 g ac/ha with a harvest withholding period of 'Not required when used as directed'.

One trial summary on peanuts was submitted (Williams, 1989). Although not stated it was probably a postemergence weed control application. No detectable residues (<0.01 mg/kg) were found in the kernels or the nut in the shell 109 days after an application of 0.09 or 0.112 kg a.i/ha.

Although the available data for peanuts is weak, data for other crops (rice and maize) also suggest that residues are not expected at harvest. An MRL of *0.05 mg/kg is recommended for SO 0697 Peanut to cover this use. The supported harvest withholding period is 'Not required when used as directed'.

The recommended MRL for diquat use on peanuts at crop establishment is:

• SO 0697 Peanut

*0.05 mg/kg

*0.05 mg/kg

Safflower

The use on safflower is at crop establishment at 368 g ac/ha with a harvest withholding period of 'Not required when used as directed'.

Although data for safflower is not available, data for other crops (peanuts, rice and maize) suggest that residues are not expected at harvest following a pre-emergent use. An MRL of *0.05 mg/kg is recommended for SO 0699 Safflower seed to cover this use. The supported harvest withholding period is 'Not required when used as directed'.

The recommended MRL for diquat use on safflower at crop establishment is:

SO 0699 Safflower seed

*0.05 mg/kg

Sunflower

The maximum Australian label rate for use on sunflower is for application at up to 0.6 kg ac/ha at 7–14 days before harvest, noting the harvest withholding period is 4 days.

Eight reports were submitted which contained results of eighteen trials conducted on sunflowers (Anon., no date(c); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1970(b); Anon., 1972; Anderson et al, 1995(c); Anderson and Renard, 1995(b)). One trial was conducted in Australia. The sunflower trials were all conducted at pre-harvest desiccation treatments. Residues of diquat in sunflower seed were in the range <0.05 to 1 mg/kg, after applications of 0.28 to 1.68 kg ac/ha. Eight trials had a single application of 0.6 kg ac/ha applied. Residues in the whole seed, which were calculated from the measured residues in oil and cake, were in the range 0.08 to 0.54 mg/kg with a PHI of 5–7 days. It is noted that the 2013 JMPR considered some of these studies submitted for review along with additional European sunflower studies and recommended an MRL of 0.9 mg/kg based on a GAP of 0.6 kg ac/ha, PHI 6 days (in the additional 5 JMPR trials matching this GAP residues in seed were <0.05–0.10 mg/kg). The combined data set for sunflower seed at 5–7 days after application at approximately 0.6 kg ac/ha is <0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.11, 0.11, 0.15, 0.19, 0.41, 0.46 and 0.54 mg/kg. The OECD MRL calculator recommends an MRL of 0.9 mg/kg (n = 14, STMR = 0.11 mg/kg). The current Australian MRL is Oilseeds at 5 mg/kg. A diquat sunflower MRL of 1 mg/kg is appropriate based on this data in conjunction with a 7 day withholding period instead of the currently registered withholding period of 4 days.

The available diquat residues data supports continued use sunflowers with a 7 day harvest withholding period. The recommended MRL is:

• SO 0702 Sunflower seed

Linseed

The maximum Australian label rate for use of diquat on linseed is for a pre-harvest desiccation application at up to 0.6 kg ac/ha when the majority of seed head are mature. A harvest withholding period is not specified.

Nine reports were submitted, which contained results of 18 trials conducted on linseed; however, one report, which measured residues in cake and oil only, was not considered further (Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1972; Earl and Anderson, 1989(b); Anderson and Elsworth, 1994; Anderson and Moons, 1995; Anderson and Renard, 1995(a), Dick et al., 1995(f)). No Australian trials were submitted. Two trials were conducted as post-emergence weed control treatments (no detectable residues occurred), and the remainder were pre-harvest desiccation treatments, which is Australian GAP. For the pre-harvest desiccation trials, the range of diquat residues in the seed was <0.05 to 5.5 mg/kg 7–16 days after an application of 0.07 to 2.24 kg ac/ha (scaled HR 2.75 mg/kg). After applications approximating the Australian maximum rate of 0.6 kg ac/ha, residues were <0.05 to 3.9 mg/kg. The available linseed trials did not address a sampling time less than 7 days. The current Australian MRL is Linseed at *0.01 mg/kg should be increased to 5 mg/kg.

The available diquat residues data supports continued use in linseed. The recommended MRL is:

• SO 0693 Linseed

1 mg/kg

Current labels do not specify a harvest withholding period for linseed. A 7 day harvest withholding period is recommended for linseed in line with the sampling times from the available residue trials.

Canola (rapeseed)

The maximum Australian label rate for use on canola is for a pre-harvest desiccation application at 0.6 kg ac/ha in conjunction with a 4 day harvest withholding period.

Seven reports of rapeseed residues trials were submitted (McKenna, 1966; Anon., no date(c); Anon., 1972; Anon., 1980(a); Swaine, 1981(b); Kennedy, 1984(c); Kennedy, 1988(b)). No Australian trials were submitted. Applications in all the trials were made as pre-harvest desiccation treatments. Diquat residues in rapeseed were in the range <0.05 to 1.5 mg/kg, from applications of 0.28 to 3.8 kg ac/ha, although most results were less than 1 mg/kg. In trials where applications of 0.6 kg ac/ha were applied 5–20 days prior to harvest all residues were <0.05 to 0.48 mg/kg.

Additional data for diquat on rape seed is available from the 2013 JMPR. Residues in rape seeds from trials conducted in Europe approximating German GAP (0.6 kg ac/ha, PHI 5 days) were (n=16): 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 (0.56 kg ac/ha, PHI 7 days) 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. Based on the combined dataset considered by the 2013 JMPR the OECD MRL calculator recommends an MRL of 1.5 mg/kg (n = 25, STMR = 0.27 mg/kg).

The available diquat residues data supports continued use in canola. Based on the overseas rape seed data an MRL of 2 mg/kg is supported for diquat on SO 0495 Rape seed [canola] in conjunction with a 7 day harvest withholding period. This MRL would be in closer alignment to those established by Codex, Japan and Korea (compared to the current MRL for oilseeds at 5 mg/kg), reducing the potential risk to trade.

The recommended MRL is:

• SO 0495 Rape seed [canola]

2 mg/kg

The supported harvest withholding period for canola is 7 days.

Poppies

The maximum Australian label rate for use on poppies is for a pre-harvest desiccation application at 0.8 kg ac/ha in conjunction with a 2 day withholding period.

Two overseas trials were submitted but were not considered to be reliable (Kennedy, 1985(b); Massey, 1987(f)). Two Australian studies detailing 6 trials were considered (Haller and Winner, 2013; Udy, 2011). No diquat residues \geq LOQ (0.01 mg/kg) were found in any poppy seed sample from the 4 Tasmanian trials at any sampling period (zero, 2, 7 or 10 days after application at 0.8 kg ac/ha). No diquat residues \geq LOQ (0.02 mg/kg) were found in any poppy seed sampling period (zero, 5, 10 and 15 days after application at 0.8 kg ac/ha).

The current MRL of *0.01 mg/kg for diquat on poppy seed remains appropriate.

The available diquat residues data supports continued use in poppies. The supported MRL is:

SO 0698 Poppy seed

*0.01 mg/kg

The 2 day harvest withholding period for poppies is supported.

Sugarcane

The available diquat residue trial on sugarcane is summarised below (McKenna, 1966).

Diquat may be used over the top of plant or ratoon cane at up to 0.23 kg ac/ha with no withholding period specified. There is a pre-harvest desiccation use at up to 0.6 kg ac/ha in conjunction with a 4 day withholding period. There is also a use as an aid in establishing sugarcane or in a fallow prior to sugarcane at up to 0.368 kg ac/ha. The current Australian MRL is Sugarcane at *0.05 mg/kg.

A single summary of a trial conducted on sugarcane was submitted. No detectable residues (LOQ 0.01 mg/kg) occurred in juice from sugarcane sampled 6 months after application of 1.12–2.24 kg ac/ha diquat, which was applied to act as a desiccant preventing flowering. The submitted information does not reflect any current Australian GAP or address the raw agricultural commodity (sugarcane billets).

As residue data are not available to support the over the top use or pre-harvest desiccation of sugarcane these uses are no longer supported in the longer term but may be suitable for a phase out period.

Noting the results of the pre-emergent trials on rice and maize where residues were <0.05 mg/kg, the sugarcane MRL at *0.05 mg/kg can remain in place to support the use of diquat as an aid in establishing sugarcane or controlling weeds in a fallow prior to sugarcane. The supported withholding period for the supported pre-emergent use on sugarcane is 'Not required when used as directed'.

Hops

The available diquat residue trials on hops are detailed are summarised below (Simon, 1978). The maximum label use rate is 0.28 kg ac/ha as a directed inter-row spray prior to crop emergence from winter dormancy. The current Australian MRL is Hops, dry at 0.2 mg/kg.

Residue data for diquat on hops were provided for permit 13260 (which includes paraquat). Residues of diquat in hops were <0.05 mg/kg (n = 2) at 12-14 days after the last of 2–3 applications at 368 g ac/ha by inter row boom spray.

The available diquat residues data supports continued use in hops. The recommended MRL is:

• DH 1100 Hops, dry

*0.05 mg/kg

The recommended harvest withholding period is 'Not required when used as directed' for this use as a directed inter row spray prior to crop emerging from winter dormancy.

Processed commodities

Studies were submitted that determined the residues of diquat in products from the processing of wheat, barley, sorghum and oilseed crops. Diquat residues in wheat, barley and sorghum grain were concentrated in the bran (Calderbank and Springett, 1971; Fujie, 1988(c)). In wheat, residues were found to concentrate generally 2-fold and in sorghum were found to concentrate on average four-fold from a dry milling process. The residue levels found in wholemeal flour and bread were similar to the levels found in the grain. It is noted that use on sorghum has not been supported. For wheat, processing factors for bran were 1.3x and 2.4x. Applying these processing factors to the HR in wheat grain of 0.78 mg/kg from the desiccation use gives residues of 1.0 and 1.9 mg/kg, both below the supported wheat MRL of 2 mg/kg. A separate MRL for wheat bran is not required, noting also that wheat will be bulked and blended at processing.

The levels of residues in beer were found to be 2–3% of those found in the barley whole grain from which it was prepared.

In studies of oilseeds such as rapeseed (McKenna, 1966; Anon., no date(c); Anon., 1972; Anon., 1980(a); Swaine, 1981(b); Kennedy, 1984(c); Kennedy, 1988(b)), sunflower (Anon., no date(c); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1970(c); Anon., 1972; Anderson et al, 1995(c); Anderson and Renard 1995(b) and linseed (Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1989(b); Anderson and Elsworth, 1994; Anderson and Moons, 1995; Anderson and Renard, 1995(a)) the diquat residue is concentrated in the cake and there are no detectable residues in the oil. In an additional European rape seed processing study conducted at 2 sites and evaluated by the JMPR (2013) residues in refined oil were <0.01 mg/kg and processing factors for solvent extracted meal ranged from 0.17–0.76×.

All but one of the submitted soybean studies, where beans, meal, and oil were measured, had no detectable residues of diquat in any of these fractions. In one soybean study residues were 0.07 mg/kg in the cake and not detectable in the oil. In this study the residues in the seed were not measured. The JMPR (1994) reviewed a soybean processing study and found there was a 2.6-fold concentration of diquat residues in the hulls of treated plants. There was no concentration in any other fraction and no residues were detectable in the crude or refined oil.

The MRL of 1 mg/kg for diquat on OC 0172 Vegetable oils, crude can be replaced with an MRL of *0.01 mg/kg for OR 0172 Vegetable oil, edible as the processing studies indicate that residues are not expected to occur in oil.

The recommended MRL is:

• OR 0172 Vegetable oil, edible

*0.01 mg/kg

Use in aquatic areas

Diquat may be used to control weeds in aquatic areas with the following restraint:

Do not use treated water for human consumption, livestock watering or irrigation purposes for 10 days after application.

A WHO evaluation concluded that when diquat is added to surface waters to control aquatic weeds, residues in the water rapidly decline, owing mainly to the absorption of diquat into the aquatic plants, where it is firmly bound until the decaying weeds disintegrate into the bottom mud. The diquat is then irreversibly bound to the soil particles, leaving the water free of diquat residues. Half-lives of diquat in natural waters are generally less than 48 h (JMPR, 1994).

Use of diquat in aquatic areas with the 10 day restraint on using water for human consumption, livestock watering or irrigation purposes continues to be supported from a residues and trade perspective.

Residues in animal feeds

The only entries for diquat in Table 4 of the current MRL Standard are 'Legume Animal Feeds' at 100 mg/kg and 'Oilseed forage and fodder' at 30 mg/kg. The Australian use pattern specifies rates of 0.28–0.37 kg ac/ha for grass, clover, medic and lucerne pasture and up to 0.6 kg ac/ha for clover and lucerne seed crops and legume crops that may be grazed or cut for feed. There is no grazing restraint for cereal crop forage or fodder, and it considered that these materials can be grazed after applications up to 0.6 kg ac/ha.

Studies were submitted that included residues trials with applications to pasture, including grass and mixed pasture, and legume based pasture. Trials were also conducted on cereals and legume crops where in almost all cases only the dried plant material at harvest after desiccation was sampled. (Anon., no date(b,d,e); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Cardinali et al, 1967; Anon., 1972; Anon., 1973; Swaine and Hayward, 1982; Anon., 1987; Massey, 1987(d); Dick et al, 1995(e)).

Animal feed derived from grasses (including cereals)

The levels of diquat residues in trials conducted on grass resembled those results found in legumes. In trials conducted during 1964–65 in the UK mean diquat residues in grass were 26 and 13 mg/kg, one and 2 days, respectively, after an application of 0.3 kg a.i/ha and 43 and 25 mg/kg, one and 2 days, respectively, after an application of 0.6 kg ac/ha. A trial on tall fescue conducted in the UK had residues ranging from 0.52 to 3.6 mg/kg one to 2 days after applications of 0.24–0.42 kg ac/ha. In a trial conducted on tall fescue in Australia residues after one day ranged from 0.77 to 27 mg/kg after an application of 0.5 kg ac/ha.

Detectable residues of diquat occurred in cereal grain straw. Residues were generally higher in oats and barley and for all winter cereals ranged from 2.5 to 26 mg/kg from pre-harvest desiccation applications at the maximum Australian use rate of 0.6 kg ac/ha. Residues in maize were much lower and generally not detectable due the application timing (pre-sowing or prior to emergence), which is consistent with the maize Australian GAP. However, application to sorghum can be as a pre-harvest desiccant and trials on sorghum with residues measured in forage or straw were not submitted. Residues of up to 11 mg/kg occurred in rice straw from pre-harvest desiccation applications of 0.6 kg ac/ha.

Additional Australian data for barley, oat and wheat straw were considered by the JMPR (2018) and have been provided to the APVMA separately. Residues of diquat 2–4 days after a pre-harvest application at 0.6 kg ac/ha were 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 (dry weight).

Residues in animal feed derived from grasses are not covered by an existing Australian MRL. It is not clear if all the residue results for grass were reported on a fresh or dry weight basis, with exception of the JMPR cereal trials,

which were expressed on a dry weight basis. However, samples of cereal straw from the trials involving preharvest desiccation applications should have a high dry matter content. The available data for grass and cereal forage and fodder suggests that residues should be below 100 mg/kg, the level at which the current legume animal feed MRL is set noting that the levels of diquat residues in trials conducted on grasses and cereals were similar to those results found in legumes (see below).

Animal feed derived from legumes

Studies submitted on lucerne, clover and medic (zero to 133 day PHI), including several that addressed a zero or one day PHI, generally had diquat residues between 20 and 40 mg/kg in the desiccated plant material, although 2 results were below 0.1 mg/kg, from applications approximating the Australian maximum use rate of 0.6 kg ac/ha and a PHI of 2–4 days. The HR at one day was 66.7 mg/kg in clover after 0.56 kg ac/ha (scaling not required). At longer PHIs the HR was 92.5 mg/kg (dry weight) in white clover at 4 days after 1.12 kg ac/ha (49.6 mg/kg scaled for rate).

Diquat residues in pea and bean haulms varied widely with a maximum residue recorded of 53 mg/kg. The trial information indicates all the samples were taken as dried material at harvest, including the samples in trials conducted as post-emergence weed control applications (Anon., no date(f); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1972; Edwards, 1977; Anon., 1980(a); Culoto and de Mallmann, 1982; Swaine, 1983(a); Culoto, 1985(a,b); Kennedy, 1985(a); Kennedy, 1986(b); Massey, 1987(d); Anon., 1987; Anderson, 1990; Dodsworth, 1990; Earl, 1991(a); Earl and Hall, 1994; Roper, 1995(a,b); Dick et al., 1995(c,d); Roper, 1996).

Residues of diquat in desiccated fodder of lentils and field peas were generally higher than those recorded in peas and beans haulms, with a mean residue of 40 mg/kg, although in all cases residues were <100 mg/kg, particularly at use rates of 0.50–0.55 kg ac/ha (the HR was 90 mg/kg after application at 1.1 kg ac/ha, or 40.1 mg/kg when scaled for application rate).

Residues in soybean stalks, stems, straw or fodder were in the range <0.05 to 20 mg/kg at PHIs of 3–119 days after application at 0.28–1.12 kg ac/ha.

In the submitted trials residues in animal feed derived from legumes were below the current Australian MRL at 100 mg/kg, which remains appropriate.

Animal feeds derived from oilseeds

Limited data on feeds derived from oilseed plant material were provided to the review. Diquat residues in the stalks of linseed and sesame were <0.05 to 0.68 mg/kg at 12–98 days after application at 0.07–1.12 kg ac/ha (Anon., no date(g); Calderbank and Yuan, 1963; Calderbank and McKenna, 1964; McKenna, 1966; Anon., 1972; Earl and Anderson, 1989(b); Anderson and Elsworth, 1994; Anderson and Moons, 1995; Anderson and Renard, 1995(a,b). The current oilseed forage and fodder MRL at 30 mg/kg was established based on data for rape seed forage from the 2013 JMPR. Diquat residues in rape forage after a single application at a nominal rate of 600 g ac/ha at one day PHI (or later if higher residues were observed), in rank order were: 0.4, 1.7, 3.2, 3.5, 7.5, 8.1, 11 and 17 mg/kg (n=8). (assume DW as this was a pre-harvest desiccation use with application at BBCH 87-89). The Oilseed forage and fodder MRL is expected to remain appropriate for currently registered uses in conjunction with a one day grazing withholding period.

Other animal feeds

Residues in minor animal feed commodities form no more than 20% of the diet livestock and will not influence animal MRLs due to the higher residues of diquat in pastures, hay and fodder. Such animal feeds include citrus pulp, grape pomace, apple pomace, tomato pomace and almond hulls and the primary crops may be treated with pre-emergent or directed applications and should not result in residues in the raw commodity or animal feed. MRLs in Table 4 of the MRL standard are not considered necessary as residues above the LOQ are not expected.

Conclusion on residues in animal feeds

The use of diquat on crops or situations which produce animal feeds continues to be supported. The one day grazing withholding period on current labels remains appropriate (noting that products formulated with paraquat have a 7 day grazing withholding period for horses).

The recommended grazing withholding period statement in relation to diquat is:

• DO NOT graze or cut for stock food for one day after application.

The recommended MRLs for animal feeds are summarised in Table 13.

Code	Animal feed commodity	Current MRL	Recommended MRL
AL 0157	Legume animal feeds	100	100
	Oilseed forage and fodder	30	30
AF 0161	Forage of cereal grains and other grass-like plants	_	100
AS 0161	Straw and fodder (dry) and hay of cereal grains and other grass like plants	_	100

Table 13: Recommended MRLs for animal feeds

Animal transfer studies and animal commodity MRLs

Poultry

Four studies on diquat residues in poultry were submitted and assessed. In 2 related studies, 3 groups of 30 chickens each were fed nominally 1, 5 or 10 mg/kg diquat in the diet for 28 days (Fletcher, 1977; Lai et al, 1977). Ten chickens from each group were sacrificed on day 21 and day 28 with the remaining birds kept on a control diet for 7 days prior to sacrifice. Eggs were collected on days one, 14, 21 and 28 and the final day of the recovery diet. No residues greater than 0.005 mg/kg were detected in the egg, fat, muscle, liver or heart samples. In skin, only the day 21 sample from the 10 mg/kg dose contained residues greater than 0.005 mg/kg at 0.006 mg/kg. The gizzards contained detectable residues which ranged from 0.006 mg/kg at the lowest feeding level at day 21 to 0.022 mg/kg at the highest level at day 28. Residues in gizzards declined after cessation of feeding.

In 2 further studies, 3 groups of 40 hens each were fed nominally 2, 5 or 10 mg/kg diquat in the diet for 6 weeks (Leahey, 1975; Edwards and Smith, 1975). Samples of eggs were collected throughout the trial and tissue samples taken after 6 weeks. No detectable residues of diquat were found in the egg white or yolk, and from hens slaughtered after 16, 28 and 45 days, no detectable residues of diquat were found in the meat, liver or kidneys. The limit of detection in eggs, meat and liver was 0.05 mg/kg and in kidney was 0.2 mg/kg.

Current poultry MRLs are *0.01 mg/kg for eggs and *0.05 mg/kg for meat and offal. Data from the animal transfer studies indicate that a dietary intake of 10 mg/kg would not produce detectable residues in the meat, offal or eggs. Although not a typical diet, it is assumed either cereal grain or pulses could make up 100% of the poultry diet. In this case, the poultry dietary intake at the current maximum MRLs for cereals and pulses (5 and 1 mg/kg, respectively) would not result in violative residues in the meat, offal or eggs.

More refined dietary burden calculations for poultry broilers and layers are presented in Table 14 and Table 15 using the OECD Feed Calculator and the relevant HR or Supervised Trials Median Residue (STMR).

Poultry broiler – for MRLs							
Commodity	Codex Commodity Code ¹²	Residue (mg/kg)	Basis	Dry matter (%)	Residue dry weight (mg/kg)	Diet content (%)	Residue contribution (ppm)
Alfalfa forage	AL	100	HR	100	100.0	-	_
Rice grain	VD	2.1	STMR	88	2.4	50	1.2
Sorghum, grain	GC	1.1	STMR	86	4.3	50	0.6
Barley grain	GC	1.1	STMR	88	1.3	-	-
Corn, field grain	GC	0.05	STMR	88	0.01	-	_
Total						100	1.8

Table 14: Calculation of poultry broiler dietary burden of diquat

¹² See <u>crop groups</u>, available on the APVMA website.

Poultry broiler – for MRLs							
Commodity	Codex Commodity Code	Residue (mg/kg)	Basis	Dry matter (%)	Residue dry weight (mg/kg)	Diet content (%)	Residue contribution (ppm)
Barley straw	AF/AS	26	HR	100	26	_	-
Rape forage	AM/AV	17	HR	100	17	-	_
Rice grain	GC	2.1	STMR	88	2.4	50	1.2
Sorghum, grain	GC	1.1	STMR	86	1.3	50	0.6
Barley grain	GC	1.1	STMR	88	1.3	-	-
Corn, field grain	GC	0.05	STMR	88	1.1	_	-
Total						100	1.8

Table 15: Calculation of poultry broiler dietary burden of diquat

As diquat residues above the LOQ of 0.01 mg/kg for eggs and 0.05 mg/kg for meat and offal were not observed in the feeding study conducted at a feeding level of 10 ppm, finite residues are not expected from the feeding level associated with current uses (1.8 ppm). The current poultry commodity MRLs remain appropriate.

Ruminants

Several studies in ruminants were submitted and assessed. In one study, 12 Friesian cows were fed for 30 days with diets including pelleted grass nuts containing nominally zero, 20, 50 or 100 mg diquat/kg diet dry weight (Edward et al, 1976). The grass nuts were prepared from grass sprayed with diquat at a rate of 4 kg ac/ha and cut after 4 days. The cut grass was pelleted and stored at ambient temperature for up to 2 years. Residues in the grass immediately after treatment were 940 mg/kg dry weight, in the nuts after pelleting were 212 mg/kg dry weight, and a mean of 209 mg/kg in the nuts during the feeding study. Milk was collected and analysed 3 times per week, and after 30 days 2 animals from each treatment group were slaughtered and tissues analysed. The remaining animal from each group was maintained on a control diet for 7 days then slaughtered. No residues of diquat above 0.001 mg/kg were detected in the milk and no residues >0.01 mg/kg were detected in tissues (liver, kidney, fat and muscle).

In another study, a single cow was dosed orally with 10 grams diquat and milk collected at 0, 24, 48, 72 and 96 hours for analysis (Daniel, 1962). The dose administered is equivalent to 1,000 mg/kg diquat in the diet. No detectable residues of diquat were found (the limit of detection was 0.01 mg/kg).

In another study, 3 groups of 5 cows were fed either rapeseed cake containing 50 mg/kg diquat, sunflower cake containing 55 mg/kg diquat, or rapeseed cake from the field containing 0.45 mg/kg diquat, for a period of 31 days (Sipos, 1973). Samples of milk were taken daily and analysed throughout the feeding period and no detectable residues of diquat were found (residues were <0.005 mg/kg). No detectable residues of diquat were found in the

tissues (liver, kidney, kidney fat, heart, brain, bone marrow, stomach or meat) of sacrificed cows at the conclusion of the feeding period. The limit if detection was 0.01 mg/kg for the kidney, kidney fat, heart and meat, 0.02 mg/kg for the liver and stomach, 0.02–0.025 mg/kg for the brain, and 0.03 mg/kg for the bone marrow.

In a study involving cattle and sheep 6 acres of Italian ryegrass was sprayed with diquat at a rate of approximately 0.3kg ac/ha (Black et al, 1966). The crop was harvested 4 days later, and a silo filled with about 50 tonnes of herbage. After 5 months samples of silage were analysed for diquat residues, and a mean value of 3.6 mg/kg dry weight was obtained. A Hereford steer was sacrificed after being fed a daily ration incorporating 18–23 kg of silage for one month, and no diquat residues were detected (residues were <0.01 mg/kg) in the meat and organs. A Dairy Shorthorn fed the same ration had milk collected and analysed on alternate days for a period of 2 weeks, 2 weeks after commencement of feeding, and similarly, no residues of diquat were detected (residues were <0.003 mg/kg).

Twenty sheep in the same study (Black et al, 1966) were fed silage (mixed grass/clover) containing diquat residues of either 6.6 or 13.3 mg/kg (dry) for a period of 8 days. The concentration of diquat in the urine and faeces was determined over a 3 day period. The amount of diquat excreted in the faeces was 40–50% of the intake and <10% in the urine. No detectable residues of diquat (residues were <0.01 mg/kg) were found in samples of brain, liver and kidneys.

In an additional experiment, Black et al, (1966) incubated diquat with rumen liquor or faeces. In faeces, a 35% loss was reported after 2 days but no further loss on prolonged incubation. There was little degradation of diquat in the rumen liquor after incubation for 10 hours but thereafter there was 'an appreciable loss', although this was not quantified.

Cardinali et al (1967) applied diquat as a pre-harvest desiccant to lucerne at a rate of 1.12 kg ac/ha. Samples of hay were analysed 9 days later and found to have diquat residues of 19.3 mg/kg (wet), 23.12 mg/kg (dry). A cow was fed treated hay for 29 days (consuming a total of 7.163 grams of diquat). Milk taken and analysed after 8 days or after 29 days did not have detectable residues of diquat (residues were <0.01 mg/kg). Samples of meat and liver also had no detectable residues of diquat (residues were <0.01 mg/kg). Sheep fed the treated hay for 29 days (consuming a total of 427 mg of diquat) did not have detectable residues in samples (residues were <0.01 mg/kg) of flesh and liver.

Two lactating cows were fed 5 kg each of ground sunflower seed daily, containing 0.2 mg/kg diquat, for 185 days (Lembinski et al, 1972). The total amount of diquat consumed during the feeding period was 185 and 225 mg. Samples of milk, urine and faeces were collected at intervals during the feeding period, and the calf of one cow was slaughtered 7 days after birth. There were no detectable residues of diquat in any of the samples of milk, faeces or urine analysed, or in the liver and kidneys of the calf. Three one year old wethers were fed 0.5 kg of ground sunflower seed daily, containing 0.2 mg/kg diquat, for 141 days. The total quantity consumed was about 14.1 mg diquat. There were no detectable residues of diquat in the livers or kidneys of the wethers at the end of the feeding period. The limits of detection were 0.01 mg/kg for milk and urine, and 0.03 mg/kg for faeces, liver and kidneys.

Diquat dietary burdens calculations for beef and dairy cattle are presented in Table 16 and Table 17 using the OECD livestock feed calculator using relevant HR or STMR. Residues in legume animal feeds and pastures are assumed to be at the MRL as a worst case, rather than the HR.

Beef cattle – for MRLs							
Commodity	Codex Commodity Code ¹³	Residue (mg/kg)	Basis	Dry matter (%)	Residue dry weight (mg/kg)	Diet content (%)	Residue contribution (ppm)
Alfalfa forage	AL	100	HR	100	100.0	100	100.0
Barley straw	AF/AS	26	HR	100	26.0	-	-
Rice grain	GC	2.1	STMR	88	2.4	_	-
Sorghum, grain	GC	1.1	STMR	86	1.3	-	-
Barley grain	GC	1.1	STMR	88	1.3	_	-
Potato culls	VR	0.2	HR	20	1.0	_	_
Corn, field grain	GC	0.05	STMR	88	0.1	_	-
Total						100	100

Table 16: Calculation of beef cattle dietary burden of diquat

Table 17: Calculation of dairy cattle dietary burden of diquat

Dairy cattle – for MRLs							
Commodity	Codex Commodity Code ¹⁴	Residue (mg/kg)	Basis	Dry matter (%)	Residue dry weight (mg/kg)	Diet content (%)	Residue contribution (ppm)
Alfalfa forage	AL	100	HR	100	100.0	100	100
Bean vines	AL	100	HR	100	100.0	40	40.0
Barley straw	AF/AS	26	HR	100	26.0	-	-
Oat straw	AF/AS	26	HR	100	26.0	_	_

¹³ See <u>crop groups</u>, available on the APVMA website.

 $^{^{\}rm 14}$ See $\underline{\rm crop\ groups},$ available on the APVMA website.

Dairy cattle – for MRLs							
Commodity	Codex Commodity Code ¹⁴	Residue (mg/kg)	Basis	Dry matter (%)	Residue dry weight (mg/kg)	Diet content (%)	Residue contribution (ppm)
Rape straw	AM/AV	17	HR	100	17	-	-
Rice grain	GC	2.1	STMR	88	2.4	-	-
Sorghum, grain	GC	1.1	STMR	86	1.3	-	_
Barley grain	GC	1.1	STMR	88	1.3	-	-
Corn, field grain	GC	0.05	STMR	88	0.1	_	-
Total						100	100

Required animal commodity MRLs

Current MRLs are *0.05 mg/kg for meat (mammalian) and edible offal (mammalian) and *0.01 mg/kg for milks. Data from the animal transfer studies indicate that a dietary intake of 100 ppm would not produce detectable residues in the meat or offal and a dietary intake of 1,000 ppm would not produce detectable residues in the milk. The submitted residues studies support the current Table 4 entries of 100 mg/kg for Legume Animal Feeds and 30 mg/kg for Oilseed forage and fodder or a new entry to account for residues in grass pasture or cereal forage and fodder of 100 mg/kg. Therefore, finite residues in meat, offal and milks are not expected to occur based on the current maximum dietary intake for ruminants and pigs. The current mammalian commodity MRLs remain appropriate.

Crop rotation

In a confined accumulation study radiolabelled diquat was applied to soil at 1.5x the maximum Australian use rate and seeds of carrots, lettuce and wheat were planted 30, 120 and 365 days after treatment and grown to maturity. Detectable residues only occurred in the carrot leaf and wheat straw samples but were attributed to soil contamination (Lee, 1989).

Additional studies were conducted where small plots of carrot, lettuce and wheat at a site in Florida (Fujie, 1989(a)), and small plots of carrot, lettuce and oats at a site in California (Fujie, 1989(b)) were irrigated at approximately ¹/₄, ¹/₂, ³/₄ and maturity with water containing diquat at a nominal concentration of 0.1 mg/L. Crops were sampled one day prior to the first irrigation and at maturity one day after the last irrigation, except for wheat and oats, which were allowed to dry in the field prior to harvesting as per normal agricultural practice. No diquat residues were detected in any of the crop samples analysed.

The conclusion that diquat residues are not expected in rotational crops from the Australian use patterns is in line with the JMPR (2013) evaluation which concluded that crops grown in rotation with diquat-treated crops are not expected to contain residues of diquat. Diquat residues in soil should contribute little to residue levels in rotational crops.

Spray drift

Data from the animal transfer studies indicate that a dietary intake of 100 ppm would not produce detectable residues in the meat or offal of animals grazing treated areas or fed a diet containing treated plant material. The Regulatory Acceptable Level for calculation of no spray downwind buffer zones for the protection of international trade will be taken as 100 ppm.

Dietary risk assessment

Chronic dietary exposure assessment

The chronic dietary exposure to diquat is estimated by the National Estimated Daily Intake (NEDI) calculation encompassing all registered/temporary uses of the chemical and the mean daily dietary consumption data derived primarily from the 2011–12 National Nutritional and Physical Activity Survey. The NEDI calculation is made in accordance with WHO Guidelines and is a conservative estimate of dietary exposure to chemical residues in food. The NEDI for diquat is equivalent to <30% of the ADI.

It is concluded that the chronic dietary exposure of diquat is acceptable.

Acute dietary exposure assessment

The acute dietary exposure is estimated by the National Estimated Short Term Intake (NESTI) calculation. The NESTI calculations are made in accordance with the deterministic method used by the JMPR with 97.5th percentile food consumption data derived primarily from the 2011–12 National Nutritional and Physical Activity Survey. NESTI calculations are conservative estimates of short-term exposure (24 hour period) to chemical residues in food.

The highest acute dietary intake was estimated at <10% of the ARfD. It is concluded that the acute dietary exposure is acceptable.

Residue related aspects of trade

The overseas MRLs presented in Table 18 are established for commodities considered to be major export commodities.

Commodity	Australia	Codex ¹⁵	EU ¹⁶	Japan ¹⁷	Korea ¹⁸	Taiwan ¹⁹	USA ²⁰
Residue definition	Diquat cation	Diquat ion	Diquat	Diquat ion	-	_	Calculated as the cation
Barley	5 (current)	5	*0.02	5	-	_	0.02 (cereal grain)
Oats	5 (current) 2 (proposed)	-	2	2 (other cereal grains)	-	-	0.02 (cereal grain
Wheat	2 (current)	_	*0.02	0.1	_	_	0.02 (cereal grain
Maize	*0.05 (proposed)	-	*0.02	0.02	-	_	0.02 (cereal grain
	0.1 (current)						
Rye	2 (current)	1.5	*0.02	2	_	-	_
Sorghum	2 (current)	-	*0.02	-	-	-	-
	Proposed *0.05 after a phase out period						
Rice	5 (current)	-	*0.02	0.03 (brown rice)	-	-	0.02 (cereal grain
	Proposed *0.05 after a phase out						

Table 18: International MRLs for Australian major export commodities (December 2023)

¹⁵ Food and Agriculture Organization of the United Nations (FAO), 2023. <u>Codex Alimentarius, International Food Standards</u>, FAO website, accessed December 2023.

¹⁶ European Commission (EC), <u>EU Pesticides Database</u>, EC website, accessed December 2023.

¹⁷ Japanese Food Chemistry Research Foundation (JFCRPF), 2023. <u>Table of MRLs for Agricultural Chemicals</u>, JFCRPF website, accessed December 2023.

¹⁸ Ministry of Food and Drug Safety Korea, 2023. <u>MRLs in Pesticides</u>, accessed December 2023.

¹⁹ Laws & Regulations Database of the Republic of China (Taiwan),2023. <u>Standards for Pesticide Residue Limits in Foods</u>, accessed December 2023.

²⁰ Electronic Code of Federal Regulations (eCFR), 2023. <u>USA Electronic Code of Federal Regulations</u>, eCFR website, accessed December 2023.

Commodity	Australia	Codex ¹⁵	EU ¹⁶	Japan ¹⁷	Korea ¹⁸	Taiwan ¹⁹	USA ²⁰
	period						
Rice, polished	1 (current) Proposed for deletion after a phase out period	_	_	_	_	_	0.02 (cereal grain
Cotton seed	Cotton seed proposed for deletion after a phase out period	-	*0.01 (cotton seed)	-	-	-	0.2 (cotton seed)
Rape seed [canola]	2 (proposed for rape seed)	1.5 (rape seed)	1.5 rapeseeds/c anola seeds)	2 (rapeseeds)	–1.5 (rape seed)	-	2 (canola seed)
Pulses	1 (current)	0.4 (dry beans subgroup) 0.9 (dry peas subgroup, Chick-pea (dry))	0.2 (beans) 0.2 (lentils) 0.3 (peas)	0.4 (soybeans, dried) 0.9 (beans, dried, Peas) 0.9 (other legumes pulses)	0.9 (lentil) 0.9 (pea) 0.3 (soybean)	-	0.05 (vegetable, seed and pod)
Sugar cane	*0.05 (current)	_	*0.01	0.02	_	_	0.2
Fruits	*0.05 (proposed for citrus) *0.01 (proposed for berries, pome fruit, stone fruit) *0.05 (current Fruits)	*0.02 (citrus fruits) *0.02 (pome fruits) *0.02 (stone fruits)	0.02 (citrus fruits) *0.01 (grapes) 0.02 (pome fruits) 0.02 (stone fruit)	0.02 (lemon) 0.02 (orange) 0.02 (grapefruit) 0.02 (lime) 0.02 (apple) 0.02 (pear) 0.02 (peach, nectarine, apricot, plum, cherry) 0.01 (grape)	-	-	0.05 (grape) 0.05 (citrus group 10) 0.02 (pome group 11) 0.02 (stone group 12)
Edible offal (mammalian)	*0.05 (current)	*0.01	*0.05 (bovine)	0.01 (cattle liver) 0.01 (cattle kidney)	_	0.05	0.05 (cattle meat byproducts)
Meat	*0.05 (current)	*0.01	*0.05	0.01 (cattle	_	0.05	0.05 (cattle
Commodity	Australia	Codex ¹⁵	EU ¹⁶	Japan ¹⁷	Korea ¹⁸	Taiwan ¹⁹	USA ²⁰
-------------	-----------------	---------------------	------------------	----------------------	---------------------	----------------------	----------------------
[mammalian]			(bovine)	muscle)			meat)
				0.01 (cattle fat)			0.05 (cattle fat)
Milks	*0.01 (current)	*0.001	*0.01	0.001	_	0.01	0.02

Export of treated produce containing finite (measurable) residues of diquat may pose a risk to Australian trade in situations where either no residue tolerance (import tolerance) is established in the importing country or where residues in Australian produce are likely to exceed a residue tolerance (import tolerance) established in the importing country.

It is noted that following the 2019 Codex Committee on Pesticide Residues (CCPR) the Codex MRL's for oats (2 mg/kg); wheat (2 mg/kg); wheat bran, unprocessed (2 mg/kg); wheat flour (0.5 mg/kg); and wheat wholemeal (2 mg/kg) were revoked. These MRLs were revoked following the 2018 JMPR assessment that concluded that a MRL could not be recommended as they did not have data that matched the critical GAP which was assessed by the JMPR.

The cereal use patterns have not changed, and no changes have been proposed to the barley, wheat and rye MRLs. The barley MRL is at the same levels as that established by Codex but, as noted, the Codex MRLs for oats and wheat (including processed fractions) were withdrawn in 2019. The Australian MRL for oats is proposed to be reduced to 2 mg/kg, which is the same as established in the EU and Japan, but higher than the USA. The maize MRL will be reduced to *0.05 mg/kg reflecting the supported use pattern at crop establishment. Although the supported MRLs for several cereal grains (with pre-harvest use) are higher than the standards in several markets this risk to trade has been managed in the past. It is noted that the pre-harvest uses on rice and sorghum are no longer supported in the long term and will be subject to a phase out period.

Use on cotton will not be supported in the long term and will also be subject to a phase out period. A longer withholding period will be recommended for canola which will allow the diquat rapeseed MRL to be reduced to 2 mg/kg which is similar to those MRLs established by Codex and in most overseas markets (except Taiwan).

No changes have been proposed to the current diquat pulse MRL at 1 mg/kg which again is higher than the tolerances established overseas. As no changes have been proposed to current use patterns, this risk is also unchanged.

The current Fruits and sugar cane MRLs for diquat are both established at the LOQ for the analytical method. No changes are proposed to the sugar cane MRL. The fruits MRL will be expanded into the Codex fruit commodity groups at the relevant LOQ for each crop. The risk to trade in these commodities is low.

No changes have been recommended to the current animal commodity MRLs for diquat which are established at the LOQ for the analytical method. The risk to trade in commodities of animal origin is low.

Oaten hay is also a major export commodity, noting that an MRL of 100 mg/kg has been recommended for diquat on AS 0162 Hay and fodder of grasses (dry). Approximately 85% of exports are oaten hay, while 10% is straw and the balance is predominantly lucerne hay and chaff. Approximately 85% of Australian export hay is destined for

Japan, while the volume of hay exported to China and the UAE is increasing. An animal feed MRL of 100 mg/kg has been established for diquat on grass in Japan²¹ As before this risk to trade is unchanged.

For cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay, finite residues of diquat are expected from the Australian uses which were supported by this residues and trade assessment. As the potential trade risk associated with diquat residues expected in cereal grains (barley, oats, rye, triticale and wheat), pulses, canola, and oaten hay have been managed by industry, and because international standards for diquat have not significantly changed in recent years (except for the removal of the Codex MRLs for wheat and oats in 2019), it is currently considered that the trade risk associated with the uses of diquat in cereal grains, pulses, canola and oaten hay is not undue. However, as the Australian MRLs are higher than those set by Codex or major export destinations, it is recommended that the following trade advice statement should be added to the labels of products containing pre-harvest uses on cereals (barley, oats, rye, triticale and wheat), pulses, canola:

EXPORT OF TREATED PRODUCE: Growers should note that maximum residue limits (MRLs) or import tolerances may not exist in all markets for [edible produce name] treated with [chemical product name]. If you are growing [edible produce name] for export, please check with [company name, industry body, etc.] for the latest information on MRLs and import tolerances before using [chemical product name].

As the Australian MRLs for cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay are higher than some of those set by Codex and major export destinations, the APVMA should seek comments from members of the grain and fodder industries on their ability to manage the risk to international trade associated with diquat during the Proposed Regulatory Decision consultation for diquat before a final decision against the trade criteria is made for pre-harvest uses on cereal grains other than maize, pulses, canola and oaten hay.

Conclusions from the residues and trade assessment

The Residues and Trade section recommends that the APVMA should be satisfied that the continued approval of the use patterns as currently described would not pose an undue hazard to the safety of people consuming anything containing its residues, according to the safety criteria as defined by Section 5A nor an undue risk to international trade as described by Section 5C of the Schedule to the Code Act, with the following exceptions.

The following crops were considered against the broad claims for 'orchards (including bananas) and vineyards' and 'row crops, vegetables and market gardens'.

Orchards (including bananas) and vineyards:

²¹ Japanese Food Chemistry Research Foundation (JFCRPF), 2023. <u>Table of MRLs for Agricultural Chemicals</u>, JFCRPF website, accessed December 2023.

• Citrus, Grapes, Pome fruit, Stone fruit, Tree nuts, Tropical fruit (edible peel), Tropical fruit (inedible peel, except pineapple).

Row crops, vegetables and market gardens:

 Berries and other small fruit (except grapes), Brassica vegetables, Bulb vegetables, Fruiting vegetables (cucurbits), Fruiting vegetables (other than cucurbits), Leafy vegetables, Legume vegetables, Pineapple, Root and tuber vegetables, Stalk and stem vegetables and herbs and spices.

The directions for use tables on product labels should be amended to indicate the specified crops/crop groups as above for the 'orchards (including bananas) and vineyards' and 'Row crops, vegetables and market garden uses' noting also the following recommendations for uses which are not supported (but may be suitable for a phase out period).

- Use on pineapple is not supported in the absence of specific residue data.
- For bulb vegetables, use is only supported for the bulb onions subgroup as residue data for green onions, which may have a higher residue potential, were not available.
- For brassica vegetables use is only supported for the crops with specific residue data, i.e. broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe-tsai).
- Use on fruiting vegetables, cucurbits is not supported in the absence of specific residue data.
- Use on stalk and stem vegetables (including a specific label use for asparagus) is not supported in the absence of reliable residue data.
- Use on herbs and spices is not supported in the absence of specific residue data.

Other uses that are no longer supported from a residues perspective

- There was insufficient reliable data for sorghum to confirm the current MRL for pre-harvest desiccation uses and assess dietary risk. Pre-harvest desiccation use on sorghum is no longer supported in the long term but may be suitable for a phase out period. Use at crop establishment continues to be supported for sorghum from a residues perspective.
- There was insufficient reliable data for rice to confirm the current MRLs for pre-harvest desiccation uses and assess dietary risk. Pre-harvest desiccation use on rice is no longer supported in the long term but may be suitable for a phase out period. The pre-emergent use on rice is however supported from a residues perspective.
- There is insufficient residue data to support the registered use on cotton which is no longer supported in the long term but may be suitable for a phase out period.
- As residue data are not available to support the over the top use or pre-harvest desiccation of sugarcane these uses are no longer supported but may be suitable for a phase out period. The pre-emergent use on sugar cane is however supported from a residues perspective.

Winter cereals

Labels with the winter cereal use pattern should specify the crops as barley, oats, rye, triticale and wheat. The broad term of winter cereals should be removed from product labels as it does not align with the APVMA crop group guidance.

Supported withholding periods

- The supported harvest withholding period for orchards and row crops for pre-emergent applications or applications by a shielded spray is 'Not required when used as directed'.
- The supported harvest withholding periods for the pre-harvest desiccation of potatoes and sweet potatoes are 7 and 14 days respectively.
- The supported harvest withholding period for pre-harvest desiccation of all pulse crops with this use (dry beans, dry peas, lentils, chickpeas, faba beans, lupins, mung beans, pigeon peas and soya beans) is 4 days.
- The supported harvest withholding period for barley, oats, rye, triticale and wheat for pre-harvest weed control is 4 days.
- The supported harvest withholding period for maize is 'Not required when used as directed'.
- The supported harvest withholding period for rice for the supported pre-emergent use pattern is 'Not required when used as directed'.
- The supported harvest withholding period for canola, linseed and sunflower is 7 days.
- The supported harvest withholding period for poppies is 2 days.
- The supported harvest withholding period for establishing sugarcane or controlling weeds in a fallow prior to sugarcane is 'Not required when used as directed'.
- The supported harvest withholding period for hops is 'Not required when used as directed'.
- The supported withholding period for crop establishment uses (canola, chickpeas, cereals (wheat, barley, oats, rye, triticale, sorghum, maize, millet), cotton, field beans, field peas, lentils, linseed, lupins, fodder rape, mung beans, navy beans, peanuts, pigeon peas, safflower, soybeans, sunflower, pasture (clover, grass, lucerne, medic), vetch) is 'Not required when used as directed'.
- The supported grazing withholding period statement in relation to diquat is:
 - DO NOT graze or cut for stock food for one day after application.

(noting that diquat products that also contain paraquat require a 7 day grazing withholding period for horses).

Aquatic areas

Use of diquat in aquatic areas with the 10 day restraint on using water for human consumption, livestock watering or irrigation purposes continues to be supported.

Spray drift

The livestock area RAL is 100 ppm. Mandatory no-spray zones for protection of international trade are not required for either ground or aerial application based on this RAL. This assessment was based on a droplet size of fine.

Trade

For cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay, finite residues of diquat are expected from the Australian uses. As the potential trade risk associated with diquat residues expected in cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay, have been managed by industry, and because international standards for diquat have not significantly changed in recent years (except for the removal of the Codex MRLs for wheat and oats), it is currently considered that the trade risk associated with the uses of diquat in cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay is not undue.

However, as the Australian MRLs are higher than those set by Codex or major export destinations, it is recommended that the following trade advice statement should be added to the labels of products containing preharvest uses on cereals (barley, oats, rye, triticale and wheat), pulses, canola:

EXPORT OF TREATED PRODUCE: Growers should note that maximum residue limits (MRLs) or import tolerances may not exist in all markets for [edible produce name] treated with [chemical product name]. If you are growing [edible produce name] for export, please check with [company name, industry body, etc.] for the latest information on MRLs and import tolerances before using [chemical product name].

As the Australian MRLs for cereal grains (barley, oats, rye, triticale and wheat), pulses, canola and oaten hay are higher than some of those set by Codex and major export destinations, the APVMA should seek comments from members of the grain and fodder industries on their ability to manage the risk to international trade associated with diquat during the Proposed Regulatory Decision consultation for diquat before a final decision against the trade criteria is made for pre-harvest uses on cereal grains other than maize, pulses, canola and oaten hay.

Required MRL changes

Table 19 and Table 20 show the changes required to the Agricultural and Veterinary Chemicals (MRL Standard for Residues of Chemical Products) Instrument 2023, based on the uses supported by the risk assessment outcomes in this Residues and Trade assessment of diquat. It should be noted that the outcome of other risk assessments conducted by the APVMA will be applied to determine which use patterns remain supported overall.

Code	Commodity	Current MRL	Recommended MRL
FT 0026	Assorted tropical and sub-tropical fruits – edible peel	_	*0.1
FI 0030	Assorted tropical and sub-tropical fruits – inedible peel {except pineapple}	-	*0.02

Table 19: Amendments to Table 1 of the MRL Standard

Code	Commodity	Current MRL	Recommended MRL
GC 0640	Barley	5	5
VP 0061	Beans, except broad bean and soya bean	1	Delete
FB 0018	Berries and other small fruits	_	*0.05
VP 0522	Broad bean (green pods and immature seeds)	1	Delete
VB 0400	Broccoli	_	*0.02
VA 2031	Bulb onions	_	0.2
VB 0041	Cabbages, head	_	*0.02
VB 0404	Cauliflower	_	*0.02
VB 0467	Chinese cabbage (type Pe-tsai)	_	*0.02
FC 0001	Citrus fruits	_	*0.05
SO 0691	Cotton seed	_	T5 during phase out, *0.05 after phase out
MO 0105	Edible offal (Mammalian)	*0.05	*0.05
PE 0112	Eggs	*0.01	*0.01
VO 0050	Fruiting vegetables, other than cucurbits	_	*0.01
	Fruits	*0.05	Delete
DH 1100	Hops, dry	0.2	*0.05
VL 0053	Leafy vegetables	_	0.2
VP 0060	Legume vegetables	_	*0.05
SO 0693	Linseed	*0.01	5
GC 0645	Maize	0.1	*0.05
MM 0095	Meat [mammalian]	*0.05	*0.05
ML 0106	Milks	*0.01	*0.01
GC 0646	Millet	_	*0.05
GC 0647	Oats	5	2
SO 0088	Oilseed [except linseed and poppy seed]	5	Delete
SO 0305	Olives for oil production	_	*0.1

Code	Commodity	Current MRL	Recommended MRL
VA 0385	Onion, Bulb	0.1	Delete
SO 0697	Peanut	_	*0.05
VP 0063	Peas	0.1	Delete
FP 0009	Pome fruits	_	*0.01
SO 0698	Poppy seed	*0.01	*0.01
VR 0589	Potato	0.2	0.2
PO 0111	Poultry, Edible offal of	*0.05	*0.05
PM 0110	Poultry meat	*0.05	*0.05
VD 0070	Pulses	1	1
SO 0495	Rape seed [canola]	_	2
GC 0649	Rice	5	T5 during phase out, *0.05 after phase out
CM 1205	Rice, polished	1	Delete (T1 during phase out)
VR 0075	Root and tuber vegetables {except Potato; Sweet potato}	_	0.1
GC 0650	Rye	2	2
SO 0699	Safflower	_	*0.05
GC 0651	Sorghum	2	T2 during phase out, *0.05 after phase out
FS 0012	Stone fruits	_	*0.01
VR 0596	Sugar beet	0.1	Delete
GS 0659	Sugar cane	*0.05	*0.05
SO 0702	Sunflower seed	_	1
VR 0508	Sweet potato	_	0.2
TN 0085	Tree nuts	*0.05	*0.05
GC 0653	Triticale	2	2
	Vegetables [except beans; broad bean; lupin (dry); onion, bulb; peas; potato; soya bean (dry); sugar beet]	*0.05	Delete

Code	Commodity	Current MRL	Recommended MRL
OC 0172	Vegetable oils, crude	1	Delete
OR 0172	Vegetable oil, edible	_	*0.01
GC 0654	Wheat	2	2

Table 20: Amendments to Table 4 of the MRL Standard

Code	Animal feed commodity	Current MRL	Recommended MRL
AL 0157	Legume animal feeds	100	100
	Oilseed forage and fodder	30	30
AF 0161	Forage of cereal grains and other grass-like plants	-	100
AS 0161	Straw and fodder (dry) and hay of cereal grains and other grass like plants	_	100

Consideration of proposed APVMA reconsideration outcomes for diquat

The APVMA's risk assessments for human and environmental exposure to diquat based on currently approved uses indicate that many of those uses will not continue to be supported. The uses that are supported are presented in Table 21 and

Table 22. These uses are within the application rate range indicated on currently approved labels.

Table 21: Diquat uses supp	ported by human health	n, environment, and r	residues and trade ris	k assessments
		/ /		

Crop use or situation	Weeds controlled/ use	Application method	Assessment outcome
Hops	Annual broadleaf and grass weeds	Inter-row spray	Supported
Lucerne	Capeweed and Erodium spp.	Boomspray	Supported up to 88 g ac/ha per season
Oil seed poppies	General weed control	Boomspray	Supported up to 283 g ac/ha per season
Pasture renovation and establishment	Capeweed (very young seedling, 2– 3 leaf stage only)	Boomspray	Supported up to 88 g ac/ha per season
Row crops, vegetables and market gardens (berries and other small fruit (except grapes)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (brassica vegetables: broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe- tsai)	Broadleaf weeds	Boomspray, handwand inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (bulb vegetables :bulb onions)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens(fruiting vegetables: other than cucurbits)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (leafy vegetables)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (legume vegetables)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)

Crop use or situation	Weeds controlled/ use	Application method	Assessment outcome
Row crops, vegetables and market gardens (root and tuber vegetables)	Broadleaf weeds	Boomspray, handwand, inter-row spray (shielded)	Supported up to 283 g ac/ha per season (noting crop group change required by residues)
Wheat, oats (3-4 leaf to early tillering)	Capeweed (small seedlings)	Boomspray	Supported up to 122 g ac/ha per season

Table 22: Paraquat and diquat combination uses that are supported by human health, environment and residues and trade risk assessments

Сгор	Weeds controlled/use	Application method	Assessment outcome (risk area)
Aid to cultivation (Southern Australia – full disturbance) Winter Canola, chickpeas, wheat,	Seedling grasses: annual ryegrass (lolium rigidum), barley grass (hordeum spp.), brome grass (bromus spp.), volunteer cereals, wild oats (avena spp.) (2–3 leaf)	Boomspray	Supported up to 175 g/ha of combined active constituents per season (700 ml of product/ha)
barley, oats, rye, triticale, field beans, field peas, lentils, linseed (linola), lupins, vetch	Vulpia (silver grass, sand fescue) (vulpia spp.) (2–3 leaf)		
Spring/summer			
Fodder rape, pigeon peas, safflower, sorghum, soybeans, sunflower			
Pasture			
Clover grass, lucerne, medics			

Hops (supported use: 0.28 kg ac/ha)

The use on hops is as a directed inter-row spray at 0.28 kg ac/ha to crop emerging from winter dormancy. The withholding period is 'Not required when used as directed'. The current Australian MRL is Hops, dry at 0.2 mg/kg.

Residue data for diquat on hops were provided. Residues of diquat in hops were <0.05 mg/kg (n = 2) at 12-14 days after the last of 2–3 applications at 0.368 kg ac/ha by inter row boom spray.

The available diquat residues data supports continued use in hops. The recommended MRL is:

• DH 1100 Hops, dry

*0.05 mg/kg

The recommended harvest withholding period is 'Not required when used as directed' for this use as a directed inter row spray prior to crop emerging from winter dormancy. The recommended grazing withholding period for sprayed vegetation is one day.

Lucerne (supported use: 0.088 kg ac/ha)

The use on lucerne is for application at up to 0.088 kg ac/ha. Heavy grazing is necessary to reduce lucerne to 2 cm in height before spraying. The grazing withholding period is one day. The current entry for diquat in Table 4 of the MRL Standard is 'Legume Animal Feeds' at 100 mg/kg.

Studies submitted on lucerne, clover and medic (zero to 133 day PHI, with applications of 0.1 to 6 kg ac/ha), including several that addressed a zero or one day PHI, generally had diquat residues between 20 and 40 mg/kg

in the desiccated plant material, from the approximate rate of 0.6 kg ac/ha and a PHI of 2–4 days. The HR at one day was 66.7 mg/kg in clover after 0.56 kg ac/ha (10.5 mg/kg scaled for the supported rate of 0.088 kg ac/ha). At longer PHIs the HR was 92.5 mg/kg (dry weight) in white clover at 4 days after 1.12 kg ac/ha (7.3 mg/kg scaled for the supported rate of 0.088 kg ac/ha).

Noting that when scaled for the supported rate of 0.088 kg ac/ha the HR was 10.5 mg/kg, MRLs of 20 mg/kg would be appropriate for diquat on AL 1020 Alfalfa [lucerne] fodder and AL 1021 Alfalfa [lucerne] forage (green) in conjunction with a one day grazing withholding period. However, a Primary feed commodities MRL at 20 mg/kg is recommended to cover this use and the pasture and crop establishment uses considered below.

Oilseed poppies

The current MRL at the LOQ of *0.01 mg/kg for diquat on poppy seed was considered appropriate for the higher registered rate considered earlier. The MRL should therefore remain appropriate for the reduced rate supported by the environmental assessment. The available diquat residues data supports continued use in poppies. The supported MRL is:

SO 0698 Poppy seed

*0.01 mg/kg

The supported harvest withholding period for poppies is 2 days.

Pasture renovation and establishment

The use supported by the environmental assessment for pasture renovation and establishment is for application at 88 g ac/ha. It was noted earlier that it is not clear if all the residue results for grass were reported on a fresh or dry weight basis, with exception of the JMPR cereal trials which were expressed on a dry weight basis. It was however also noted earlier that the levels of diquat residues in trials conducted on grasses and cereals were similar to those results found in legumes. Based on the assessment for lucerne above which was supported at the same application rate a Primary feed commodities MRL at 20 mg/kg will be established to cover these uses and will also cover crop establishment uses. The recommended grazing withholding period is one day.

Berries and other small fruit (except grapes)

The entry recommended earlier into the MRL Standard for berries and small fruits, was at the LOQ with finite residues not expected to occur. This entry should therefore remain appropriate for the reduced rate supported by the environmental assessment but should exclude grapes as a use on grapes has not been supported.

• FB 0018 Berries and other small fruits {except grapes} *0.05 mg/kg

As the use is targeting inter-row weeds and not the crop, a harvest withholding period statement of 'Not Required when used as directed' is supported for berries and other small fruit.

Brassica vegetables: broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe-tsai)

The entries into the MRL Standard recommended earlier for selected Brassica vegetables were at the LOQ with finite residues not expected to occur. These entries should remain appropriate for the reduced rate supported by the environmental assessment:

•	VB 0400	Broccoli	*0.02 mg/kg
•	VB 0041	Cabbages, head	*0.02 mg/kg
•	VB 0404	Cauliflower	*0.02 mg/kg
•	VB 0467	Chinese cabbage (type Pe-tsai)	*0.02 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for broccoli, cauliflower, cabbage and Chinese cabbage.

Bulb vegetables: bulb onions

The highest residues reported in bulb onions which was relevant to the Australian use rate of 0.8 kg ac/ha was 0.10 mg/kg after 3 applications of 0.8 kg ac/ha. Scaled for the application rate of 283 g ac/ha supported by the environmental assessment, the estimated HR is 0.035 mg/kg.

The recommended entry into the MRL Standard for bulb onions is:

VA 2031 Bulb onions

Although the HR was observed at 6–7 days after application at 0.8 kg ac/ha, a 'Not required when used as directed' withholding period is considered suitable for shielded spray application post emergence, noting also that lower residues were observed immediately after application and that an MRL has been recommended to cover the observed HR.

0.07 mg/kg

Fruiting vegetables other than cucurbits

The entry into the MRL Standard recommended earlier for fruiting vegetables, other than cucurbits was at the predominant LOQ in the available trials of 0.01 mg/kg, noting that finite residues were not expected to occur. This entry should remain appropriate for the reduced rate supported by the environmental assessment.

• VO 0050 Fruiting vegetables, other than cucurbits *0.01 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for fruiting vegetables, other than cucurbits.

Leafy vegetables

In trials that involved one to 2 applications at rates approximate to the Australian rate (0.7–1 kg ac/ha), residues were <0.01, 0.01, <0.02 (2), 0.03, 0.05 and 0.07 mg/kg at a 7–10 day PHI. Application rates were approximately 3x that supported by the environment assessment. Scaled for the supported rate residues are estimated as

<0.01 (2), <0.02 (2), 0.01 and 0.02 (2) mg/kg. The OECD MRL Calculator recommends an MRL of 0.04 mg/kg. The recommended entry into the MRL Standard for Leafy vegetables based on the rate supported by the environmental assessment is:

VL 0053 Leafy vegetables 0.05 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for leafy vegetables.

Legume vegetables

The entry recommended earlier into the MRL Standard for legume vegetables was at the LOQ, with finite residues not expected to occur. This entry should remain appropriate for the reduced rate supported by the environmental assessment:

VP 0060 Legume vegetables *0.05 mg/kg

As the use is pre-emergence or by shielded spray, a harvest withholding period statement of 'Not Required when used as directed' is supported for legume vegetables.

Root and tuber vegetables

There were 13 overseas carrot trials conducted as pre-emergence and post-emergence weed control. Residues of diquat in these trials were generally <0.02 mg/kg, with a maximum of 0.07 mg/kg recorded in samples taken 14 days after an application of 1.0 kg ac/ha (3.5× the rate supported by environment). The maximum residue recorded after application at 0.8 kg ac/ha (2.8× the maximum rate supported by environment) was 0.04 mg/kg in the same trial (14 day PHI). In another trial, residues were all <0.02 mg/kg in samples taken one, 7, 13 and 20 days after an inter-row weed control application of 0.8 kg a.i/ha. The PHI in all these trials ranged from one to 123 days and the shorter intervals would not reflect typical agronomic practice where application as a pre-emergence weed control is earlier in the crop growth cycle, or via shielded sprayer later in the growing cycle.

Diquat residues in root and tuber vegetables after pre-emergent or post emergent shielded spray application will be covered by an MRL recommended at 0.05 mg/kg in conjunction with a 'Not required when used as directed' harvest withholding period (the sugar beet MRL at 0.1 mg/kg will be deleted). This group MRL will cover the HR of 0.07 mg/kg observed in carrots after a pre-emergence application when scaled for application rate (HR = 0.02 mg/kg when scaled for the supported application rate of 0.283 kg ac/ha).

The supported MRL is:

• VR 0075 Root and tuber vegetables

0.05 mg/kg

Pre-emergent application to wheat and oats and as a cultivation aid for pastures and selected cereals, pulses and oilseeds

The supported use in combination with paraquat as a cultivation aid is for diquat application at 80.5 g ac/ha. The supported pre-emergent use to wheat and oats is for application at 122 g ac/ha. Although data for all crops are not

available, the data for peanuts, rice and maize considered earlier along with the confined crop rotation study suggest that finite residues are not expected at harvest following a pre-emergent use. The recommended MRLs are:

•	GC 0080	Cereal grains	*0.05 mg/kg
•	VD 0070	Pulses	*0.05 mg/kg
•	SO 0088	Oilseeds {except poppy seed}	*0.05 mg/kg

The supported harvest withholding period is 'Not required when used as directed'.

The primary feed commodities MRL at 20 mg/kg should be sufficient to cover these uses with a grazing withholding period of one day, noting for the pre-emergent uses grazing would not be expected to occur so soon after treatment.

Animal commodities

Current MRLs are *0.05 mg/kg for meat (mammalian) and edible offal (mammalian) and *0.01 mg/kg for milks. Data from the animal transfer studies indicate that a dietary intake of 100 ppm would not produce detectable residues in the meat or offal and a dietary intake of 1,000 ppm would not produce detectable residues in the milk. The submitted residues studies support Table 4 entries of 20 mg/kg for primary feed commodities. Therefore, finite residues in meat, offal and milks are not expected to occur based on the current maximum dietary intake for ruminants and pigs. The current mammalian commodity MRLs remain appropriate.

The poultry commodity MRLs at the LOQ can also remain in place to indicate that finite diquat residues should not occur in poultry commodities for the supported uses. All other MRLs for diquat can be deleted after a phase out period as no other uses are supported.

Trade

Cereals, pulses and oilseeds include major export commodities. However, residue is not expected to occur at harvest following the supported pre-emergent uses. Hops are not considered to be a major export commodity and detectable residues are not expected to occur in hops. The supported vegetable crops are also not major export commodities. Residues should also not occur in livestock grazing treated crops or pasture. The risk to trade from the supported uses is considered to be low.

Revised dietary exposure assessment

Chronic dietary exposure assessment

The chronic dietary exposure to diquat is estimated by the National Estimated Daily Intake (NEDI) calculation encompassing all registered/temporary uses of the chemical and the mean daily dietary consumption data derived primarily from the 2011–12 National Nutritional and Physical Activity Survey. The NEDI calculation is made in accordance with WHO Guidelines and is a conservative estimate of dietary exposure to chemical residues in food. The NEDI for diquat is equivalent to <15% of the ADI, for the uses proposed to be supported by the APVMA chemical review.

It is concluded that the chronic dietary exposure of diquat is acceptable.

Acute dietary exposure assessment

The acute dietary exposure is estimated by the National Estimated Short Term Intake (NESTI) calculation. The NESTI calculations are made in accordance with the deterministic method used by the JMPR with 97.5th percentile food consumption data derived primarily from the 2011–12 National Nutritional and Physical Activity Survey. NESTI calculations are conservative estimates of short-term exposure (24 hour period) to chemical residues in food.

The highest acute dietary intake was estimated at <1% of the ARfD, for the uses proposed to be supported by the APVMA chemical review. It is concluded that the acute dietary exposure is acceptable.

Revised MRL changes

The amendments shown in Table 23 and Table 24: Revised amendments to Table 4 of the MRL Standard

Code	Animal feed commodity	Current MRL	Recommended MRL
AL 0157	Legume animal feeds	100	Delete
	Oilseed forage and fodder	30	Delete
	Primary feed commodities	-	20

should be made to the Agricultural and Veterinary Chemicals (MRL Standard for Residues of Chemical Products) Instrument 2023, at the end of any phase out period, to reflect uses which are proposed to remain at the completion of the APVMA chemical review.

Code	Commodity	Current MRL	Recommended MRL
GC 0640	Barley	5	Delete
VP 0061	Beans, except broad bean and soya bean	1	Delete
FB 0018	Berries and other small fruits {except grapes}	-	*0.05
VP 0522	Broad bean (green pods and immature seeds)	1	Delete
VB 0400	Broccoli	_	*0.02
VA 2031	Bulb onions	-	0.07
VB 0041	Cabbages, head	-	*0.02
VB 0404	Cauliflower	-	*0.02
GC 0080	Cereal grains	-	*0.05
VB 0467	Chinese cabbage (type Pe-tsai)	-	*0.02
MO 0105	Edible offal (Mammalian)	*0.05	*0.05
PE 0112	Eggs	*0.01	*0.01
VO 0050	Fruiting vegetables, other than cucurbits	-	*0.01
	Fruits	*0.05	Delete
DH 1100	Hops, dry	0.2	*0.05
VL 0053	Leafy vegetables	-	0.05
VP 0060	Legume vegetables	-	*0.05
SO 0693	Linseed	*0.01	Delete
GC 0645	Maize	0.1	Delete
MM 0095	Meat [mammalian]	*0.05	*0.05
ML 0106	Milks	*0.01	*0.01
GC 0647	Oats	5	Delete
SO 0088	Oilseed [except linseed and poppy seed]	5	Delete

Table 23: Revised amendments to Table 1 of the MRL Standard

Code	Commodity	Current MRL	Recommended MRL
SO 0088	Oilseed {except poppy seed}	-	*0.05
VA 0385	Onion, Bulb	0.1	Delete
VP 0063	Peas	0.1	Delete
SO 0698	Poppy seed	*0.01	*0.01
VR 0589	Potato	0.2	Delete
PO 0111	Poultry, Edible offal of	*0.05	*0.05
PM 0110	Poultry meat	*0.05	*0.05
VD 0070	Pulses	1	*0.05
GC 0649	Rice	5	Delete
CM 1205	Rice, polished	1	Delete
VR 0075	Root and tuber vegetables	_	0.05
GC 0650	Rye	2	Delete
GC 0651	Sorghum	2	Delete
VR 0596	Sugar beet	0.1	Delete
GS 0659	Sugar cane	*0.05	Delete
TN 0085	Tree nuts	*0.05	Delete
GC 0653	Triticale	2	Delete
	Vegetables [except beans; broad bean; lupin (dry);	*0.05	Delete
	onion, bulb; peas; potato; soya bean (dry); sugar beet]		
OC 0172	Vegetable oils, crude	1	Delete
GC 0654	Wheat	2	Delete

Table 24: Revised amendments to Table 4 of the MRL Standard

Code	Animal feed commodity	Current MRL	Recommended MRL
AL 0157	Legume animal feeds	100	Delete
Oilseed forage and fodder 30		30	Delete
	Primary feed commodities	-	20

Environmental safety

Assessment scenarios

Many diquat products are registered for control of aquatic weeds. The products can be injected below the surface to achieve a target concentration of 1.0 mg ac/L (for control of cattails and pond weeds) or applied as a surface spray at 1,000 to 2,000 g ac/ha with a minimum retreatment interval of 7 days (to control floating weeds). A second spray application may be necessary for control of dense infestations. Oxygen depletion of decaying weeds may occur; therefore, no more than a quarter of the area should be treated as a surface spray per application to ensure adequate oxygen supply for aquatic life (i.e. environmental exposure across the entire water body is equivalent to 250 to 500 g ac/ha).

Many diquat products are also registered as pre-harvest desiccants in a variety of crops at rates up to 800 g ac/ha.

Diquat products are also registered for general weed control in a variety of crop and pasture situations at rates up to 800 g ac/ha. Applications are generally before planting or before crop emergence (i.e., bare soil scenarios); however, applications can also occur at later crop stages as directed sprays or inter-row.

There is one diquat/paraquat combination product that is registered as a pre-harvest desiccant in cotton at a diquat rate of 184 g ac/ha. There are many diquat/paraquat combination products that are registered for general weed control at diquat rates up to 368 g ac/ha in a broad range of situations, including crops, pasture, forestry, public service areas, and rights of way. Spot spray application is also possible in tropical fruit orchards up to 27.6 g ac/100L (each application is equivalent to 276 g ac/ha assuming a spray volume of 1,000 L/ha). Assuming a maximum of 40% of an orchard is treated, environmental exposure across the entire orchard is equivalent to 110 g ac/ha. Please note this assessment addresses the risks of diquat only; environmental risks of paraquat and the diquat/paraquat combination.

The environmental risk assessment scenarios considered in the assessment are summarised in Table 25. Environmental risks were determined according to contemporary methodology outlined in the <u>APVMA Risk</u> <u>Assessment Manual – Environment</u>. All endpoints are expressed in terms of the diquat cation as the active constituent.

Category	Situation	Risk assessment scenario
Aquatic areas	Water injection	1× 1.0 mg ac/L
	Surface spray	2× 500 g ac/ha 7-day retreatment interval
Pre-harvest crop desiccation	Poppies, potatoes, sweet potatoes	1× 600–800 g ac/ha
	Oilseeds, lupins, lucerne, pulses	1× 300–600 g ac/ha

Table 25: Environmental risk assessment scenarios for diquat

Category	Situation	Risk assessment scenario
	Cereals, cotton, rice, sugarcane, sunflowers	1× 400–600 g ac/ha
General weed control	Row crops, vegetables, market gardens	1× 280–800 g ac/ha
	Wheat and oats	1× 110–140 g ac/ha
	Pasture	1× 70–300 g ac/ha
	Infested areas	1× 560 g ac/ha
	Oilseeds	1× 60–300 g ac/ha
	Orchards, vineyards	1× 300 g ac/ha
	Hops	1× 140–280 g ac/ha
	Lucerne	1× 70–140 g ac/ha
Combination products containing paraguat	Cotton desiccation	1× 138–184 g ac/ha
	Spray topping in grasses	1× 92–173 g ac/ha
	Bananas, duboisia ²² , public service areas, rights of way, market gardens, nurseries, potatoes, rice, vegetables	1× 276–368 g ac/ha
	Vineyards	1× 368 g ac/ha
	Forests, orchards, plantations	1× 184–368 g ac/ha
	Fallow (minimal disturbance)	2× 138–368 g ac/ha 7-day retreatment interval
	Fallow (full disturbance), lucerne	1× 276 g ac/ha

²² Spot spray also possible in duboisia

Category	Situation	Risk assessment scenario
	Spot application in avocado, custard apples, lychees, mangos ²³	2× 276 g ac/ha 14-day retreatment interval
	Sugarcane, pasture	1× 138–368 g ac/ha

Fate and behaviour in the environment

Diquat has low volatility and high solubility in water. Its octanol-water partition coefficient (Table 3) indicates low potential for bioaccumulation. One UV-VIS absorption maximum of diquat was observed above 290 nm, suggesting some photochemical degradation is possible under natural light.

The rate of dissipation of diquat on ground invertebrates that may be eaten by birds was determined at 3 separate sites in Northern France. Cereal stubble was sprayed with an SL 200 g/L formulation at 1,000 g ac/ha and residues were measured on pitfall trapped beetles. DT₅₀ values for beetles sampled at the 3 sites were 3.2, 1.5 and 1.8 days (mean DT₅₀ 2.2 days). Similarly in Canada, sites comprising a field (lentils), slough (small wetland) and upland were sprayed directly by aircraft at the rate of 550 g ac/ha. Reliable DT₅₀ values for insects captured in pitfall traps at 4 of the sites were 1.6, 3.9, 1.6 and 1.9 days (mean DT₅₀ 2.3 days). DT₅₀ values ranged 1.0–2.1 days in terrestrial vegetation and 2.9–17 days in seeds. Dissipation rates were also determined in the foliage of oilseed rape plants (not seeds or pods) based on data available from European residue trials. DT₅₀ values were 0.42–3.0 days (Austria), 0.97–3.9 days (northern France), 1.7 days (Spain), 2.8 days (Italy) and 2.0–4.0 days (southern France).

Under aerobic laboratory conditions in the dark, diquat was very persistent in soil (geomean DT₅₀ 1108 days), with no metabolites forming >5% AR. Mineralisation to carbon dioxide accounted for less than 5% AR and bound residues accounted for 0.4–16 % AR after 90–120 days. A laboratory soil photolysis study showed photolysis occurs in irradiated moist soil and formation of TOPPS at a maximum of 9.9% AR at the study end (30 DAT). TOPPS was persistent in laboratory soil under aerobic conditions in the dark (geomean DT₅₀ 224 days). Batch equilibrium studies indicate diquat bind strongly to clay particles rendering it largely non-bioavailable and nonmobile in soil. Adsorption of diquat to sand soils (mean Kf 2932 mL/g, \leq 10% clay) was considerably lower than agricultural soils with higher clay content (mean Kf 11298 mL/g, >10% clay). The metabolite TOPPS is also nonmobile in soil (mean Kf 147 mL/g, 1/n 0.73). Under field conditions, diquat was very persistent at sites in the UK and the United States.

Diquat is stable to hydrolysis but may photodegrade in natural water. Two photoproducts, TOPPS and AQ1, were formed in aqueous photolysis studies up to 19 and 12% AR, respectively. In water/sediment systems, diquat

²³ Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard

partitions rapidly to particulate matter and sediment, where it is strongly sorbed, non-bioavailable, and very persistent. There is no apparent desorption of diquat back into the water.

Based on a theoretical calculation of the potential for photooxidation of diquat dibromide in the atmosphere, using a OH radical concentration of 1.5×10^6 cm⁻³ (12-hour day), a first order half-life of 0.46 days (5.5 hours) was estimated. However, diquat concentrations in air following application would be negligible, given it is highly sorbed to soil and sediment, fully ionised in aqueous conditions, very soluble in water, and has low volatility.

The key regulatory endpoints for the environmental exposure assessment are summarised in Table 26. A full listing of endpoints is provided in <u>Appendix B</u>.

Compartment Value Reference Animal food items Foliage: DT₅₀ 1.8 d Edwards, et al, 1991; Kennedy, 1984(a); Langridge, 2011a; 2011b; Massey, 1987(c) Insects: DT₅₀ 2.2 d Edwards, et al, 1991; Jutsum, 2011 Seeds: DT₅₀ 7.9 d Edwards et al, 1991 Soil DT₅₀ 1000 d Default for persistent substances Sands:Kf 2932 mL/g, 1/n 0.63 Dixon & Gilbert, 2012(b); Mônego, 2005; Pack, 1987 Non-sands: Kf 11298 mL/g, 1/n 0.78 Water DT₅₀ 0.50 d Fujie, 1988(d) Sediment DT₅₀ 1000 d Default for persistent substances Kf 136759 mL/g Mônego, 2005; Pack, 1987 Air DT₅₀ 5.5 h Hayes, 2001

Table 26: Key regulatory endpoints for environmental exposure assessment

Effects on non-target species

Diquat has moderate toxicity to mammals (LD_{50} 120 mg ac/kg bw, *Rattus norvegicus*) and high toxicity to birds (geomean LD_{50} 70 mg ac/kg bw, 3 species). Therefore, the following protection statement is required on diquat product labels (followed by an appropriate risk management statement).

Toxic to birds.

Following long-term dietary exposure in a multi-generation reproductive toxicity study, fewer F1 pups/litter and reduced F1 body weight gain in mammals during lactation were observed at doses as low as 12 mg ac/kg bw/d (NOAEL 4.0 mg ac/kg bw/d, *Rattus norvegicus*).

Higher tier reproductive toxicity studies are available on the most sensitive species of bird (*Anas platyrhynchos*) that considered 9 weeks of exposure (3 weeks prior to full egg production and 6 weeks during full egg production). Biologically relevant reductions in egg production were observed at dietary concentrations as low as 40 mg ac/kg food (NOEC 20 mg ac/kg food; equivalent to NOEL 3.2 mg ac/kg bw/d). An additional study suggested that egg production can recover providing that the exposure is early on in the egg production period and the egg laying period of exposed birds is sufficiently long (Temple et al. 2009).

Diquat has moderate toxicity to fish (lowest LC_{50} 750 µg ac/L, *Stizosterdion vitreum*) and aquatic invertebrates (lowest LC_{50} 420 µg ac/L, Stizosterdion vitreum), and high toxicity to sediment dwellers (LC_{50} 84 µg ac/L, *Hyallella azteca*), algae (lowest ErC_{50} 1.2 µg ac/L, *Navicula pelliculosa*) and aquatic plants (EC_{50} 3.2 µg ac/L, *Lemna gibba*). Therefore, the following protection statement is required on diquat product labels.

Very toxic to aquatic life. DO NOT contaminate wetlands or watercourses with this product or used containers.

Following life-cycle exposure of pond snails to contaminated water, increased embryonic stage duration, delayed first spawning and reduced food consumption were observed at concentrations as low as 3.2 µg ac/L (NOEC 1.1 µg ac/L, *Lymnaea stagnalis*). Reduced growth of fish and aquatic invertebrates was observed at concentrations as low as 320 µg ac/L (NOEC 120 µg ac/L, *Pimephales promelas*) and 110 µg ac/L (NOEC 52 µg ac/L, *Americamysis bahia*), respectively.

Following long-term exposure of amphipods to contaminated sediment, reduced reproduction was observed at concentrations as low as 23 mg ac/kg dry sediment (NOEC 11 mg ac/kg dry sediment, *Hyallela azteca*). It is noted that the clay content in the test sediment was relatively low (3%). No adverse effects were observed in 2 species of midges at the highest sediment concentrations tested (NOEC 37 mg ac/kg dry sediment, *Chironomus dilutus*; NOEC 100 mg ac/kg dry sediment, *Chironomus riparius*), noting the clay content in the test sediments ranged 20–25%.

The effects of spray application or water injection of an SL 240 g/L formulation on non-target aquatic plants were investigated under field conditions in Florida and Wisconsin. A wide range of sensitivities was observed between the tested aquatic plants. These sensitivities were often related to the ability of the plant to recover over a 4– 5 week observation period following application. Duckweed (*Spirodela punctata*) was the most sensitive species following exposure both as a foliar spray (ER₅₀ 3.5 g ac/ha) and water injection (ER₅₀ 3.1 μ g ac/L). Sediment seemed to afford some protection to sub-soil vegetative portions of plants that are not free-floating (for example, hydrilla and torpedograss). This indicates that perennial plants with a significant underground biomass could be resistant to diquat, with the exception of some temporary damage.

A measured BCF of 1.0 in bluegill sunfish shows that diquat is unlikely to accumulate in fish (Hamer et al. 1987).

Noting primary producers are most sensitive to diquat, an SSD analysis was performed on the laboratory data (EC_{50} values). Diquat dissipates quickly from the water column under natural conditions due to rapid adsorption to sediment and suspended particulates; therefore, the endpoints were adjusted to account for the expected dissipation under natural conditions (Table 27). After considering the exposure periods for each of the aquatic

endpoints and the water DT_{50} of 0.50 days under field conditions, an HC₅ of 2.1 µg ac/L was derived, which is lower than the lowest EC₅₀ value. In addition, the lower limit HC5 is more than one third of the median HC₅. As such, 2.1 µg ac/L was set as the RAL for the protection of natural aquatic areas.

To assess risks in aquatic situations where aquatic weeds are targeted, the most conservative RAL of 47 μ g ac/L for aquatic animals was selected, which was also adjusted to account for rapid dissipation under natural conditions.

Diquat has low toxicity to bees by contact exposure (LD_{50} 105 µg ac/bee, *Apis mellifera*) and moderate toxicity by oral exposure (LD_{50} 22 µg ac/bee, *Apis mellifera*). The RAL for spray drift assessment is 17,500 g ac/ha based on the contact LD_{50} 105 µg ac/bee and a conversion factor of LOC 0.4 / ExpE 2.4 * 1000 as per the APVMA's <u>Spray drift risk assessment manual</u> (SDRAM).

In tier 1 (glass plate) laboratory tests on the toxicity of an SL formulation of diquat to the indicator species of predatory arthropods (predatory mite *Typhlodromus pyri*) and parasitic arthropods (parasitic wasp *Aphidius rhopalosiphi*), the respective LR₅₀ values were 2.9 and 3.2 g ac/ha. Exposure under tier 2 (natural substrate) conditions did not influence toxicity to the predatory mite (LR₅₀ 4.1 g ac/ha, *Typhlodromus pyri*). However, toxicity to the parasitic wasp was reduced (LR₅₀ 758 g ac/ha, *Aphidius rhopalosiphi*). Soil dwelling arthropods such as carabid beetles, spiders and rove beetles were unaffected at field relevant rates.

Diquat has moderate toxicity to soil macro-organisms such as earthworms (LC₅₀ 94 mg ac/kg dry soil, *Eisenia fetida*). Following long-term exposure, reduced reproduction of collembolans was observed at concentrations as low as 12 mg ac/kg dry soil (NOEC 9.4 mg ac/kg dry soil, *Folsomia candida*). No adverse effects were observed on other soil macro-organisms at the highest tested soil concentrations (NOEC 37 mg ac/kg dry soil, *Eisenia fetida*; NOEC 50 mg ac/kg dry soil, *Hypoaspis aculeifer*). It is noted that the laboratory tests were conducted in artificial soils containing 20% clay, which may not represent realistic worst-case exposure systems (i.e. compared to soils with lower capacity to adsorb and deactivate diquat). It is also noted that effects on earthworm numbers and weight were observed under representative field conditions after one year; however, no differences were observed for several years thereafter.

Following long-term exposure to the metabolite TOPPS, reduced reproduction and biomass of earthworms were observed at soil concentrations as low as 160 mg/kg dry soil (NOEC 80 mg ac/kg dry soil, *Eisenia fetida*), and reduced reproduction of collembolans was observed at concentrations as low as 259 mg/kg dry soil (NOEC 144 mg/kg dry soil, *Folsomia candida*). No adverse effects were observed on soil mites at the highest tested soil concentration (NOEC 320 mg/kg dry soil, *Hypoaspis aculeifer*).

Diquat did not adversely affect soil processes such as nitrification at soil concentrations up to 500 mg ac/kg dry soil. Similarly, a litter-bag study showed that exaggerated soil concentrations have no functional impairment on the soil organisms contributing to organic matter breakdown.

A representative SL formulation of diquat had low toxicity to non-target terrestrial plants following pre-emergent exposure to soil residues under laboratory conditions (lowest ER₂₅ 25 kg ac/ha, *Zea mays*). However, because diquat is a non-selective contact herbicide, foliar exposure is the exposure route of greatest concern. Under laboratory conditions, cabbage was the most sensitive species following foliar exposure (ER₅₀ 15 g ac/ha, *Brassica oleracea*). Under field conditions, a natural stand of yellow nutsedge was the most sensitive based on visual injury

(ER₅₀ 35 g ac/ha, *Cyperus esculentus*); sunflower was the next most sensitive species based on dry weight (ER₅₀ 50 g ac/ha, *Helianthus annuus*).

Noting dicots are more sensitive than monocots, an SSD analysis was performed on the post-emergent ER_{50} values for the 10 dicotyledonous species (Table 28). An HR_5 of 12 g ac/ha was derived, which is lower than the lowest ER_{50} value. As such, 12 g ac/ha was set as the RAL for the protection of vegetation areas.

The 3-hour EC₅₀ of diquat on activated sewage sludge was >220 mg ac/L (Clarke 2009).

In terms of endocrine disrupting properties of diquat, there is strong evidence for adverse in vivo effects on sexually reproducing molluscs, but the effects were not necessarily caused by endocrine disruption. Results in remaining non-mammalian species are largely equivocal. No targeted studies were available to mechanistically understand the reproductive toxicity to non-mammalian species; therefore, it is not possible to assess whether any observed effects were endocrine-mediated. Therefore, no firm conclusion can be drawn regarding endocrine effects of diquat.

The regulatory acceptable levels for the environmental risk assessment are proposed in the table below. The RAL values for the spray drift assessment are 2.1 μ g ac/L for the protection of natural aquatic areas, 17,500 g ac/ha for the protection of pollinator areas, and 12 g ac/ha for the protection of vegetation areas.

Species	Exposure days	Measured EC ₅₀	Adjusted EC ₅₀	Notes
Navicula pelliculosa	3 d	0.0012 mg ac/L	0.0051 mg ac/L	
Nitzschia palea	4 d	0.0052 mg ac/L	0.029 mg ac/L	
Raphidocelis subcapitata	4 d	0.0055 mg ac/L	0.031 mg ac/L	
Achnanthidium minutissimum	4 d	0.0073 mg ac/L	0.041 mg ac/L	
Lemna gibba	14 d	0.0032 mg ac/L	0.062 mg ac/L	
Anabaena flos-aquae	3 d	0.025 mg ac/L	0.11 mg ac/L	
Pseudanabaena foetida	4 d	0.23 mg ac/L	1.3 mg ac/L	
Synechococcus leopoliensis	4 d	0.29 mg ac/L	1.6 mg ac/L	
Fistulifera pelliculosa	4 d	0.33 mg ac/L	1.8 mg ac/L	
Desmodesmus subspicatus	4 d	3.2 mg ac/L	18 mg ac/L	
Skeletonema costatum	3 d	12 mg ac/L	51 mg ac/L	
	HC ₅	0.00030 mg ac/L	0.0021 mg ac/L	(11 species)
		(95% CI 0.000046-0.00020)	(95% CI 0.00038-0.011)	

Table 27: Toxicity endpoints for aquatic primary producers used in SSD analysis

Endpoints from Table 61 in Appendix B have been adjusted to account for rapid dissipation from the water column under natural conditions (adjusted EC_{50} = measured EC_{50} / (1–EXP (exposure days * (-ln(2)/DT₅₀ 0.5 days))) * (exposure days * ln(2)/DT₅₀ 0.5 days)

Table 28: Post-emergent toxicity endpoints for dicots used in SSD analysis based on data from laboratory and field studies

Species	ER25	ER 50	Note
Brassica oleracea	7.3 g ac/ha	15 g ac/ha	
Beta vulgaris	9.6 g ac/ha	38 g ac/ha	
Helianthus annuus	19 g ac/ha	53 g ac/ha	(Geomean of 3 studies)
Daucus carota	25 g ac/ha	53 g ac/ha	
Gossypium hirsutum	12 g ac/ha	55 g ac/ha	
Brassica napus	17 g ac/ha	57 g ac/ha	
Glycine max	37 g ac/ha	138 g ac/ha	(Geomean of 3studies)
Pinus strobes	74 g ac/ha	150 g ac/ha	
Pinus elliottii	19 g ac/ha	293 g ac/ha	
Phaseolus vulgaris	293 g ac/ha	884 g ac/ha	
HR₅	3.2 g ac/ha	12 g ac/ha	(10 species)
	(95% CI 1.0-9.9)	(95% CI 5.5–26)	

Table 29: Regulatory acceptable levels for non-target species

Group	Exposure	Endpoint	AF	RAL	Reference
Mammals	Acute	LD_{50} 120 mg/kg bw	10	12 mg/kg bw	Rittenhouse 1979
	Chronic	NOAEL 4.0 mg/kg bw/d	1	4.0 mg/kg bw/d	Hodge 1990
Birds	Acute	LD_{50} 70 mg/kg bw	10	7.0 mg/kg bw	Fink et al. 1982, Hubbard 2013, Roberts & Fairley 1980
	Chronic	NOEL 3.2 mg/kg bw/d	1	3.2 mg/kg bw/d	Temple et al. 2004a, 2004b
Aquatic animals	Acute	LC50 468 µg/L*	1	47 µg/L	Bender 2006a
Aquatic primary producers	Chronic	HC₅ 2.1 μg/L*	1	2.1 µg/L	Magor & Shillabeer 2001, Nagai 2019, Smyth et al. 1998a, 1998b, 1998c
Sediment dwellers	Chronic	NOEC 11 mg/kg ds	1	11 mg/kg ds	Bradley 2013a
Adult bees	Acute contact	LD ₅₀ 105 µg/bee	2.5	42 µg/bee	Gough et al. 1987
	Acute oral	LD ₅₀ 22 µg/bee	2.5	8.8 µg/bee	Gough et al. 1987

Group	Exposure	Endpoint	AF	RAL	Reference
Foliar arthropods	Contact	LR ₅₀ 4.1 g/ha	1	4.1 g/ha	Austin & Elcock 1999b
Ground arthropods	Contact	ER ₅₀ >1000 g/ha	1	1000 g/ha	Beech 1997
Soil macro- organisms	Acute	LC_{50} 94 mg/kg ds	10	9.4 mg/kg ds	Bender 2006b
	Chronic	NOEC 9.4 mg/kg ds	1	9.4 mg/kg ds	Friedrich 2007b
Soil micro-organisms	Chronic	NOEC 500 mg/kg ds	1	500 mg/kg ds	Schultz 2007b
Terrestrial plants	Post-emergent	HR₅ 12 g ac/ha	1	12 g/ha	Bellet 1990b, Martin 2013, Porch & Krueger 1999

*Aquatic endpoints have been adjusted to account for rapid dissipation from the water column under natural conditions (adjusted endpoint = measured endpoint / (1-EXP (exposure days * (-In(2)/DT₅₀ 0.5 days))) * (exposure days * In(2)/DT₅₀ 0.5 days))) * (exposure days * In(2)/DT₅₀

Risks to non-target species

Terrestrial vertebrates

Direct dietary exposure of terrestrial vertebrates to diquat is considered negligible following application to aquatic areas. Therefore, risks to terrestrial vertebrates are acceptable for application in aquatic areas.

Direct dietary exposure is possible for uses of diquat as a pre-harvest crop desiccant or for general weed control in a wide range of situations. A full assessment for terrestrial vertebrates for the different use patterns is presented in <u>Appendix B</u>. Acceptable risks of diquat could only be concluded for general weed control in hops, lucerne, fallow (full disturbance only), and sugarcane (Table 30). Cotton desiccation is also supported at rates up to 352 g ac/ha, noting it is only registered for rates lower than this when applied in combination with paraquat. The following protection labelling is appropriate for the supported uses (including uses in aquatic areas).

Toxic to birds. However, the use of this product as directed is not expected to have adverse effects on birds.

The remaining uses are not supported unless application is restricted to one per season at the maximum supported rate(s) indicated in Table 30.

Diquat is not expected to bioaccumulate in biota based on its low octanol-water partition coefficient and low BCF in fish; therefore, a food chain assessment was not necessary.

Category	Situation	Rate range (g ac/ha)	Wild mammal assessment	Bird assessment	Max seasonal rate supported
Pre-harvest crop desiccation	Poppies	600–800	Not supported	Not supported	283 g ac/ha
	Potatoes, sweet potatoes	600–800	Acceptable risk Not supported		278 g ac/ha
	Oilseeds	300–600	Not supported Not supported		283 g ac/ha
	Cotton	400–600	Not supported	Acceptable risk	352 g ac/ha
	Sunflower	400–600	Not supported Not supported		323 g ac/ha
	Cereals, rice, sugarcane	400–600	Not supported Not supported		54 g ac/ha
	Lupins. lucerne, pulses	300–600	Not supported Not supported		278 g ac/ha
General weed control	Row crops, vegetables, market gardens	280-800	Acceptable risk Acceptable up to 283 g ac/ha		283 g ac/ha
	Wheat and oats	110–140	Acceptable risk Acceptable up to 122 g ac/ha		122 g ac/ha
	Oilseeds	60–300	Acceptable risk Acceptable up to 283 g ac/ha		283 g ac/ha
	Hops	140–280	Acceptable risk	Acceptable risk	-
	Lucerne	70–140	Acceptable up to 88 g ac/ha	Acceptable up to 230 g ac/ha	88 g ac/ha
	Infested areas	560	Not supported	Not supported	88 g ac/ha
	Pasture	70–300	Acceptable up to 88 g ac/ha	Acceptable up to 230 g ac/ha	88 g ac/ha
	Orchards	300	Not supported	Not supported	88 g ac/ha
	Vineyards	300	Not supported	Not supported	88 g ac/ha

Table 30: Summary of risk assessment outcomes for terrestrial vertebrates

Category	Situation	Rate range (g ac/ha)	Wild mammal assessment	Bird assessment	Max seasonal rate supported
Combination products containing	Fallow (minimal disturbance)	138–368	Acceptable risk	Acceptable up to 283 g ac/ha	283 g ac/ha
paraquat	Bananas, duboisia, market gardens, nurseries, potatoes, rice, vegetables	276–368	Acceptable risk	Acceptable up to 283 g ac/ha24	283 g ac/ha
	Fallow (full disturbance)	69–368	Acceptable risk	Acceptable up to 283 g ac/ha	283 g ac/ha
	Lucerne	184–276	Not supported	Not supported	88 g ac/ha
	Sugarcane	138–368	Acceptable risk	Acceptable up to 283 g ac/ha	283 g ac/ha
	Public service areas, rights of way, pasture	276–368	Not supported	Not supported	88 g ac/ha
	Spray topping in grasses	92–173	Not supported	Not supported	88 g ac/ha
	Forests, orchards, plantations	184–368	Not supported	Not supported	88 g ac/ha
	Spot application in avocado, custard apples, lychees, mangos ²⁵	276	Not supported	Acceptable risk	220 g ac/ha
	Vineyards	368	Not supported	Not supported	88 g ac/ha
	Cotton desiccant	138–184	Acceptable risk	Acceptable risk	-

 ²⁴ Spot spray acceptable in duboisia up to maximum rate of 368 g ac/ha
 ²⁵ Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard; maximum supported rate in this instance is specific to spot application

Aquatic species

As indicated in Table 29 the RAL for the spray drift assessment is 2.1 µg ac/L for the protection of natural aquatic areas. Risks of spray drift are addressed separately, as needed.

For uses in aquatic areas, the risk assessment considered direct treatment of a shallow aquatic habitat. For acceptable risk, there must be no concerns identified for aquatic animals (RAL 47 µg ac/L) under this scenario. Acceptable risks of diquat could not be concluded for water injection at 1.0 mg ac/L or spray applications at rates as low as 1,000 g ac/ha (Table 31). An even lower spray rate is registered when used in combination with Agral Spray Adjuvant (product no. 54116); however, this adjuvant contains ethoxylated nonylphenol which is considered to be harmful to aquatic life and should not be used in aquatic situations (Brooke 1993, ECHA 2014, Lussier et al. 2000). Therefore, use of diquat products in aquatic areas is no longer supported.

For terrestrial uses, a runoff assessment according to APVMA's method to refine estimates of pesticide runoff to waterways²⁶ considered the lowest RAL values of 2.1 μ g ac/L and 11 mg ac/kg dry sediment and assumed a runoff event occurs 3 days after the last application. Because the assessment assumes that a runoff event occurs 3 days after application, the following restraints are recommended for the supported uses.

DO NOT apply if heavy rains or storms are forecast within 3 days.

DO NOT irrigate to the point of field runoff for at least 3 days after application.

The Tier 1 (screening) level of assessment is a worst-case scenario where slope is fixed at 8%, which is considered protective of 95% of agricultural activities in Australia. The rainfall value is set at 8 mm, with results in the maximum receiving water concentration using the standard water body of 1 ha and 15 cm initial depth when the worst-case Australian soil profile is used; the catchment is 10 ha. Further, for this worst-case scenario, a fallow/bare soil runoff profile is assessed.

Acceptable risks could be concluded at the screening level for soils that contain >10% clay (Table 33). For sand soils containing \leq 10% soil, the maximum supported annual peak soil concentration is 3.3 mg ac/kg dry soil²⁷ at the screening level, which is equivalent to an annual rate of 560 g ac/ha over 20 years. As such, the uses supported by the terrestrial vertebrate assessment which are applied at annual rates up to 280 g ac/ha have acceptable runoff risks for all soil types.

²⁶ See Appendix B, Attachments 1 and 2 of <u>https://apvma.gov.au/node/46416</u>

²⁷ Back-calculated from 2480 g ac/ha and soil depth of 5-cm (2480/750)

Table 31: Assessment of risks to non-target aquatic species for aquatic use situations

Scenario	PEC	RAL	RQ
Water injection	1,000 µg ac/L	47 µg ac/L	21
One surface spray application (lowest rate)	167 µg ac/L	47 µg ac/L	3.5

Water injection PEC is based on target concentration of 1.0 mg ac/L

Surface spray application is based on 250 g ac/ha across whole pond (25% of 1000 g ac/ha) and 15-cm water depth

RAL = regulatory acceptable level for aquatic animals (from Table 29)

RQ = risk quotient = PEC / RAL, where acceptable RQ \leq 1

Table 32: Soil exposure estimates

Category	Situation	Application rate & frequency	Foliar interception fraction	Peak annual soil concentration (mg/kg)	Steady state soil concentration (mg/kg)
Pre-harvest crop	Poppies	1× 800 g ac/ha	0.70	1.4	1.1
desiccation	Potatoes	1× 800 g ac/ha	0.80	1.0	0.74
	Cotton, sunflower	1× 600 g ac/ha	0.75	0.89	0.69
	Cereals, lupins, oilseeds, rice, sugarcane	1× 600 g ac/ha	0.80	0.71	0.55
	Lucerne, pulses	1× 600 g ac/ha	0.85	0.53	0.41
General weed control	Row crops, vegetables, market gardens	1× 800 g ac/ha	0	4.7	3.7
	Cereals	1× 600 g ac/ha	0	3.6	2.8
	Oilseeds, orchards, vineyards	1× 300 g ac/ha	0	1.8	1.4
	Hops	1× 280 g ac/ha	0	1.6	1.3
	Lucerne	1× 140 g ac/ha	0	0.83	0.64
	Pasture, infested areas	1× 560 g ac/ha	0.90	0.33	0.26
Combination products containing	Fallow (minimal disturbance)	2× 368 g ac/ha 7d interval	0	4.4	3.4

Category	Situation	Application rate & frequency	Foliar interception fraction	Peak annual soil concentration (mg/kg)	Steady state soil concentration (mg/kg)
paraquat and diquat	Bananas, duboisia, forests, industrial vegetation management, market gardens, nurseries, orchards, plantations, potatoes, rice, vegetables, vineyards	1× 368 g ac/ha	0	2.2	1.7
	Fallow (full disturbance), lucerne	1× 276 g ac/ha	0	1.6	1.3
	Sugarcane	1× 230 g ac/ha	0	1.4	1.1
	Spot application in avocado, custard apples, lychees, mangos ²⁸	2x 276 g ac/ha 14d interval	0	1.3	1.0
	Cotton desiccant	1× 184 g ac/ha	0.75	0.27	0.21
	Pasture	1× 368 g ac/ha	0.90	0.22	0.17

Risk assessment scenarios as described in Table 25; foliar interception values are based on EFSA (2020) defaults for similar situations; soil exposure estimates based on indicated application rate and frequency applied annually for 20 years with indicated interception and soil DT_{50} 1,000 d.

Table 33: Assessment of runoff risks to aquatic species for terrestrial use situations

Parameter		Worst-case scenario	Max supported	
		Non-sands (clay >10%)	Sands (clay ≤10%)	Sands (clay ≤10%)
Soil				
Exposure rate	(g/ha)	3,525	3,525	2,480
Soil DT ₅₀	(d)	1,000	1,000	1,000

²⁸ Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard

Parameter		Worst-case scenario	Max supported	
		Non-sands (clay >10%)	Sands (clay ≤10%)	Sands (clay ≤10%)
Kf	(L/kg)	11,298	2,932	2,932
Rainfall-P	(mm)	8.00	8.00	8.00
Runoff–Q	(mm)	1.34	1.34	1.34
Cr _{soil surface}	(fraction)	0.000088	0.00034	0.00034
slope factor-F	(fraction)	0.26	0.26	0.26
Runoff	(% applied)	0.00038	0.0015	0.0015
Water				
PEC	(µg/L)	0.083	0.32	0.22
RAL	(µg/L)	2.1	2.1	2.1
Risk quotient	(fraction)	0.04	0.15	0.11
Sediment				
PEC	(mg/kg)	4.3	16	12
RAL	(mg/kg)	11	11	11
Risk quotient	(fraction)	0.39	1.5	1.0

Worst-case scenario based on 1×800 g ac/ha applied annually for 20 years with no interception and indicated soil DT₅₀ Exposure rate is back-calculated from maximum predicted annual peak concentration in top 5-cm for worst-case scenario (4.7 mg ac/kg dry soil for general weed control in row crops, vegetables, and market gardens from Table 32)

Soil DT₅₀ and Kf from Table 55

Rainfall P value is default for Tier 1

 $\begin{aligned} & \mathsf{Runoff}\ Q\ \mathsf{value} = (((-0.000196^*(\mathsf{rain}^3)) + (0.0232^*(\mathsf{rain}^2))) + (-0.00520^*\mathsf{rain}));\ \mathsf{runoff}\ \mathsf{curve}\ \mathsf{for}\ \mathsf{worst-case}\ \mathsf{Australian}\ \mathsf{soil}\ \mathsf{profile}\ \mathsf{Cr}_{\mathsf{soil}\ \mathsf{surface}} = \mathsf{EXP}(-3^*\mathsf{In}(2)/\mathsf{DT}_{\mathsf{50soil}})^*(1/(1+\mathsf{Kf})) \end{aligned}$

Slope factor F = (0.02153 * slope + 0.001423 * slope²), where default screening level slope is 8%

Runoff (% applied) = Q/P * F * $Cr_{soil surface}$ * 0.5

PEC (water) = application rate * %runoff/100 * 10/(1500+134) *1000

PEC (sediment) = PEC (water) * (0.8+(0.2*Kf/1000*2400))/1280, where Kf is 136759 (from Table 26)

RAL = regulatory acceptable level (from Table 29)

RQ = risk quotient = PEC/RAL, where acceptable RQ \leq 1

Bees

Exposure of bees is expected to be negligible for water injection in aquatic areas. Therefore, risks to bees are acceptable for this use pattern.

For spray applications, risks to bees foraging in treated areas are assessed using a tiered approach. A screening level risk assessment assumes the worst-case scenario of a direct overspray of blooming plants that are frequented by bees in order to identify those substances and associated uses that do not pose a risk. Risks of exposure to foliar residues (contact exposure) were acceptable at the highest application rate of 2,000 g ac/ha; however, acceptable risks of oral exposure (via pollen and nectar) to foraging bees could only be concluded at rates up to 300 g ac/ha. To mitigate risks of oral exposure, the following protection statement is advised for all spray uses of diquat products where rates exceed 300 g ac/ha.

Harmful to bees. DO NOT apply to flowering weeds or crops at rates exceeding [300 g ac/ha]. DO NOT allow spray drift to flowering weeds or crops in the vicinity of the treatment area. Before spraying, notify beekeepers to move hives to a safe location with an untreated source of nectar and pollen, if there is potential for managed hives to be affected by the spray or spray drift.

Life stage	Scenario	Exposure	Rate (g/ha)	Predicted total dose (µg/bee)	RAL (µg/bee)	RQ
Adults	Aquatic areas (surface spray)	Acute contact	2 000	4.8	42	0.11
		Acute oral	2 000	57	8.8	6.5
	Desiccation or general weed control	Acute oral	800	23	8.8	2.6
			600	17	8.8	2.0
			560	16	8.8	1.8
		_	368	11	8.8	1.2
			300	8.6	8.8	0.98

Table 34: Screening level assessment of risks to bees

Predicted total dose calculated using USEPA BeeREX tool for adult worker bee foraging for nectar and larval drone within the hive

RAL = regulatory acceptable level (from Table 29)

RQ = risk quotient = PEC / RAL, where acceptable RQ ≤1

Other arthropod species

Exposure of other terrestrial arthropods species to diquat is considered negligible following application to aquatic areas. Therefore, risks of diquat to other terrestrial arthropods are acceptable for aquatic use situations.

Commercial use of predatory or parasitic arthropods in integrated pest management programs can occur in a wide range of agricultural industries. For broad-spectrum herbicides such as diquat, exposure of natural populations of arthropod species that are beneficial to agricultural systems is also possible. The risk assessment assumes that arthropods are exposed to fresh-dried residues within the treatment area immediately after the last application. Risks to ground-dwelling arthropods are acceptable for all desiccation and general weed control scenarios; however, acceptable risks to foliar-dwelling arthropods could not be concluded for any of these scenarios. Therefore, the following protection statement is advised for products used for pre-harvest crop desiccation or general weed control.

Toxic to beneficial foliar arthropods. Not compatible with integrated pest management (IPM) programs utilising beneficial foliar arthropods. Minimise spray drift to reduce harmful effects on beneficial foliar arthropods in non-crop areas.

Scenario	Group	Exposure	Rate (g/ha)	RAL (g/ha)	RQ
Worst-case (1× 800 g ac/ha)	Foliar arthropods	Contact	800	4.1	195
	Ground arthropods	Contact	800	1 000	0.80
Best-case (1× 140 g ac/ha)	Foliar arthropods	Contact	140	4.1	34
	Ground arthropods	Contact	140	1 000	0.14

Table 35: Assessment of risks to other non-target arthropods

RAL = regulatory acceptable level (from Table 29)

RQ = risk quotient = PEC / RAL, where acceptable RQ \leq 1

Soil organisms

Exposure of soil organisms to diquat is considered negligible following application to aquatic areas. Therefore, risks of diquat to soil organisms are acceptable for aquatic use situations.

For desiccation and general weed control uses, the risk assessment assumes soil organisms are exposed to accumulated residues in the top 5 cm after 20 years of use. Assuming annual use at the highest rate of 800 g ac/ha with no foliar interception, the peak concentration was predicted to be 4.7 mg ac/kg dry soil (acute exposure scenario), while the steady state concentration was predicted to be 3.7 mg ac/kg dry soil (chronic exposure scenario). Risks to soil organisms were determined to be acceptable under this worst-case scenario (Table 36), and no protection statements are therefore required.

Group	Exposure	Annual rate (g/ha)	PEC (mg/kg dry soil)	RAL (mg/kg dry soil)	RQ
Macro-organisms	Acute	800	4.7	9.4	0.50
	Chronic	800	3.7	9.4	0.39
Micro-organisms	Chronic	800	3.7	500	0.01

Table 36: Screening level assessment of risks to soil organisms (worst-case scenario)

Worst-case scenario based on 1× 800 g ac/ha applied annually for 20 years with no interception and soil DT $_{\rm 50}$ 1000 d

Acute PEC is based on maximum predicted annual peak concentration in top 5-cm

Chronic PEC is based on steady state concentration predicted in top 5-cm

RAL = regulatory acceptable level (from Table 29)

RQ = risk quotient = PEC / RAC, where acceptable RQ \leq 1

Non-target terrestrial plants

As indicated in Table 29, the RAL for the spray drift assessment is 12 g ac/ha for the protection of vegetation areas. Risks of spray drift are addressed separately, as needed.

Combination toxicity

Assessment scenarios

In a separate assessment, the risks of paraquat were determined to be acceptable at a maximum rate of 179 g ac/ha as a cotton desiccant and 231 g ac/ha in fallow and sugarcane situations. For the combination products containing 115 g/L diquat and 135 g/L paraquat, these correspond to rates of 1.3 L/ha and 1.7 L/ha, respectively. Risks of diquat were also determined to be acceptable at these rates. For the lower rates of the combination products in these situations (starting from 600 mL/ha in some fallow situations), risks of combination toxicity to non-target species have also been assessed.

Crop/situation	Product rate range (L/ha)	Diquat rate range (g ac/ha)	Paraquat rate range (g ac/ha)	Total actives rate range (g acs/ha)
Desiccant to aid harvest in cotton	1.2 to 1.3	138 to 150	162 to 176	300 to 325
As an aid to cultivation in fallow (full disturbance)	0.6 to 1.7	69 to 196	81 to 230	150 to 425
As an aid to cultivation in fallow (minimum disturbance)	0.8 to 1.7	92 to 196	108 to 230	200 to 425
Crop/situation	Product rate range (L/ha)	Diquat rate range (g ac/ha)	Paraquat rate range (g ac/ha)	Total actives rate range (g acs/ha)
--	------------------------------	--------------------------------	-------------------------------------	---
As an aid in establishing sugarcane or controlling weeds in a fallow prior to sugarcane	1.2 to 1.7	138 to 196	162 to 230	300 to 425
As an aid in post-harvest weed control in fallow (minimum disturbance)	1.6 to 1.7	184 to 196	216 to 230	400 to 425
Sugarcane plant and ratoon	1.6 to 1.7	184 to 196	216 to 230	400 to 425

Effects on non-target species

A representative combination product containing 115 g/L diquat and 135 g/L paraquat had moderate toxicity to rats (LD₅₀ 119 mg acs/kg bw, *Rattus norvegicus*). No data are available on the toxicity of a representative combination product containing 115 g/L diquat and 136 g/L paraquat to any other non-target species. Therefore, combination toxicity to non-target species was estimated assuming additive toxicity of the active constituents. All combination toxicity endpoints are expressed in terms of total active constituents (acs). Please refer to Table 68 through to Table 73 in <u>Appendix B</u> for all predicted combination toxicity values for non-target species. For further details on the estimation method, please refer to the <u>APVMA Risk Assessment Manual – Environment</u>.

Based on available data, the diquat/paraquat combination products were predicted to have high toxicity to mammals (geomean LD₅₀ 76 mg acs/kg bw, 4 mammal species) and birds (geomean LD₅₀ 4.2 mg acs/kg bw, 2 bird species). Therefore, the following hazard statement is required on diquat/paraquat combination product labels (followed by an appropriate risk management statement).

Toxic to birds and native mammals.

In aquatic systems, diquat and paraquat dissipate quickly from the water column under natural conditions due to rapid adsorption to sediment and suspended particulates; therefore, the aquatic endpoints were first adjusted to account for their expected dissipation under natural conditions prior to deriving the combination toxicity estimates. Although field data on diquat suggest a more rapid half-life, the more conservative water DT_{50} of 7.0 days for paraquat has been utilised for both chemicals to avoid artificially skewing the relative toxicity contributions toward paraquat.

After considering the exposure periods for each of the aquatic endpoints and rapid dissipation under natural conditions, the diquat/paraquat combination products were predicted to have moderate toxicity to fish (LC_{50} 1.7 mg acs/L for most sensitive species) and aquatic invertebrates (lowest LC_{50} 0.15 mg acs/L, *Hyalella azteca*), and high toxicity to primary producers (geomean E_rC_{50} 0.0066 mg acs/L, 3 algal and 2 aquatic plant species). Therefore, the following protection statement is required on diquat/paraquat combination product labels.

Very toxic to aquatic life. DO NOT contamination wetlands or watercourses with this product or used containers.

Based on available data, the diquat/paraquat combination products were predicted to have moderate toxicity to bees by contact exposure (LD_{50} 26 µg acs/bee, *Apis mellifera*) and oral exposure (LD_{50} 16 µg acs/bee, *Apis mellifera*). For the protection of pollinator areas, the RAL for the spray drift assessment is 4,333 g acs/ha based on the predicted contact LD_{50} 26 µg acs/bee and a conversion factor of LOC 0.4 / ExpE 2.4 * 1,000 as per the APVMA's Spray drift risk assessment manual (SDRAM).

Based on the available data, the LR₅₀ values for the indicator species of predatory arthropods (predatory mite *Typhlodromus pyri*) were predicted to be 2.3 g acs/ha (tier 1) and 5.6 g acs/ha (tier 2). Insufficient data were available on the indicator species of parasitic arthropod (parasitic wasp *Aphidius rhopalosiphi*) to estimate combination toxicity. The diquat/paraquat combination products were not expected to be toxic to ground arthropods such as rain beetles (*Pterostichus melanarius*), wolf spiders (*Pardosa* sp.), and rove beetles (*Aleochara bilineata*).

Based on available data, any toxicity to soil macro-organisms such as earthworms would be attributed to diquat. The diquat/paraquat combination products are not expected to adversely influence soil processes such as nitrification.

Because both diquat and paraquat have low toxicity to non-target terrestrial plants following pre-emergent exposure (seedling emergence tests), only post-emergent exposure data (vegetative vigour tests) were considered. Based on available data, predicted ER₅₀ values following post-emergent exposure ranged 19 g acs/ha for the most sensitive species (cabbage or rough cocklebur) to 224 g acs/ha for soybean. An SSD analysis was performed on the post-emergent ER₅₀ values for 7 non-target terrestrial plant species. An HR₅ of 18 g acs/ha was derived (Table 38), which is lower than the lowest ER₅₀ value. As such, 18 g acs/ha was selected as the RAL for the protection of vegetation areas.

The regulatory acceptable levels for the environmental risk assessment are proposed in Table 39, which are based on predicted toxicity values. The RAL values for the spray drift assessment are 0.66 µg acs/L for the protection of natural aquatic areas, 4,333 g acs/ha for the protection of pollinator areas, and 18 g acs/ha for the protection of vegetation areas.

Species Predicted ER₅₀ Sensitive species (Brassica oleracea/Xanthium strumarium) 19 g acs/ha Beta vulgaris 50 g acs/ha Lolium perenne 61 g acs/ha Brassica napus 88 g acs/ha Allium cepa 173 g acs/ha Zea mays 206 g acs/ha Glycine max 224 g acs/ha HR₅ 18 g acs/ha (95% CI 9.0-38)

Table 38: Diquat/paraquat combination products – Predicted toxicity endpoints for non-target terrestrial plants (post-emergent exposure) used in SSD analysis

Group	Exposure	Endpoint	AF	RAL
Mammals	Acute	LD ₅₀ 76 mg acs/kg bw	10	7.6 mg acs/kg bw
Birds	Acute	LD ₅₀ 42 mg acs/kg bw	10	4.2 mg acs/kg bw
Aquatic species	Acute	EC ₅₀ 6.6 μg acs/L*	10	0.66 µg acs/L
Adult bees	Contact	LD ₅₀ 26 µg acs/bee	2.5	10 µg acs/bee
	Oral	LD ₅₀ 16 µg acs/bee	2.5	6.4 µg acs/bee
Foliar arthropods	Contact	LR₅₀ 5.6 g acs/ha	1	5.6 g acs/ha
Ground arthropods	Contact	Not expected to be toxic		
Soil macro-organisms	Acute	Any toxicity would be attributed to	diquat	
Soil micro-organisms	Chronic	Not expected to be toxic		
Terrestrial plants	Post-emergent	HR₅ 18 g acs/ha	1	18 g acs/ha

Table 39: Diquat/paraquat combination products: regulatory acceptable levels for non-target species

*Aquatic endpoints have been adjusted to account for rapid dissipation from the water column under natural conditions (adjusted endpoint = measured endpoint / $(1-EXP (exposure days * (-ln(2)/DT_{50} 7.0 days))) * (exposure days * ln(2)/DT_{50} 7.0 days))$

Risks to non-target species

The risk assessment for combination products considers only short-term risks to non-target species following direct exposure to combined residues of the active constituents (diquat + paraquat cations) immediately after one application.

The assessment for terrestrial vertebrates assumes 100% of food items are obtained from the treatment area on the day of application. The use patterns were divided up into groups which consist of crops that have similar growing patterns (Table 40). Weed control largely occurs at the early growth stages of crops (or in fallow) and fall under a 'bare soil' scenario. Cotton desiccation occurs at the latest growth stage of the crop (BBCH \geq 90).

Risks to wild mammals were determined to be acceptable except for small herbivorous mammals in cotton desiccation situations. Risks were not acceptable at the lowest rate of 300 g ac/ha (1.2 L/ha) in this situation. The EFSA representative species in this group is a vole; Australian species at risk in this group might include a hopping mouse, native rat, possum, or bettong species.

When used for weed control, risks to birds were only acceptable at the lower rates in the registered range with granivorous birds being at greatest risk. The maximum supported rate was 175 g acs/ha (700 mL/ha) in this

situation. The EFSA representative species in this group is a finch which is relevant to Australia; additional Australian species in this group might include dove, button-quail, parrot, quail or pigeon species.

Risks of runoff of diquat and paraquat to aquatic species are considered separately and have been considered in their respective risk assessments. Both require the following restraints which also apply to the diquat/paraquat combination products.

DO NOT apply if heavy rains or storms are forecast within 3 days.

DO NOT irrigate to the point of field runoff for at least 3 days after application.

The assessment for bees assumes the worst-case scenario of a direct overspray of blooming plants that are frequented by bees in order to identify those substances and associated uses that do not pose a risk. Risks of exposure to foliar residues (contact exposure) were acceptable at the highest rate of 425 g acs/ha (1.7 L/ha); however, acceptable risks of oral exposure (via pollen and nectar) to foraging bees could only be concluded at rates up to 225 g ac/ha (900 mL/ha). To mitigate risks of oral exposure, the following protection statement is advised for any combination product containing 115 g/L diquat and 135 g/L paraquat where rates exceed 225 g acs/ha (900 mL/ha).

Harmful to bees. DO NOT apply to flowering weeds or crops at rates exceeding 900 mL/ha. DO NOT allow spray drift to flowering weeds or crops in the vicinity of the treatment area. Before spraying, notify beekeepers to move hives to a safe location with an untreated source of nectar and pollen, if there is potential for managed hives to be affected by the spray or spray drift.

The assessment for other arthropod species assumes that predatory and parasitic arthropods are exposed to fresh-dried residues within the treatment area immediately after application. The combination product is not expected to be toxic to ground arthropods; however, risks to foliar arthropods could not be concluded at the lowest rate (Table 13). Therefore, the following protection statement is advised for all combination products containing 115 g/L diquat and 135 g/L paraquat.

Toxic to beneficial arthropods. Not compatible with integrated pest management (IPM) programs utilising beneficial arthropods. Minimise spray drift to reduce harmful effects on beneficial arthropods in non-crop areas.

No protection statements are required for soil organisms to address risks of diquat or paraquat alone, as per their individual environmental assessments. When considering their combination (115 g/L diquat + 135 g/L paraquat), toxicity to soil macro-organisms such as earthworms would be attributed to diquat. The combination products are not expected to adversely affect soil processes such as nitrogen transformation and therefore risks are considered to be acceptable.

As indicated in the <u>Effects on non-target species</u> section, the RAL values for the spray drift assessment are 0.66 μ g acs/L for the protection of natural aquatic areas, 4,333 g acs/ha for the protection of pollinator areas, and 18 g acs/ha for the protection of vegetation areas. Risks of spray drift are addressed separately, as needed.

Table 40: Diquat/paraquat combination products: crop groups for terrestrial vertebrate assessment

EFSA 2009 crop group	Crop/situation	Application rates
Bare soil	As an aid to cultivation in fallow (full or minimum disturbance), as an aid in establishing sugarcane or controlling weeds in a fallow prior to sugarcane, as an aid in post-harvest weed control in fallow (minimum disturbance), sugarcane plant and ratoon	from 150 to 425 g acs/ha
Cotton	Dessicant to aid in harvest in cotton	from 300 to 325 g acs/ha

Risk assessment scenarios as described in Table 37; seasonal exposure rates based on indicated application rate, frequency and DT_{50}

Table 41: Diquat/paraquat combination products: acute risks to terrestrial vertebrates

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
Wild mamm	als (RAL 7.6 mg acs/	/kg bw)				
Bare soil	Small omnivore	BBCH <10	14.3	425	6.1	0.80
Cotton	Small herbivore	BBCH ≥50	34.1	300	10	1.3
	Small insectivore	BBCH ≥20	5.4	325	1.8	0.23
	Small omnivore	BBCH ≥50	4.3	325	1.4	0.18
Birds (RAL 4	.2 mg acs/kg bw)					
Bare soil	Small granivore	BBCH <10	24.7	200	4.9	1.2
				175	4.3	1.0
	Small omnivore	BBCH <10	17.4	275	4.8	1.1
				250	4.4	1.0
	Small insectivore	BBCH <10	10.9	425	4.6	1.1
				400	4.4	1.0
Cotton	Small omnivore	BBCH ≥50	4.4	325	1.4	0.34
	Small insectivore	BBCH ≥20	3.0	325	0.98	0.23

Crop groups as indicated in Table 9; generic focal species and shortcut values for indicated crop groups from EFSA (2009)

DDD = daily dietary dose (mg/kg bw/d) = shortcut value * rate (kg ac/ha)

RAL = regulatory acceptable level from Table 39

RQ = risk quotient = DDD/RAL, where acceptable RQ \leq 1

Table 42: Summary of risk assessment outcomes for risks of combination products containing 115 g/L diquat and 135 g/L paraquat to terrestrial vertebrates

Crop/situation	Product rate (L/ha)	Wild mammal assessment	Bird assessment	Max application rate supported
Desiccant to aid harvest in cotton	from 1.2 to 1.3 L/ha (300–325 g acs/ha)	Not supported	Acceptable risk	900 mL/ha (225 g acs/ha)
As an aid to cultivation in fallow (full disturbance)	from 0.6 to 1.7 L/ha (150–425 g acs/ha)	Acceptable risk	Acceptable up to 175 g acs/ha	700 mL/ha (175 g acs/ha)
As an aid to cultivation in fallow (minimum disturbance)	from 0.8 to 1.7 L/ha (200–425 g acs/ha)	Acceptable up to 225 g acs/ha	Not supported	700 mL/ha (175 g acs/ha)
As an aid in establishing sugarcane or controlling weeds in a fallow prior to sugarcane	from 1.2 to 1.7 L/ha (300–425 g acs/ha)	Not supported	Not supported	700 mL/ha (175 g acs/ha)
As an aid in post-harvest weed control in fallow (minimum disturbance)	from 1.6 to 1.7 L/ha (400–425 g acs/ha)	Not supported	Not supported	700 mL/ha (175 g acs/ha)
Sugarcane plant and ratoon	from 1.6 to 1.7 L/ha (400–425 g acs/ha)	Not supported	Not supported	700 mL/ha (175 g acs/ha)

Table 43: Screening level assessment of risks of combination products containing 115 g/L diquat and 135 g/L paraquat to bees

Life stage	Exposure	Rate (g/ha)	Predicted total dose (µg/bee)	RAL (µg/bee)	RQ
Adults	Acute contact	425	1.0	10	0.10
	Acute oral	425	12	6.4	1.9
		250	7.2	6.4	1.1
		225	6.4	6.4	1.0

Predicted total dose calculated using USEPA BeeREX tool for adult worker bee foraging for nectar and larval drone within the hive

RAL = regulatory acceptable level from Table 39

RQ = risk quotient = PEC / RAC, where acceptable RQ ≤1

Table 44: Assessment of risks to other non-target arthropods

Group	Exposure	Scenario	Rate (g acs/ha)	RAL (g acs/ha)	RQ
Foliar arthropods	Contact	Worst-case	425	5.6	76
		Best-case	150	5.6	27

RAL = regulatory acceptable level from Table 39

RQ = risk quotient = PEC / RAL, where acceptable RQ \leq 1

Recommendations

Uses supported from the viewpoint of environmental safety are listed in Table 45 with the required protection statements and restraints. Uses that are not supported from the viewpoint of environmental safety are listed in Table 46. These recommendations include consideration of the environmental risks of the diquat/paraquat combination products, as needed.

Table 45: Supported uses of diquat from the viewpoint of environmental safety

Situation	Protection statements and restraints
All supported situations	DO NOT apply if heavy rains or storms are forecast within 3 days. DO NOT irrigate to the point of field runoff for at least 3 days after application.
	Very toxic to aquatic life. DO NOT contaminate wetlands or watercourses with this product or used containers.
	Toxic to beneficial arthropods. Not compatible with integrated pest management (IPM) programs utilising beneficial arthropods. Minimise spray drift to reduce harmful effects on beneficial arthropods in non-crop areas.
General weed control in hops	Toxic to birds. However, the use of this product as directed is not expected to have adverse effects on birds.
General weed control in row crops, vegetables, market gardens, oilseeds at rates up to 283 g diquat/ha	
General weed control in wheat and oats at rates up to 122 g diquat/ha	
General weed control in pasture and lucerne up to 88 g diquat/ha	

Situation

Protection statements and restraints

Combination products containing 115 g/L diquat and 135 g/L paraquat as an aid to cultivation in fallow (full disturbance) up to 700 mL/ha

Toxic to birds and native mammals. However, the use of this product as directed is not expected to have adverse effects on birds and native mammals

Table 46: Uses of diquat not supported from the viewpoint of environmental safety

Situation	Basis
Use in aquatic areas	Unacceptable risk to non-target aquatic species
Pre-harvest crop desiccation in poppies, oilseeds, sunflower, cereals, rice, sugarcane, lupins, lucerne, pulses	Unacceptable risk to wild mammals and birds
General weed control in infested areas, orchards, and vineyards	
Combination products containing 115 g/L diquat and 135 g/L paraquat for general weed control in lucerne, public service areas, rights of way, pasture, spray topping in grasses, forests, orchards, plantations, vineyards, or sugarcane plant & ratoon; as an aid in establishing sugarcane or controlling weeds in a fallow prior to sugarcane; as an aid in post-harvest weed control in fallow (minimum disturbance)	
Pre-harvest crop desiccation in cotton (400–600 g diquat/ha)	Unacceptable risk to wild mammals
General weed control in pasture and lucerne at rates exceeding 88 g diquat/ha	
Spot application of combination products containing 115 g/L diquat and 135 g/L paraquat in avocado, custard apples, lychees, mangos	
Combination products containing 115 g/L diquat and 135 g/L paraquat as a desiccant to aid harvest in cotton	
Pre-harvest crop desiccation in potatoes	Unacceptable risk to birds
General weed control in row crops, vegetables, market gardens, and oilseeds at rates exceeding 283 g ac/ha	
General weed control in wheat and oats at rates exceeding 122 g ac/ha	

Situation	Basis
Combination products containing 115 g/L diquat and 135 g/L paraquat as an aid to cultivation in fallow (minimal disturbance)	_

Combination products containing 115 g/L diquat and 135 g/L paraquat as an aid to cultivation in fallow (full disturbance) at rates exceeding 700 mL/ha

Spray drift

The APVMA's approach to spray drift management set out in the <u>APVMA Spray Drift Policy, July 2019</u> specifies consideration of spray drift in bystander areas, livestock areas, natural aquatic areas, pollinator areas and vegetation areas. The regulatory acceptable levels (RALs) for each area are summarised in Table 47, which is the maximum amount of spray drift exposure that is not expected to cause undue harm to sensitive areas.

Area considered	Regulatory acceptable level
Natural aquatic areas	2.1 µg ac/L
Pollinator areas	17,500 g ac/ha
Vegetation areas	12 g ac/ha
Bystander areas	3.87 g ac/ha
Livestock areas	100 mg/kg

Table 47: Regulatory acceptable levels of diquat resulting from spray drift

The APVMA has only considered spray drift implications for uses of diquat that are supported by worker health and safety, residues, trade and environmental risk assessments.

The APVMA has also considered the spray drift risk resulting from combined toxicity of paraquat and diquat present in chemical products co-formulated with both active constituents. The regulatory acceptable levels of the co-formulated products, accounting for the combined toxicity of both paraquat and diquat are listed in Table 48.

Table 48: Regulatory acceptable levels of paraquat and diquat resulting from spray drift of chemical prod	ucts co-
formulated with both active constituents	

Area considered	Regulatory acceptable level
Natural aquatic areas	0.66 µg ac/L
Pollinator areas	4333 g ac/ha
Vegetation areas	18 g ac/ha
Bystander areas	4.49 g ac/ha
Livestock areas	17.8 mg/kg

Uses of products that contain both paraquat and diquat which are supported by worker health and safety, residues, trade and environmental risk assessments are limited to fallows establishment and aid to cultivation at rates up to 175 g combined active constituents (acs) per hectare (175 g acs/ha).

Based on the acceptable uses, the following spray drift restraints and downwind buffer zones would be required for application of diquat products at the rates listed below.

SPRAY DRIFT RESTRAINTS

Specific definitions for terms used in this section of the label can be found at apvma.gov.au/spraydrift

DO NOT allow bystanders to come into contact with the spray cloud.

DO NOT apply in a manner that may cause an unacceptable impact to native vegetation, agricultural crops, landscaped gardens and aquaculture production, or cause contamination of plant or livestock commodities, outside the application site from spray drift. The advisory buffer zones in the relevant buffer zone table/s below provide guidance but may not be sufficient in all situations. Wherever possible, correctly use application equipment designed to reduce spray drift and apply when the wind direction is away from these sensitive areas.

DO NOT apply unless the wind speed is between 3 and 20 kilometres per hour at the application site during the time of application.

DO NOT apply if there are surface temperature inversion conditions present at the application site during the time of application. These conditions exist most evenings one to 2 hours before sunset and persist until one to 2 hours after sunrise.

DO NOT apply by a boom sprayer unless the following requirements are met:

- Spray droplets not smaller than a MEDIUM spray droplet size category.
- Minimum distances between the application site and downwind sensitive areas (see 'Mandatory buffer zones' section of the following table titled 'Buffer zones for boom sprayers') are observed.

Diquat–buffer zones for boom sprayers (metres; MEDIUM droplet size)						
Application rate	Boom height above the target canopy	Bystander areas	Natural aquatic areas	Pollinator areas	Vegetation areas	Livestock areas
	0.5 m or lower	20	30	0	5	0
Up to 283 g ac/ha	1.0 m or lower	60	75	0	30	0
122 g ac/ha or	0.5 m or lower	0	10	0	0	0
lower	1.0 m or lower	30	40	0	15	0
	0.5 m or lower	0	10	0	0	0
oo g ac/na lower	1.0 m or lower	20	35	0	10	0

Table 49: Diquat – buffer zones for boom sprayers

DO NOT apply by a vertical sprayer.

DO NOT apply by aircraft unless the following requirements are met:

- Spray droplets not smaller than a MEDIUM spray droplet size category.

 For maximum release heights above the target canopy of 3m or 25% of wingspan or 25% of rotor diameter whichever is the greatest, minimum distances between the application site and downwind sensitive areas (see 'Mandatory buffer zones' section of the following table titled 'Buffer zones for aircraft') are observed.

Diquat-buffer zones for aircraft (metres; MEDIUM droplet size)					
Type of aircraft (rate)	Bystander areas	Natural aquatic areas	Pollinator areas	Vegetation areas	Livestock areas
Fixed-wing (283 g ac/ha)	275	350	0	120	0
Fixed-wing (122 g ac/ha)	140	170	0	65	0
Fixed-wing (88 g ac/ha)	110	140	0	50	0
Helicopter (283 g ac/ha)	180	220	0	90	0
Helicopter (122 g(ac/ha)	110	130	0	55	0
Helicopter (88 g ac/ha)	80	100	0	45	0

Table 50: Diquat – buffer zones for aircraft (metres; MEDIUM droplet size)

Table 51: Diquat/paraquat co-formulated product buffer zones for boom sprayers

Diquat-paraquat co-formulated chemical products – buffer zones for boom sprayers							
Application rate Boom height above the target canopy	Boom height		Mandatory downwind buffer zones (metres)				
	Bystander areas	Natural aquatic areas	Pollinator areas	Vegetation areas	Livestock areas		
175 g acc/ba	0.5 m or lower	5	45	0	0	0	
175 y acs/na	1.0 m or lower	35	120	0	15	0	
150 g acs/ha or	0.5 m or lower	5	40	0	0	0	
lower	1.0 m or lower	30	110	0	15	0	

Storage and disposal

Storage

Products containing only diquat require the following storage statement.

Store in the closed, original container in a cool, well-ventilated area. DO NOT store for prolonged periods in direct sunlight.

Schedule 7 Poisons require the following storage statement, including a direction to store the product in a locked room or place. The following storage statement is required for products containing both paraquat and diquat

Store in a locked room or place away from children, animals, food, feedstuffs, seed and fertilisers. Store in the closed, original container in a cool, well-ventilated area. DO NOT store for prolonged periods in direct sunlight.

Disposal

Disposal statements are matched against the specification of the product and container. As the worker health and safety advised that the products should only be used through closed mixing and loading, containers suitable for closed mixing and loading would require the following disposal instructions:

Empty contents fully into application equipment. Close all valves and return to [point of supply/designated collection point/other specific collection details] for refill or storage.



Appendix

Appendix A – Summary of assessment outcomes

Table 52: Risk assessment outcomes	for	products	containing	diquat
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Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
Cotton (short stapled varieties only)		Boomspray	not supported (environment, residues)
Dry Beans		Boomspray	not supported (environment, residues)
Dry Peas		Boomspray	not supported (environment)
Lentils		Boomspray	not supported (environment)
Chickpeas		Boomspray	not supported (environment)
Faba Beans		Boomspray	not supported (environment)
Linseed		Boomspray	not supported (environment)
Lupins		Boomspray	not supported (environment)
Mung beans		Boomspray	not supported (environment)
Perennial legume seed crops (Lucerne)	Pre-harvest crop desiccation	Boomspray	not supported (environment)
Perennial legume seed crops (Red clover)		Boomspray	not supported (environment)
Perennial legume seed crops (White clover)		Boomspray	not supported (environment)
Pigeon peas		Boomspray	not supported (environment)
Poppies		Boomspray	not supported (environment)
Potato (Haulm desiccation)		Boomspray	not supported (environment)
Potato (Ground stored-preharvest weed control)		Boomspray	not supported (environment)
Canola (Rape)		Boomspray	not supported (environment)
Rice		Boomspray	not supported (environment, residues)
Sorghum		Boomspray	not supported (environment, residues)

Сгор	Weeds controlled/use	Application method	Assessment outcome (risk area)
Soya Beans		Boomspray	not supported (environment)
Sugar Cane		Boomspray	not supported (environment, residues)
Sunflower		Boomspray	not supported (environment)
Sweet potatoes		Boomspray	not supported (environment)
Aquatic areas	Duck weeds, red azolla, water hyacinth, salvinia marsilea, water lillies, water lettuce	Boomspray	not supported (environment)
	Cattail and Pond Weeds	Injection below surface, Surface spray	not supported (environment)
Asparagus	Broadleaf weeds (prior to spear emergence)	Boomspray	not supported (residues, environment above 283 g ac/ha per season)
Hops	Annual broadleaf and grass weeds	Inter-row spray	supported
Infested areas	Cotton Thistle (Onopordum acanthium)	Spot spray	not supported (environment)
	Saffron Thistle	Spot spray, Boomspray	
Lucerne	Capeweed and Erodium spp.	Boomspray	supported up to 88 g ac/ha per season
Oil seed poppies	General weed control	Boomspray	supported up to 283 g ac/ha per season
Orchards (including bananas) and Vineyards: Citrus, Grapes, Pome fruit, Stone fruit, Tree nuts, Tropical fruit (edible peel), Tropical fruit (inedible peel, except pineapple)	Capeweed	Directed spray, inter-row spray, Butt spray	not supported (environment)
	Capeweed and Erodium spp. (Storksbill)		not supported (environment)
Pasture renovation and establishment	Barlet grass, brome grass, silver grass and sweet vernal grass	Boomspray	not supported (environment)
	Capeweed (very young seedling, 2-3 leaf stage		supported up to 88 g ac/ha per season

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
	only)		
Row crops, vegetables and market gardens (Berries and other small fruit (except grapes)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (Brassica vegetables: broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe-tsai)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (Brassica vegetables: other than broccoli, head cabbages, cauliflower and Chinese cabbage (type Pe-tsai)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Row crops, vegetables and market gardens (Bulb vegetables :bulb onions)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (Bulb vegetables: other than bulb onions)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Row crops, vegetables and market gardens (Fruiting Vegetables: cucurbits))	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Row crops, vegetables and market gardens(Fruiting Vegetables: other	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
than cucurbits)			
Row crops, vegetables and market gardens (Leafy vegetables)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (Legume vegetables)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (pineapple)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Row crops, vegetables and market gardens (Root and tuber vegetables)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	supported up to 283 g ac/ha per season (noting crop group change required by residues)
Row crops, vegetables and market gardens (Stalk and stem vegetables, including asparagus)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Row crops, vegetables and market gardens (herbs and spices)	Broadleaf weeds	Boomspray, handwand, inter- row spray (shielded)	not supported (residues, environment above 283 g ac/ha per season)
Wheat, Oats	Capeweed	Boomspray	supported up to 122 g ac/ha per season
Wheat	Pre-harvest weed control	Boomspray	not supported (environment)
Wheat	Suppression of wild radish (GS 10–12)	Boomspray	not supported (environment)
Winter Cereals (Barley, oats, rye, triticale and wheat)	Pre-harvest weed control	Boomspray	not supported (environment)

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
Aid to cultivation (Southern Australia–full disturbance) <u>Winter</u> Canola, Chickpeas, Wheat, Barley,	Seedling Grasses: Annual Ryegrass (Lolium rigidum), Barley Grass (Hordeum spp.), Brome Grass (Bromus spp.), Volunteer Cereals, Wild Oats (Avena spp.) (2-3 leaf)		
Oats, Rye, Triticale, Field Beans, Field Peas, Lentils, Linseed (Linola), Lupins, Vetch <u>Spring/Summer</u>		Boomspray	supported up to 175 g/ha of combined active constituents per season (700 mL of product/ha)
Fodder Rape, Pigeon Peas, Safflower, Sorghum, Soybeans, Sunflower	Vulpia (Silver Grass, Sand Fescue) <i>(Vulpia</i> <i>spp.)</i> (2-3 leaf)		producting
Pasture			
Clover Grass, Lucerne, Medics			
	Seedling Grasses: Annual Ryegrass (Lolium rigidum), Barley Grass (Hordeum spp.), Brome Grass (Bromus spp.), Volunteer Cereals, Wild Oats (Avena spp.)		
Aid to cultivation (Southern Australia– fallow/minimum disturbance)	Seedling Grasses: Annual Ryegrass (Lolium rigidum), Barley Grass (Hordeum spp.), Brome Grass (Bromus spp.), Volunteer Cereals, Wild Oats (Avena spp.)	Boomspray	not supported (environment)
	Vulpia (Silver Grass, Sand Fescue) <i>(Vulpia</i> <i>spp.)</i>		
	Seedling Brassica Weeds		
	Other Seedling Broadleaved Weeds		

Table 53: Risk assessment outcomes for products containing paraquat and diquat

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
	Deadnettle (Lamium amplexicaule), Fumitory (Fumitory spp.), Melilotus (Melilotus spp.), Pimpernel (Anagallis spp.), Poppy (Papaver spp.), Saffron Thistle (Carthmus lanatus), Sheepweed (Buglossoides arvensis)		
	Wireweed (Polygonum aviculare)		
	Marshmallow (Malva parviflora)		
	Volunteer Beans, Peas & Lupins		
	Medic (Medicago spp.), Sub-Clover (Trifolium subterraneum)		
	Sub-Clover (<i>Trifolium</i> subterraneum)–split application		
	Perennial Ryegrass (Lolium perenne)-split application		
	Most Annual Weeds- split application		
	Potato Weed (Heliotropium europaeum)		
	Seedling Grasses		
	Sorghum (Sorghum bicolour), Stink Grass (Eragrostis cilianensis)		
Aid to cultivation (Northern Australia–full disturbance)	Seedling Broadleaved Weeds	Boomspray	not supported (environment)
	Native Jute (Corchorus trilocularis)		
	Annual Ground Cherry (<i>Physalis angulata</i>), Turnip Weed (<i>Rapistrum</i> <i>rugosum</i>)		

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)
	Boggabri (Amaranthus mitchellii), Hexham Scent (Melilotus indicus), Wild Carrot (Daucus glochidiatus), Speedy Weed (Flaveria australasica)		
	Seedling Grasses		
	Seedling Broadleaved Weeds		
Aid to cultivation (Northern Australia– fallow/minimum	Volunteer Cotton (including Roundup® Ready Cotton) (Gossypium hirsulum)	Boomspray	not supported (environment)
disturbance)####	Boggabri (Amaranthus mitchellii), Hexham Scent (Melilotus indicus), Wild Carrot (Daucus glodcidiatus), Phyllanthus (Phyllanthus spp.)		
Aid in Post-Harvest weed control (Nothern Australia – after Winter Cereals)	Volunteer Barley (Hordeum vulgare), Volunteer Wheat (Triticum aestivum), Bladder Ketmia (Hibiscus trionum), Milk Thistle (Sonchus oleraceus), New Zealand Spinach (Tetragonia tetragonioides)	Boomspray	not supported (environment)
Sugarcane-	Seedling Grasses: (not regrowth or rhizomes) Barnyard Grass (<i>Echinochloa spp.</i>), Liverseed Grass (<i>Urochloa panicoides</i>), Stink Grass (<i>Eragrostis</i> <i>cilianensis</i>)	Boomspray	not supported (environment)
fallows prior to planting	Seedling Broadleaved Weed		not supported (environment)
	Seedling Phyllanthus (Phylanthus spp.)		not supported (environment)
	Mature grasses, broadleaf weeds and Phyllanthus (<i>Phylanthus</i>	Boomspray	not supported (environment)

Сгор	Weeds controlled/use	Application method	Assessment outcome (risk area)	
	spp.)			
	Most Seedling Broadleaf Weeds including Sicklepod (Senna (Cassia) obtusifolia), Bluetop (Ageratum houstonianum), Phyllanthus (Phyllanthus spp.), Calopo (Calapogonium muconoides)			
Sugarcane–plant and ratoon	Most Seedling Grasses including Awnless Barnyard Grass (Echinochloa colona), Summer Grass (Digitaria ciliaris),Guinea Grass (Panicum maximum),Hamil Grass (Panicum maximum cv Hamil),Green Summer Grass (Brachiaria miliiformis)	Boomspray or directed interrow spray	not supported (environment, residues [post-emergent boomspray])	
Cotton	Desiccant to aid harvest	Boomspray	not supported (environment, residues)	
Lucerne (established at least 1 year old)	Most annual weeds including Capeweed and Erodium. For improved grazing, hay or seed production or over sowing, enhanced control of some broadleaf weeds, and short term residual weed control.	Boomspray	not supported (environment)	
Public Service Areas, Rights-of- Way, Market Gardens and Nurseries, Orchards (including Bananas), Vineyards and Forests-ring weeding around trees with brown bark and strip spraying in Orchards and Vineyards	Most Annual Grasses and Broadleaved Weeds	High Volume or Power Sprayer	not supported (environment)	

Crop	Weeds controlled/use	Application method	Assessment outcome (risk area)	
Vegetable crops	Weed control prior to crop emergence-most Annual Grasses and Broadleaved Weeds	High Volume or Power Sprayer	not supported (environment)	
	General weed control– most Annual Grasses and Broadleaved Weeds	High Volume or Power Sprayer		
Potatoes	Weed destruction prior to digging–most Annual Grasses and Broadleaved Weeds	High Volume or Power Sprayer	not supported (environment)	
Avocados, Custard Apples, Lychees, Mangoes	Most Annual and Perennial Broadleaf Weeds and Grasses	High Volume or Power Sprayer	not supported (environment)	
	Annual Weeds including Barnyard Grass (on rice stubble after burning)			
Rice (pre-emergent use only)	Clover control	Boomspray	not supported (environment)	
	Annual Pasture-not properly managed			
Pasture (Kikuyu/paspalum)	To suppress growth to oversow winter feed	Boomspray	not supported (environment)	
Pasture (Established– Perennial Grass Crops, Cocksfoot, Perennial Ryegrass, Phalaris and Demeter Fescue)	Control of annual weeds including: capeweed and erodium for improved grazing, hay or seed production.	Boomspray	not supported (environment)	
Pasture (Improvement)	To increase the perennial grass and/or the sub-clover or white clover content	Boomspray	not supported (environment)	
Grasses (particularly Annual Ryegrass)	To control grass seed set (Spray Top technique)	Boomspray	not supported (environment)	
Duboisia		Direct spray	not supported (environment)	
υαροιδία		Spot Spray	not supported (environment)	
Tea Trees (Melaleuca alternifolia)	Grasses and broadleaf weeds	Boomspray	not supported (environment)	

Appendix B – Listing of environmental endpoints

Substance	Matrix	Result		Reference
Diquat	Insects	Beetles:	DT ₅₀ 2.2 d	Jutsum 2011
		Mixed:	DT ₅₀ 2.3 d	Edwards et al. 1991
		Geomean DT ₅₀ 2.2 d		
	Foliage	Lettuce:	DT ₅₀ 1.4 d	Kennedy 1984, Massey 1987(c)
		AT oilseed rape:	DT ₅₀ 1.7 d	Langridge 2011a
		n-FR oilseed rape:	DT ₅₀ 2.4 d	
		ES oilseed rape:	DT ₅₀ 1.7 d	Langridge 2011b
		IT oilseed rape:	DT ₅₀ 2.8 d	
		s-FR oilseed rape:	DT ₅₀ 3.0 d	
		Corn sowthistle:	DT ₅₀ 2.1 d	Edwards et al. 1991
		Sedges:	DT ₅₀ 1.8 d	
		Climbing false buckwheat:	DT ₅₀ 1.4 d	
		Reed canary grass:	DT ₅₀ 1.0 d	
		Geomean DT ₅₀ 1.8 d		
	Seeds	Sedges:	DT ₅₀ 17 d	Edwards et al. 1991
		Reed canary grass:	DT ₅₀ 10 d	
		Lentils:	DT ₅₀ 2.9 d	
		Geomean DT ₅₀ 7.9 d		

Table 55: Diquat – fate and behaviour in soil

Substance	Study	Result		Reference
Diquat	Soil photolysis	Moist soil:	DT ₅₀ 36 d	Dixon & Gilbert 2012a
		Dry soil:	DT ₅₀ 197 d	
		0.2% mineralisation	after 30 d	
		1.5% bound residue	es after 30 d	
Diquat	Soil photolysis	Moist soil: Dry soil: 0.2% mineralisation 1.5% bound residue	DT_{50} 36 d DT_{50} 197 d after 30 d es after 30 d	Dixon & Gilbert 2012a

Diquat Aerobic laboratory soil Sandy loam: stable Johnston 1988a Loam: DT ₅₀ 598 d Dixon 2012a Sandy clay loam: DT ₅₀ 2330 d Silty clay: DT ₅₀ 6174 d Sandy clay loam: DT ₅₀ 3516 d Mônego 2006a Clay: DT ₅₀ 290 d Sandy loam: DT ₅₀ 568 d Sandy clay loam: DT ₅₀ 568 d Mônego 2006a Clay: DT ₅₀ 568 d Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d < -5% mineralisation after 119-120 d 0.4-16% bound residues after 119-120 d Dixon 2012b	Substance	Study	Result				Reference
Diquat Aerobic laboratory soil Sandy loam: stable Johnston 1988a Loam: DT ₅₀ 598 d Dixon 2012a Sandy clay loam: DT ₅₀ 2330 d Silty clay: Silty clay: DT ₅₀ 6174 d Sandy clay loam: Sandy clay loam: DT ₅₀ 3516 d Mônego 2006a Clay: DT ₅₀ 290 d Sandy loam: DT ₅₀ 290 d Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d For 500 568 d Geomean DT ₅₀ 1108 d Anaerobic laboratory Loam: DT ₅₀ 1019 d Dixon 2012b			Max 9.9% TOPPS				
Loam: DT_{50} 598 d Dixon 2012a Sandy clay loam: DT_{50} 2330 d Silty clay: DT_{50} 6174 d Sandy clay loam: DT_{50} 3516 d Mônego 2006a Sandy clay loam: DT_{50} 976 d Mônego 2006a Clay: DT_{50} 976 d Sandy clay loam: Sandy loam: DT_{50} 468 d Sandy loam: Sandy loam: DT_{50} 568 d Geomean DT_{50} 1108 d <5% mineralisation after 119-120 d	Diquat	Aerobic laboratory soil	Sandy loam: stable				Johnston 1988a
Sandy clay loam: DT ₅₀ 2330 d Silty clay: DT ₅₀ 6174 d Sandy clay loam: DT ₅₀ 3516 d Sandy clay loam: DT ₅₀ 976 d Mônego 2006a Clay: DT ₅₀ 290 d Sand: DT ₅₀ 290 d Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d			Loam:	DT ₅₀ 5	598 d		Dixon 2012a
Silty clay: DT ₅₀ 6174 d Sandy clay loam: DT ₅₀ 3516 d Sandy clay loam: DT ₅₀ 976 d Mônego 2006a Clay: DT ₅₀ 290 d Sand: Sandy clay loam: DT ₅₀ 290 d For 468 d Sandy loam: DT ₅₀ 568 d Sandy loam: Geomean DT ₅₀ 1108 d			Sandy clay loam:	DT ₅₀ 2	2330 d		
Sandy clay loam: DT ₅₀ 3516 d Sandy clay loam: DT ₅₀ 976 d Mônego 2006a Clay: DT ₅₀ 290 d Sand: Sandy loam: DT ₅₀ 468 d Sandy loam: Sandy loam: DT ₅₀ 568 d Sandy loam: Geomean DT ₅₀ 1108 d			Silty clay:	DT ₅₀ 6	6174 d		
Sandy clay loam: DT ₅₀ 976 d Mônego 2006a Clay: DT ₅₀ 290 d Sand: Sand: DT ₅₀ 468 d Sandy loam: Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d - <5% mineralisation after 119-120 d			Sandy clay loam:	DT ₅₀ 3	3516 d		
Clay: DT_{50} 290 dSand: DT_{50} 468 dSandy loam: DT_{50} 568 dGeomean DT_{50} 1108 d<5% mineralisation after 119-120 d			Sandy clay loam:	DT ₅₀ 9	976 d		Mônego 2006a
Sand: DT ₅₀ 468 d Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d			Clay:	DT ₅₀ 2	290 d		
Sandy loam: DT ₅₀ 568 d Geomean DT ₅₀ 1108 d			Sand:	DT ₅₀ 4	468 d		
Geomean DT ₅₀ 1108 d <5% mineralisation after 119-120 d			Sandy loam:	DT ₅₀ 5	568 d		
<5% mineralisation after 119-120 d 0.4-16% bound residues after 119-120 d Anaerobic laboratory Loam: DT ₅₀ 1019 d Dixon 2012b			Geomean DT ₅₀ 11	08 d		_	
0.4-16% bound residues after 119-120 d Anaerobic laboratory Loam: DT ₅₀ 1019 d Dixon 2012b			<5% mineralisation after 119-120 d				
Anaerobic laboratory Loam: DT ₅₀ 1019 d Dixon 2012b			0.4-16% bound re	sidues a	fter 119-		
		Anaerobic laboratory	Loam: DT ₅₀ 1019 d				Dixon 2012b
Soli Sandy clay loam: DT ₅₀ 3642 d		SOII	Sandy clay loam: DT ₅₀ 3642 d				
Silty clay: DT ₅₀ 1431 d			Silty clay:	: DT ₅₀ 1431 d			
Sandy clay loam: DT ₅₀ 12743 d			Sandy clay loam: DT ₅₀ 12743 d				
Geomean DT ₅₀ 2868 d			Geomean DT ₅₀ 28	368 d			
<5% mineralisation after 120 d			<5% mineralisatio	n after 1	20 d		
0.4-9.5% bound residues after 120 d			0.4-9.5% bound re	esidues a	after 120		
Adsorption/ desorption Soil % clay Kf 1/n		Adsorption/ desorption	Soil	<u>% clay</u>	<u>Kf</u>	<u>1/n</u>	
Loam 12 144 0.59 Dixon & Gilbert 2012b			Loam	12	144	0.59	Dixon & Gilbert 2012b
Sandy clay loam 25 9011 0.89			Sandy clay loam	25	9011	0.89	
Silty clay 39 12932 0.93			Silty clay	39	12932	0.93	
Sandy loam 19 70308 1.06			Sandy loam	19	70308	1.06	
Sandy clay loam 46 507 0.56 Mônego 2005			Sandy clay loam	46	507	0.56	Mônego 2005
Clay 61 1519 0.69			Clay	61	1519	0.69	
Sand 10 910 0.68			Sand	10	910	0.68	
Sandy loam 21 484 0.59			Sandy loam	21	484	0.59	

Substance	Study	Result					Reference
		Sand		2	36	0.40	Pack 1987
		Sand		4	42	0.45	
		Sandy	clay loam	21	4895	0.94	
		Loam		9	10740	1.00	
		Sandy	loam	13	1882	0.75	
		Mean k	(f 2932 mL	./g, 1/n 0.	.63 for ≤	10% clay	_
		Mean k	(f 11298 m	nL/g, 1/n (0.78 for	>10% clay	
	Terrestrial field	UK	SAC-WB 5	50%:	DT ₅₀ 4	11 years	Cole et al. 1991, Dyson &
	dissipation	UK	SAC-WB 1	10%:	DT_{50} 11 years		Chapman 1995
		UK	SAC-WB 4	400%:	DT_{50} 14 years		
		USA	SAC-WB 5	50%:	DT ₅₀ 3	3.6 years	Dyson et al. 1995a, 1995b
		USA	SAC-WB 1	00%:	DT ₅₀ 3	3.0 years	
		USA	SAC-WB 2	200%:	DT ₅₀ 1	.2 years	
		USA	potato:stal	ble			Fujie 1991
TOPPS	Aerobic laboratory soil	Loam:		DT ₅₀ 28	d		Dixon & Dove 2012, Patterson
		Sandy clay loam: DT_{50} 750 d			0 d	2012	
		Silty cla	ay:	DT ₅₀ 15	9 d		
		Loam:		DT ₅₀ 75	7 d		
		Geomean DT ₅₀ 224 d					
TOPPS	Adsorption/ desorption	<u>Soil</u>		<u>%0C</u>	<u>Kf</u>	<u>1/n</u>	Dixon & Gilbert 2012c
		Loam		2.1	3.4	0.72	
		Sandy	clay loam	2.3	43	0.74	
		Silty cla	ау	0.8	52	0.54	
		Loam		1.5	207	0.56	
		Sandy	loam	2.5	430	0.57	
		Mean k	Vean Kf 147 mL/g, 1/n 0.63				

Table 56: Diquat – fate and behaviour in water and sediment

Substance	Study	Result	Reference
Diquat	Hydrolysis	pH 4, 50°C: stable pH 7, 50°C: stable	Dixon & Alderman 2012, White 2010b

Substance	Study	Result	Reference
		pH 9, 50°C: stable	
	Aqueous photolysis	DT_{50} 11 d (pH 7 buffer, mid-European spring sunlight)	Moffatt 1993
		DT_{50} 10 d (natural water, spring sunlight at 35°N)	Dean 2000
		DT ₅₀ 2.0 d (natural water, summer sunlight at 40°N) 3.8% mineralisation after 3d Max 23% TOPPS Max 12% AQ1	Oliver & Webb 2005
	Degradation in aerobic water/sediment	$\begin{array}{llllllllllllllllllllllllllllllllllll$	Ford et al. 2012
		BR fine water $DT_{50} 0.033 d$ BR coarse water $DT_{50} 0.046 d$	Mônego 2006b
		Florida system stable	Cranor & Daly 1988
		Geomean DT ₅₀ 0.12 d in water Geomean DT ₅₀ 1141 d in system	-
		Max 100% diquat in sediment 0.32% mineralisation after 90-100 d 1.4-2.8% bound residues after 90-100 d	-
	Degradation in anaerobic water/sediment	Cal Abbey water $DT_{50} 0.72 d$ Swiss L water $DT_{50} 0.85 d$ Geomean $DT_{50} 0.78 d$	Ford et al. 2012
		Cal Abbey system DT_{50} 2028 d Swiss L system DT_{50} 1794 d Geomean DT_{50} 1907 d	-
		Florida system stable	Johnston 1988b
		Max 100% diquat in sediment <0.05% mineralisation after 100 d	-

Substance	Study	Result				Reference
		1.7-2.9% b	ound res	sidues aft	er 100 d	_
	Adsorption/ desorption	<u>Sediment</u>	<u>%0C</u>	<u>Kf</u>	<u>1/n</u>	
		Fine	4.9	400809	1.41	Mônego 2005
		Coarse	0.7	9452	1.02	
		Sand	0.7	15	0.52	Pack 1987
		Mean Kf 13	36759 ml	.98		
	Aquatic field dissipation	DT ₅₀ 0.50 (d in Flori	da pond	water	Fujie1988(d)

Table 57: Diquat – fate and behaviour in air

Substance	Study	Result	Reference
Diquat	Photochemical oxidative degradation	DT ₅₀ 5.5 h	Hayes 2001

Table 58: Diquat – monitoring data

Substance	Medium	Result	Reference
Diquat	Insects	Max 5.0 mg/kg in beetles following cereal stubble application at 1000 g ac/ha	Jutsum 2011
		Edwards et al. 1991	
	Foliage	Max 0.23 mg/kg in lettuce following interrow application at 750 g ac/ha	Kennedy 1984
		Max 0.91 mg/kg in lettuce following interrow application at 960 g ac/ha	Massey 1987(c)
		Max 17 mg/kg in oilseed rape following application at BBCH 87- 89 at 600 g ac/ha	Langridge 2011a, 2011b
		Max 56 mg/kg in various seeds following lentil application at 550 g ac/ha	Edwards et al. 1991
	Soil	Max 0.86 mg/kg following long-term use as crop desiccant at 300- 1400 g ac/ha (46 trials)	Devine 2004

Substance Medium	Result	Reference
	Max 0.11 mg/kg, average 0.03 mg/kg following long-term use as crop desiccant at 500-1000 g ac/ha; average 25% carry over (39 trials)	Anderson & Earl 1996

Table 59: Diquat – effects on terrestrial vertebrates

Test substance	Group	Exposure	Species	Toxicity value ²⁹	Reference
Diquat	Mammals	Acute	Rattus norvegicus	LD_{50} 120 mg ac/kg bw	Rittenhouse 1979
		Chronic	Rattus norvegicus	NOAEL 4.0 mg ac/kg bw/d	Hodge 1990
	Birds	Acute	Anas platyrhynchos LD ₅₀ 71 mg ac/kg bw Fi		Fink et al. 1982
			<i>Taeniopygia guttata</i> LD ₅₀ 31 mg ac/kg bw		Hubbard 2013
			Perdix perdix	LD_{50} 158 mg ac/kg bw	Roberts & Fairley 1980
			Geomean LD ₅₀ 70 mg	g ac/kg bw	
		Chronic	Colinus virginianus NOEL 10 mg ac/kg bw/d		Beavers & Fink 1982
			Anas platyrhynchos	NOEL 3.2 mg ac/kg bw/d	Temple et al. 2004a, 2004b

Table 60: Diquat – laboratory studies on aquatic species

Substance	Group	Exposure	Species	Toxicity value	Reference
Diquat	Vertebrates	Acute	Sander vitreus Micropterus dolomieu Micropterus salmoides	LC ₅₀ 0.75 mg ac/L Paul et al. 1994 LC ₅₀ 3.9 mg ac/L LC ₅₀ 4.9 mg ac/L	
			Cyprinodon variegatus	LC_{50} 49 mg ac/L	Nicholson 1987

²⁹ All toxicity values are reported in terms of the active constituent, which is defined as the diquat cation

Substance	Group	Exposure	Species	Toxicity value	Reference
Diquat		Chronic	Pimephales promelas	NOEC 0.12 mg ac/L	Surprenant 1987a
			Cyprinodon variegatus	NOEC 3.0 mg ac/L	Minderhout 2012
	Invertebrates	Acute	Hyalella azteca	LC ₅₀ 0.084 mg ac/L	Bender 2006a
			Americamysis bahia	LC ₅₀ 0.42 mg ac/L	Hoberg 1987
			Daphnia magna	EC ₅₀ 2.5 mg ac/L	Volz 2004
			Crassostrea virginica	EC ₅₀ 141 mg ac/L	Dionne 1987
	Invertebrates	Chronic	Daphnia magna	NOEC 0.036 mg ac/L	Surprenant 1987b
			Americamysis bahia	NOEC 0.052 mg ac/L	Claude et al. 2013
			Lymnaea stagnalis	NOEC 0.0011 mg ac/L	Ducrot et al. 2010
	Sediment- dwellers	Acute	Leptocheirus plumulosus	LC ₅₀ >110 mg ac/kg ds	Bradley 2015
		Chronic	Hyallela azteca	NOEC 11 mg ac/kg ds	Bradley 2013a
			Chironomus dilutus	NOEC 37 mg ac/kg ds	Bradley 2013b
			Chironomus riparius	NOEC 100 mg ac/kg ds	Ashwell 1999
	Algae	Chronic	Navicula pelliculosa	E _r C ₅₀ 0.0012 mg ac/L	Smyth et al. 1998a
			Nitzschia palea	EC ₅₀ 0.0052 mg ac/L	Nagai 2019
			Raphidocelis subcapitata	EC ₅₀ 0.055 mg ac/L	
			Achnanthidium minutissimum	EC ₅₀ 0.0073 mg ac/L	
			Pseudanabaena foetida	EC_{50} 0.23 mg ac/L	
			Synechococcus leopoliensis	EC_{50} 0.29 mg ac/L	
	Fistulifera pelliculosa		Fistulifera pelliculosa	EC_{50} 0.33 mg ac/L	
			Desmodesmus subspicatus	EC ₅₀ 3.2 mg ac/L	
			Anabaena flos-aquae	$E_r C_{50} 0.025 \text{ mg ac/L}$	Smyth et al. 1998b
			Skeletonema costatum	E_rC_{50} 12 mg ac/L	Smyth et al. 1998c
	Aquatic	Chronic	Lemna gibba	EC ₅₀ 0.0032 mg ac/L	Magor & Shillabeer

Substance	Group	Exposure	Species	Toxicity value	Reference
	plants				2001
TOPPS	Invertebrates	Acute	Daphnia magna	EC ₅₀ >110 mg/L	Liedtke 2011a
	Algae	Chronic	P. subcapitata	E _r C ₅₀ >110 mg/L	Liedtke 2011b
	Aquatic plants	Chronic	Lemna gibba	E _r C ₅₀ >111 mg/L	Liedtke 2011c

Table 61: Diquat – microcosm studies on aquatic species

Substance	Group	Exposure	Species	ER ₅₀ or EC ₅₀	Reference
EC 240 g/L	Aquatic plants	Spray	Spirodela punctata	3.5 g ac/ha	Bellet 1990a
		application	Eichhornia crassipes	26 g ac/ha	
			Azolla caroliniana	48 g ac/ha	
			Pistia stratiotes	125 g ac/ha	
			Pteridium aquilinum	336 g ac/ha	
			Brasenia schreberi	3504 g ac/ha	
			Panicum repens	3552 g ac/ha	
			Paspalum notatum	14064 g ac/ha	
		Water-injection	Spirodela punctata	3.1 µg ac/L	Bellet 1990a
		application	Hydrilla verticillate	60 µg ac/L	
			Azolla caroliniana	80 µg ac/L	
			Eichhornia crassipes	90 µg ac/L	
			Pistia stratiotes	90 µg ac/L	
			Panicum repens	15900 µg ac/L	

Table 62: Diquat – effects on bees

Test substance	Species	Life stage	Exposure	Toxicity value	Reference
SL 200 g/L	Apis mellifera	Adult	Acute contact	LD50 105 µg ac/bee	Gough et al. 1987
			Acute oral	LD50 22 µg ac/bee	Gough et al. 1987

Test substance	Group	Species	Test substrate	Toxicity value	Reference
SL 200 g/L	Predatory	Typhlodromus pyri	Glass plate	LR_{50} 2.9 g ac/ha	Austin & Elcock 1999a
	arthropods		Bean leaf disc	LR ₅₀ 4.1 g ac/ha ER ₅₀ >1.0 g ac/ha	Austin & Elcock 1999b
	Predatory arthropods	Poecilus melanarius	Loamy sand	LR ₅₀ >1600 g ac/ha ER ₅₀ >1600 g ac/ha	Gough et al. 1991
		Pardosa spp.	Loamy sand	LR ₅₀ >1600 g ac/ha ER ₅₀ >1600 g ac/ha	Gough et al. 1991
	Parasitic	Aphidius rhopalosiphi	Glass plate	LR_{50} 3.2 g ac/ha	Austin 1999a
	arthropods		Barley plants	LR_{50} 758 g ac/ha	Austin 1999b
		Aleochara bilineata	Artificial soil	LR ₅₀ >1000 g ac/ha ER ₅₀ >1000 g ac/ha	Beech 1997

Table 63: Diquat – effects on other non-target arthropods

Table 64: Diquat – laboratory studies on soil organisms

Test substance	Group	Exposure	Species/process	Toxicity value	Reference
Diquat	Macro-organisms	Acute	Eisenia fetida	LC_{50} 94 mg ac/kg ds	Bender 2006b
		Chronic	Eisenia fetida	NOEC 37 mg ac/kg ds	Friedrich 2007a
			Folsomia candida	NOEC 9.4 mg ac/kg ds	Friedrich 2007b
			Hypoaspis aculeifer	NOEC 50 mg ac/kg ds	Schultz 2007a
	Micro-organisms	Chronic	Nitrification	NOEC 3.4 mg ac/kg ds	Bender 2006c
				NOEC 500 mg ac/kg ds	Schultz 2007b
TOPPS	Macro-organisms	Chronic	Eisenia fetida	NOEC 80 mg/kg ds	Friedrich 2011a
			Folsomia candida	NOEC 144 mg/kg ds	Friedrich 2011b
			Hypoaspis aculeifer	NOEC 320 mg/kg ds	Schultz 2011a

Test substance	Group	Exposure	Species/process	Toxicity value	Reference
	Micro-organisms	Chronic	Nitrification	NOEC 160 mg/kg ds	Schultz 2011b

Table 65: Diquat – field studies on soil organisms

Substance	Exposure	Effect	Reference	
Diquat	90, 198 and 720 kg ac/ha (50, 110 and 400% SAC) Incorporated to 150 mm	Earthworm numbers and weight were all reduced at 1 year; however, no observed differences after 6 years	Edwards 1980	
	15, 33 and 120 kg ac/ha			
	(50, 110 and 400% SAC)			
	Incorporated to 25 mm			
	112 kg ac/ha No incorporation	No impact on earthworm numbers or weight at 5 months, 1 year or 2 years. SAC not reported.	Wilkinson & Edwards 1993	
	1700 kg ac/ha			
	Incorporated to 100 mm			
	1.0 kg ac/ha annually (plateau 22.5 kg ac/ha)	No significant impact on straw decomposition up to 9 months after litterbag burial in treated soil. SAC not reported.	Mack 2010	

Table 66: Diquat – laboratory studies on non-target terrestrial plants

Test substance	Exposure	Species	ER25	ER50	Reference
SL 200 g/L	Pre-emergent	Allium cepa	>8400 g ac/ha	>8400 g ac/ha	Shilling 1987
		Cassia obtusifolia	>8400 g ac/ha	>8400 g ac/ha	
		Datura stramonium	>8400 g ac/ha	>8400 g ac/ha	
		Echinochloa crusgalli	>8400 g ac/ha	>8400 g ac/ha	
		Glycine max	>8400 g ac/ha	>8400 g ac/ha	
		Helianthus annuus	>8400 g ac/ha	>8400 g ac/ha	
		Ipomoea hederacea	>8400 g ac/ha	>8400 g ac/ha	
		Secale cereale	>8400 g ac/ha	>8400 g ac/ha	
		Solanum tuberosum	>8400 g ac/ha	>8400 g ac/ha	
		Zea mays	>8400 g ac/ha	>8400 g ac/ha	
		Zea mays	24578 g ac/ha	>75000 g ac/ha	Balluff 2006

Test substance	Exposure	Species	ER25	ER50	Reference
		Helianthus annuus	34898 g ac/ha	>75000 g ac/ha	
		Brassica napus	>22500 g ac/ha	>75000 g ac/ha	
		Triticum aestivum	>75000 g ac/ha	>75000 g ac/ha	
	Pre-emergent	Zea mays	30900 g ac/ha	48075 g ac/ha	Peterek 2009
	28d aged residues	Helianthus annuus	62100 g ac/ha	77700 g ac/ha	
	Post-emergent	Brassica oleracea	7.3 g ac/ha	15 g ac/ha	Martin 2013
		Beta vulgaris	9.6 g ac/ha	38 g ac/ha	
		Helianthus annuus	11 g ac/ha	47 g ac/ha	
		Daucus carota	25 g ac/ha	53 g ac/ha	
		Brassica napus	17 g ac/ha	57 g ac/ha	
		Glycine max	18 g ac/ha	257 g ac/ha	
		Zea mays	125 g ac/ha	419 g ac/ha	
		Allium cepa	256 g ac/ha	425 g ac/ha	
		Lolium perenne	287 g ac/ha	445 g ac/ha	
		Avena sativa	>500 g ac/ha	>500 g ac/ha	
		Zea mays	44 g ac/ha	65 g ac/ha	Porch & Krueger 1999
		Triticum aestivum	215 g ac/ha	379 g ac/ha	

Test substance	Location	Species	ER25	ER50	Reference
SL 240 g/L	Florida	Helianthus annuus	19 g ac/ha	50 g ac/ha	Bellet 1990b
		Glycine max	7.2 g ac/ha	53 g ac/ha	
		Gossypium hirsutum	12 g ac/ha	55 g ac/ha	
		Zea mays	46 g ac/ha	120 g ac/ha	
		Cyperus esculentus	72 g ac/ha	240 g ac/ha	
		Pinus elliottii	19 g ac/ha	293 g ac/ha	
		Pterydium aquilinium	156 g ac/ha	485 g ac/ha	
		Allium cepa	247 g ac/ha	511 g ac/ha	
		Wordardia virginica	19 g ac/ha	538 g ac/ha	
	Wisconsin	Cyperus esculentus	18 g ac/ha	35 g ac/ha	Bellet 1990b
		Helianthus annuus	31 g ac/ha	63 g ac/ha	
		Allium cepa	36 g ac/ha	74 g ac/ha	
		Pinus strobes	74 g ac/ha	150 g ac/ha	
		Glycine max	395 g ac/ha	191 g ac/ha	
		Zea mays	216 g ac/ha	539 g ac/ha	
		Phaseolus vulgaris	393 g ac/ha	884 g ac/ha	

Table 67: Diquat – field studies on non-target terrestrial plants (post-emergent exposure)

Table 68: Diquat/paraquat combination products: short-term effects on terrestrial vertebrates

Group	Species	0.46 diquat ³⁰	0.54 paraquat ³¹	1.00 combination ³²
Mammals	Rattus norvegicus	LD ₅₀ 120 mg ac/kg bw Rittenhouse 1979	LD₅₀ 111 mg ac/kg bw Duerden 1994 Kimbrough & Gaines 1970	Measured: LD ₅₀ 119 mg acs/kg bw Pooles 2005
			Murray & Gibson 1972	Predicted: LD ₅₀ 115 mg acs/kg bw
				MDR 0.97

 ³⁰ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent
 ³¹ All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent
 ³² Refer to APVMA Risk Assessment Manual – Environment for calculation method to predict combination toxicity

Group	Species	0.46 diquat ³⁰	0.54 paraquat ³¹	1.00 combination ³²
	Mus musculus	LD ₅₀ 125 mg ac/kg bw Clark and Hurst 1970	LD ₅₀ 151 mg ac/kg bw Fletcher 1967	Predicted: LD ₅₀ 138 mg acs/kg bw
			Heylings & Farnworth 1992	Relative toxicity: 51% + 49%
	Cavia porcellus	LD ₅₀ ~100 mg ac/kg bw Clark and Hurst 1970	LD₅₀ 22 mg ac/kg bw Murray & Gibson 1972	Predicted: LD ₅₀ 34 mg acs/kg bw
				Relative toxicity: 16% + 84%
	Oryctolagus cuniculus	LD_{50} 101 mg ac/kg bw Clark and Hurst 1970	LD_{50} 45 mg ac/kg bw Farnworth et al. 1993	Predicted: LD₅₀ 60 mg acs/kg bw
				Relative toxicity: 28% + 72%
Geomean	LD_{50} 76 mg acs/kg bw (4	4 mammal species)		
Birds	Anas platyrhynchos	LD_{50} 71 mg ac/kg bw Fink et al. 1982	LD₅₀ 54 mg ac/kg bw Johnson 1998	Predicted: LD₅₀ 61 mg acs/kg bw
				Relative toxicity: 39% + 61%
	Taeniopygia guttata	LD₅₀ 31 mg ac/kg bw Hubbard 2013	LD ₅₀ 27 mg ac/kg bw Hubbard et al. 2014	Predicted: LD ₅₀ 29 mg acs/kg bw
				Relative toxicity: 43% + 47%

Geomean LD_{50} 42 mg acs/kg bw (2 bird species)
Group	Species	0.46 diquat ³⁴	0.54 paraquat ³⁵	1.00 combination ³⁶
Fish	Cyprinodon variegatus	meas. 4d LC ₅₀ 49 mg ac/L adj. LC ₅₀ 59 mg ac/L	meas. 4d LC_{50} >41 mg ac/L adj. LC_{50} >50 mg ac/L	Predicted: LC ₅₀ >54 mg acs/L
		Nicholson 1987	Claude et al. 2014a	Relative toxicity: ≤42% + ≥58%
	Sander vitreus	meas. 4d LC ₅₀ 0.75 mg ac/L adj. LC ₅₀ 0.91 mg ac/L	No data ³⁷	Predicted: LC ₅₀ 1.7 mg acs/L
		Paul et al. 1994		Relative toxicity: 84% + 16%
	Pimephales promelas	No data	meas. 4d LC ₅₀ 4.7 mg ac/L adj. LC ₅₀ 5.7 mg ac/L	Predicted: LC ₅₀ 1.7 mg acs/L
			Claude et al. 2014b	Relative toxicity: 84% + 16%
Invertebrates	Americamysis bahia	camysis meas. 4d LC ₅₀ 0.42 mg ac/L adj. LC ₅₀ 0.51 mg ac/L	meas. 4d LC ₅₀ 0.23 mg ac/L adj. LC ₅₀ 0.28 mg ac/L	Predicted: LC ₅₀ 0.35 mg acs/L
		Hoberg 1987	Claude et al. 2014c	Relative toxicity: 32% + 68%
	Daphnia magna	meas. 2d EC ₅₀ 2.5 mg ac/L adj. EC ₅₀ 2.8 mg ac/L	meas. 2d EC ₅₀ 4.3 mg ac/L adj. EC ₅₀ 4.8 mg ac/L	Predicted: EC ₅₀ 3.6 mg acs/L

Table 69: Diquat/paraquat combination products: short-term effects on aquatic species³³

 $^{^{33}}$ All 'measured' endpoints have been adjusted to account for rapid dissipation from the water column under natural conditions (adjusted EC₅₀ = measured EC₅₀ / (1 – EXP (exposure days * (-ln(2)/DT₅₀ 7.0 days))) (exposure days * ln(2)/DT₅₀ 7.0 days). The more conservative water DT₅₀ of 7 days for paraquat has been utilised to adjust the endpoints for both chemicals to avoid artificially skewing the relative toxicity contributions toward paraquat.

³⁴ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent0

³⁵ All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent 0

³⁶ Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity;

predicted values are based on adjusted toxicity values to account for rapid dissipation of both active constituents from the water column

³⁷ Where toxicity data are not available, the endpoint for the most sensitive species was selected to predict combination toxicity

Group	Species	0.46 diquat ³⁴	0.54 paraquat³⁵	1.00 combination ³⁶
		Volz 2004	Allison & Hamer 1990 Noack 2007	Relative toxicity: 59% + 41%
	Crassostrea virginica	meas. 4d EC ₅₀ 141 mg ac/L adj. EC ₅₀ 171 mg ac/L	meas. 4d EC ₅₀ 23 mg ac/L adj. EC ₅₀ 28 mg ac/L	Predicted: EC ₅₀ 46 mg acs/L
		Dionne 1987	Claude et al. 2014d	Relative toxicity: 12% + 88%
Invertebrates	Hyalella azteca	meas. 4d LC $_{50}$ 0.084 mg ac/L adj. LC $_{50}$ 0.10 mg ac/L	No data	Predicted: LC ₅₀ 0.15 mg acs/L
		Bender 2006a		Relative toxicity: 70% + 30%
Algae	Navicula pelliculosa	meas. 3d E _r C ₅₀ 0.0012 mg ac/L	meas. 3d E _r C ₅₀ 0.00034 mg ac/L	Predicted E _r C ₅₀ : 0.00061 mg acs/L
		adj. E_rC_{50} 0.0014 mg ac/L Smyth et al. 1998a	adj. E_rC_{50} 0.00041 mg ac/L Smyth et al. 1992a	Relative toxicity: 20% + 80%
	Raphidocelis subcapitata	meas. 4d EC ₅₀ 0.0055 mg ac/L adj. EC ₅₀ 0.0067 mg ac/L Nagai 2019	meas. 4d EC $_{50}$ 0.26 mg ac/L adj. EC $_{50}$ 0.31 mg ac/L	Predicted: EC ₅₀ 0.014 mg acs/L
			Smyth et al. 1990a, 1990b, 1992b Scheerbaum 2007b Grillo et al. 2015	Relative toxicity: 98% + 2%
	Anabaena flos- aquae	meas. 3d E_rC_{50} 0.025 mg ac/L adj. E_rC_{50} 0.029 mg ac/L	meas. 3d E_rC_{50} 0.0078 mg ac/L adj. E_rC_{50} 0.0099 mg ac/L	Predicted E _r C ₅₀ : 0.014 mg acs/L
		Smyth et al. 1998b	Smyth et al. 1992c	Relative toxicity: 23% + 77%
	Skeletonema costatum	meas. 3d E_rC_{50} 12 mg ac/L adj. E_rC_{50} 14 mg ac/L	meas. 3d E_rC_{50} 5.9 mg ac/L adj. E_rC_{50} 7.1 mg ac/L	Predicted: E _r C ₅₀ 9.2 mg acs/L
		Smyth et al. 1998c	Smyth et al. 1992d	Relative toxicity: 30% + 70%

Group	Species	0.46 diquat ³⁴	0.54 paraquat³⁵	1.00 combination ³⁶
Aquatic plants	Lemna gibba	meas. 14d EC ₅₀ 0.0032 mg ac/L adj. EC ₅₀ 0.0059 mg ac/L Magor & Shillabeer 2001	meas. 7/14d* E_rC_{50} 0.034 mg ac/L adj. E_rC_{50} 0.054 mg ac/L Mohammad et al. 2010	Predicted: EC_{50} 0.011 mg acs/L Relative toxicity:
	Lemna minor	No data	Smyth et al. 1992e meas. 7d E_rC_{50} 0.015 mg ac/L adj. E_rC_{50} 0.021 mg ac/L Tagun & Boxall 2018	89% + 11% Predicted: EC ₅₀ 0.0096 mg acs/L
				Relative toxicity: 75% + 25%

Primary producers

Geomean EC₅₀ 0.0066 mg acs/L (5 species, excl. S.costatum)

*7d $E_r C_{\rm 50}$ 0.031 and 14d $E_r C_{\rm 50}$ 0.037 mg ac/L

Table 70: Diquat/paraquat combination products: short-term effects on bees

Group	Species	0.46 diquat ³⁸	0.54 paraquat ³⁹	1.00 combination ⁴⁰
Bees (contact)	Apis mellifera	LD₅₀ 105 µg ac/bee Gough et al. 1987	LD ₅₀ 16 µg ac/bee Bull & Wilkinson 1987	Predicted: LD ₅₀ 26 µg acs/bee
				Relative toxicity: 11% + 89%
Bees (oral)	Apis mellifera	LD₅₀ 22 µg ac/bee Gough et al. 1987	LD ₅₀ 13 µg ac/bee Bull & Wilkinson 1987	Predicted: LD ₅₀ 16 μg acs/bee
				Relative toxicity: 33% + 67%

 ³⁸ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent
 ³⁹ All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent
 ⁴⁰ Refer to APVMA Risk Assessment Manual – Environment for calculation method to predict combination toxicity

Group	Species	0.46 diquat ⁴¹	0.54 paraquat ⁴²	1.00 combination ⁴³
Predatory arthropods	Typhlodromus pyri	Tier 1 LR ₅₀ 2.9 g ac/ha Austin & Elcock 1999a	Tier 1 LR₅₀ 1.9 g ac/ha Austin & Elcock 1999c	Predicted tier 1: LR ₅₀ 2.3 g acs/ha
				Relative toxicity: 36% + 64%
		Tier 2 LR ₅₀ 4.1 g ac/ha Austin & Elcock 1999b	Tier 2 LR₅₀ 8.2 g ac/ha Austin 1999c	Predicted tier 2: LR ₅₀ 5.6 g acs/ha
				Relative toxicity: 63% + 37%
	Pterostichus melanarius	ER_{50} >1600 g ac/ha Gough et al. 1991	ER_{50} >1000 g ac/ha Jackson et al. 1991	Not expected to be toxic
	Pardosa spp.	ER₅₀ >1600 g ac/ha Gough et al. 1991	ER₅₀ >1000 g ac/ha Jackson et al. 1991	Not expected to be toxic
Parasitic arthropods	Aphidius rhopalosiphi	Tier 1 LR₅₀ 3.2 g ac/ha Austin 1999a	No data	Insufficient data
		Tier 2 LR₅₀ 758 g ac/ha Austin 1999b	No data	Insufficient data
	Aleochara bilineata	ER ₅₀ >1000 g ac/ha Beech 1997	ER ₅₀ >600 g ac/ha Petto 1993	Not expected to be toxic

Table 71: Diquat/paraquat combination products: effects on other terrestrial arthropods

⁴¹ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent
 ⁴² All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent
 ⁴³ Refer to APVMA Risk Assessment Manual – Environment for calculation method to predict combination toxicity

	-	-	_	
Group	Species/process	0.46 diquat ⁴⁴	0.54 paraquat⁴⁵	1.00 combination ⁴⁶
Macro-organisms	Eisenia fetida	LC ₅₀ 94 mg ac/kg ds Bender 2006b	LC ₅₀ >1000 mg ac/kg ds Bender 2006b	Any toxicity would be attributed to diquat
Micro-organisms	Nitrification	NOEC 500 mg ac/kg ds Schulz 2007b	NOEC 120 mg ac/kg ds Drew & Davies 1980	Not expected to be toxic

Table 72: Diquat/paraquat combination products: short-term effects on soil organisms

Table 73: Diquat/paraquat combination products: effects on non-target terrestrial plants (post-emergent exposure)

Group	Species	0.46 diquat ⁴⁷	0.54 paraquat ⁴⁸	1.00 combination ⁴⁹
Monocotyledons	Zea mays	ER ₅₀ 205 g ac/ha Bellet 1990b	ER ₅₀ 207 g ac/ha Canning & White 1992	Predicted: ER₅₀ 206 g acs/ha
		Martin 2013 Porch & Krueger 1999	Martin 2014	Relative toxicity: 46% + 54%
	Allium cepa	ER₅₀ 252 g ac/ha Bellet 1990b Martin 2013	ER₅₀ 136 g ac/ha Martin 2014	Predicted: ER ₅₀ 173 g acs/ha Relative toxicity: 31% + 69%
	Lolium perenne	ER₅₀ 445 g ac/ha Martin 2013	ER₅₀ 35 g ac/ha Martin 2014	Predicted: ER ₅₀ 61 g acs/ha
				Relative toxicity: 6% + 91%

 $^{^{\}rm 44}$ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

⁴⁵ All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

⁴⁶ Refer to APVMA Risk Assessment Manual – Environment for calculation method to predict combination toxicity

⁴⁷ All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

⁴⁸ All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

⁴⁹ Refer to APVMA Risk Assessment Manual – Environment for calculation method to predict combination toxicity

Group	Species 0.46 diquat ⁴⁷ 0.54 paraquat ⁴⁸		0.54 paraquat ⁴⁸	1.00 combination ⁴⁹
	Avena sativa	ER ₅₀ >500 g ac/ha Martin 2013	ER₅₀ 108 g ac/ha Martin 2014	Predicted: ER₅₀ >169 g acs/ha
				Relative toxicity: ≤16% + ≥84%
Dicotyledons	Brassica oleracea	ER₅₀ 15 g ac/ha Martin 2013	No data ⁵⁰	Predicted: ER ₅₀ 19 g acs/ha
				Relative toxicity: 59% + 41%
	Beta vulgaris	ER ₅₀ 38 g ac/ha Martin 2013	ER ₅₀ 68 g ac/ha Canning & White 1992	Predicted: ER ₅₀ 50 g acs/ha
				Relative toxicity: 60% + 40%
	Brassica napus	ER ₅₀ 57 g ac/ha Martin 2013	ER ₅₀ 161 g ac/ha Canning & White 1992	Predicted: ER ₅₀ 88 g acs/ha
			Martin 2014	Relative toxicity: 71% + 29%
	Glycine max	ER ₅₀ 138 g ac/ha Bellet 1990b	ER ₅₀ 476 g ac/ha Canning & White 1992	Predicted: ER ₅₀ 224 g acs/ha
		Martin 2013	Martin 2014	Relative toxicity: 75% + 25%
	Xanthium strumarium	No data	ER ₅₀ 25 g ac/ha Canning & White 1992	Predicted: ER ₅₀ 19 g acs/ha

⁵⁰ Where toxicity data are not available, the endpoint for the most sensitive species was selected to predict combination toxicity

Group	Species	0.46 diquat ⁴⁷	0.54 paraquat ⁴⁸	1.00 combination ⁴⁹
				Relative toxicity: 59% + 41%

Appendix C – Terrestrial vertebrate assessments

Risks to terrestrial vertebrates following dietary exposure to contaminated food items are assessed using a tiered approach. The acute assessment assumes 100% of food items are obtained from the treatment area on the last day of application, while the chronic assessment assumes 50% of food items are obtained from the treatment area for the first 21 days after the last application (PT 0.5). Acute risks were determined to be higher risk than long-term risks for both wild mammals and birds. Therefore, the assessment in this Appendix focuses only on the acute risks.

The use patterns were divided up into groups which consist of crops that have similar growing patterns (Table 74. It is assumed that the exposure of a 'generic focal species' within each group will be the same as they relate to feeding habits and other ecological needs. A 'generic focal species' is not a real species; however, it is considered to be representative of all those species potentially at risk. The APVMA utilises the EFSA (2009) generic focal species which are considered protective of species that occur in Australia. Interception of the spray by the crop is taken into account by calculating the residue level on the several food types, depending on the growth stage of the crop. This consideration is reflected in the EFSA (2009) shortcut values.

Acute risks to wild mammals are summarised in Table 75; acute risks to birds are summarised in Table 76.

Use pattern	EFSA 2009	Situation	Application rate	Seasonal exposure rate (g/ha)		
				Insects (DT ₅₀ 2.2 d)	Foliage (DT ₅₀ 1.8 d)	Seeds (DT₅₀ 7.9 d)
Pre-harvest crop	Oilseeds	Poppies	1× 800 g ac/ha	800	800	800
desiccation		Oilseeds	1× 600 g ac/ha	600	600	600
	Potatoes	Potatoes	1× 800 g ac/ha	800	800	800
	Cotton	Cotton	1× 600 g ac/ha	600	600	600
	Sunflower	Sunflower	1× 600 g ac/ha	600	600	600
	Cereals	Cereals, rice, sugarcane	1× 600 g ac/ha	600	600	600
	Legume forage	Lupins. lucerne	1× 600 g ac/ha	600	600	600
	Pulses	Pulses	1× 600 g ac/ha	600	600	600
General weed control	Bare soil	Row crops, vegetables, market gardens	1× 800 g ac/ha	800	800	800

Table 74: Seasonal exposure estimates for diquat in animal food items

Use pattern	EFSA 2009	Situation	Application rate	Seasonal exposure rate (g/ha)		
	crop group	_		Insects (DT ₅₀ 2.2 d)	Foliage (DT ₅₀ 1.8 d)	Seeds (DT ₅₀ 7.9 d)
		Cereals	1× 600 g ac/ha	600	600	600
		Oilseeds	1× 300 g ac/ha	300	300	300
		Hops	1× 280 g ac/ha	280	280	280
		Lucerne	1× 140 g ac/ha	140	140	140
	Grassland	Pasture, infested areas	1× 560 g ac/ha	560	560	560
	Orchards	Orchards	1× 300 g ac/ha	300	300	300
	Vineyards	Vineyards	1× 300 g ac/ha	300	300	300
Combination products containing	Bare soil	Fallow (minimal disturbance)	2× 368 g ac/ha 7d interval	409	499	595
paraquat and diquat		Bananas, duboisia, market gardens, nurseries, potatoes, rice, vegetables	1× 368 g ac/ha	368	368	368
		Fallow (full disturbance), lucerne	1× 276 g ac/ha	276	276	276
		Sugarcane	1× 230 g ac/ha	230	230	230
	Grassland	Public service areas, rights of way, pasture	1× 368 g ac/ha	368	368	368
	Orchards	Forests, orchards, plantations	1× 368 g ac/ha	368	368	368

Use pattern	EFSA 2009	Situation	Application rate	Seasonal exposure rate (g/ha)		
	crob Broab		- unu nequency	Insects (DT₅o 2.2 d)	Foliage (DT ₅₀ 1.8 d)	Seeds (DT ₅₀ 7.9 d)
		Spot application in avocado, custard apples, lychees, mangos ⁵¹	2× 276 g ac/ha 14d interval	111	124	152
	Vineyards	Vineyards	1× 368 g ac/ha	368	368	368
	Cotton	Cotton desiccant	1× 184 g ac/ha	184	184	184

Risk assessment scenarios as described in Table 25; seasonal exposure rates based on indicated application rate, frequency, and DT_{50}

Table 75: Acute risks of diquat to wild mammals (RAL 12 mg/kg bw)

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
Pre-harvest desig	cation in poppies and o	ilseeds				
Oilseeds	Large herbivore	All season	35.1	600	21	1.8
	Small herbivore	BBCH ≥40	34.1	600	20	1.7
	Small omnivore	BBCH ≥40	4.3	800	3.4	0.29
Pre-harvest desiccation in potatoes						
Potatoes	Small herbivore	BBCH ≥40	10.5	800	8.4	0.70
	Small insectivore	BBCH ≥20	5.4	800	4.3	0.36
	Small omnivore	BBCH ≥40	5.2	800	4.2	0.35

⁵¹ Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
Pre-harvest desig	ccation in cotton					
Cotton	Small herbivore	BBCH ≥50	34.1	600	20	1.7
				184	6.3	0.52
	Small insectivore	BBCH ≥20	5.4	600	3.2	0.27
	Small omnivore	BBCH ≥50	4.3	600	2.6	0.22
Pre-harvest desig	cation in sunflower					
Sunflower	Small herbivore	BBCH ≥40	34.1	600	20	1.7
	Large herbivore	BBCH ≥40	8.8	600	5.3	0.44
	Small insectivore	BBCH ≥20	5.4	600	3.2	0.27
	Small omnivore	BBCH ≥40	4.3	600	2.6	0.22
Pre-harvest desig	Pre-harvest desiccation in cereals, rice and sugarcane					
Cereals	Small herbivore	BBCH ≥40	40.9	600	25	2.0
	Small omnivore	BBCH ≥40	5.2	600	3.1	0.26
Pre-harvest desig	cation in lupins and luc	erne				
Legume forage	Small herbivore	BBCH ≥50	40.9	600	25	2.0
	Small insectivore	BBCH ≥20	5.4	600	3.2	0.27
	Small omnivore	BBCH ≥50	5.2	600	3.1	0.26
Pre-harvest desig	Pre-harvest desiccation in pulses					
Pulses	Small herbivore	BBCH ≥50	40.9	600	25	2.0
	Small omnivore	BBCH 81-99	14.4	600	8.6	0.72
	Large herbivore	BBCH ≥50	10.5	600	6.3	0.53
	Small insectivore	BBCH ≥20	5.4	600	3.2	0.27

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
General weed co duboisia, nurseri	ntrol in row crops, veget es, potatoes, rice, and s	ables, market gardens, ce ugarcane	reals, oilsee	ds, hops, lucern	e, fallow, banana	as,
Bare soil ⁵²	Small granivore	BBCH <10	14.4	800	12	0.96
General weed control in pasture, infested areas, public service areas, rights of way						
Grassland	Small herbivore	All season	136.4	368	50	4.2
	Large herbivore	All season	32.6	560	18	1.5
				368	12	1.0
	Small omnivore	New sown or late season	14.4	560	81	0.67
	Small insectivore	Late season	5.4	560	3.0	0.25
General weed co	ntrol in orchards, forest	s, and plantations				
Orchards	Small herbivore	Ground directed	136.4	124	17	1.4
	Large herbivore	Ground directed	35.1	368	13	1.1
				300	11	0.88
	Small omnivore	Ground directed	17.2	368	6.3	0.53
	Small insectivore	Ground directed	5.4	368	2.0	0.17
General weed co	ntrol in vineyards					
Vineyards	Small herbivore	Ground directed	136.4	300	41	3.4
	Large herbivore	Ground directed	27.2	368	10	0.83
	Small omnivore	Ground directed	17.2	368	6.3	0.53

Crop groups as indicated in Table 74; generic focal species and shortcut values for indicated crop groups from EFSA (2009)

 $^{\rm 52}$ Only screening level scenario is presented as the assessment passes at this level

Appendix 148

Seasonal exposure rates selected from Table 74 for the indicated crop groups represent worst-case scenario (if acceptable) or best-case scenario (if not acceptable).

DDD = daily dietary dose (mg/kg bw/d) = shortcut value * rate (kg ac/ha)

RAL = regulatory acceptable level = LD_{50} 120 mg/kg bw (Rittenhouse 1979) and assessment factor of 10

RQ = risk quotient = DDD/RAL, where acceptable RQ ≤1

Table 76: Acute risks of diquat to birds (RAL 7.0 mg/kg bw)

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
Pre-harvest des	iccation in poppies and oilseed	ds				
Oilseeds	Small granivore	BBCH 80-99	24.7	600	15	2.1
	Small insectivore	BBCH 30-99	7.4	800	5.9	0.85
	Small omnivore	BBCH ≥40	6.0	800	4.8	0.69
	Medium herbivore/granivore	BBCH ≥40	2.0	800	1.6	0.23
Pre-harvest des	Pre-harvest desiccation in potatoes					
Potatoes	Small insectivore	BBCH ≥20	25.2	800	20	2.9
	Small omnivore	BBCH ≥40	7.2	800	5.8	0.82
Pre-harvest des	iccation in cotton					
Cotton	Small omnivore	BBCH ≥50	4.4	600	2.6	0.38
	Small insectivore	BBCH ≥20	3.0	600	1.8	0.26
Pre-harvest des	Pre-harvest desiccation in sunflower					
Sunflower	Small granivore/insectivore	BBCH 61-92	21.7	600	13	1.9
Pre-harvest desiccation in cereals, rice, and sugarcane						
Cereals	Small insectivore	BBCH 71-89	57.6	600	35	4.9
	Small granivore/insectivore	Late season	27.0	600	16	2.3
	Small omnivore	BBCH ≥40	7.2	600	4.3	0.62

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
Pre-harvest des	iccation in lupins, lucerne,	and pulses				
Legume forage	Small insectivore	BBCH ≥20	25.2	600	15	2.2
or pulses	Small granivore	BBCH ≥50	7.4	600	4.4	0.63
	Small omnivore	BBCH ≥50	7.2	600	4.3	0.62
General weed co bananas, dubois	General weed control in row crops, vegetables, market gardens, cereals, oilseeds, fallow (minimal disturbance), bananas, duboisia, nurseries, potatoes, rice, sugarcane, and vineyards ⁵³				,	
Bare soil	Small granivore	BBCH <10	24.7	300	7.4	1.1
	Small omnivore	BBCH <10	17.4	600	10	1.5
				368	6.4	0.91
	Small insectivore	BBCH <10	10.9	800	8.7	1.2
				600	6.5	0.93
General weed co	ontrol in hops, lucerne, fall	ow (full disturbance), and	d sugarcane			
Bare soil ⁵⁴	Small granivore	BBCH <10	25.3	280	7.1	1.0
General weed co	General weed control in pasture, infested areas, public service areas, and rights of way					
Grassland	Large herbivore	Growing shoots	30.5	368	11	1.6
	Small insectivore	Growing shoots	26.8	368	9.9	1.4
	Small granivore	Late season	24.7	368	9.1	1.3
		New sown	20.4	368	7.5	1.1

⁵³ No avian focal species have been identified for ground directed application in vineyards; therefore, a 'bare soil' scenario was considered ⁵⁴ Only screening level scenario is presented as the assessment passes at this level

Crop group	Generic focal species	Crop stage	Shortcut value	Exposure rate (g/ha)	DDD (mg/kg bw/d)	RQ
General weed c	ontrol in orchards, forests and	plantations				
Orchards	Small insectivore	Spring/summer	46.8	300	14	2.0
	Small granivore	Ground directed	27.4	300	8.2	1.2
	Small insectivore/worm feeder	Ground directed	7.4	368	2.7	0.39
Spot application	n in avocado, custard apples, ly	chees, mangos				
Orchards ⁵⁵	Small insectivore	Spring/summer	46.8	111	5.2	0.74

Crop groups as indicated in Table 74; generic focal species and shortcut values for indicated crop groups from EFSA (2009) Seasonal exposure rates selected from Table 74 for the indicated crop groups represent worst-case scenario (if acceptable) or best-case scenario (if not acceptable as indicated in red highlighted cells).

DDD = daily dietary dose (mg/kg bw/d) = shortcut value * rate (kg ac/ha)

Geomean LD₅₀ 70 mg/kg bw (Fink et al. 1982, Hubbard 2013, Roberts & Fairley 1980) and assessment factor of 10 RQ = risk quotient = DDD/RAL, where acceptable RQ \leq 1

⁵⁵ Only screening level scenario is presented as the assessment passes at this level

Appendix D – PBT and POP assessments

The Stockholm Convention provides scientifically based criteria for potential POPs (persistent organic pollutants) and a process that ultimately may lead to elimination of a POP substance globally. POPs are persistent, bioaccumulative, and toxic (PBT) and also have potential for long-range transport.

Persistence criterion

The criteria for persistence in Annex D of the convention are expressed as follows:

• Evidence that the half-life of the chemical in water is greater than 2 months (60 days), or that its half-life in soil is greater than 6 months (180 days), or that its half-life in sediment is greater than 6 months (180 days)

Or,

• Evidence that the chemical is otherwise sufficiently persistent to justify its consideration within the scope of the Convention.

As diquat is considered to be not readily biodegradable, a weight of evidence approach is followed.

- The photolytic half-lives of diquat in freshwater did not exceed 40 days. The DT₅₀ was determined to be 2.0 days at 40°N latitude in summer (Oliver & Webb 2005) and 10 days at 35°N latitude in spring (Dean 2000). Furthermore, a DT50 of 11 days was determined in pH 7 buffer under mid-European spring sunlight conditions (Moffatt 1993).
- The degradation half-life of diquat determined in a freshwater sediment simulation study exceeded 180 days. The DT₅₀ values were determined to be >1,000 days, under aerobic conditions in 2 different freshwater systems (Calwich Abbey and Swiss Lake) (Ford 2012). Diquat was also considered to be stable in a Florida water/sediment system (Cranor & Daly 1988).
- The degradation half-life of diquat was determined in 3 aerobic studies, which exceeded 180 days in all 9 soils tested (Dixon 2012a, Johnston 1988, Mônego 2006a).

Overall, these results show that the degradation of the substance in freshwater sediment and soil exceeded the persistence threshold. It can thus be concluded that diquat meets the persistence criterion.

Bioaccumulation criterion

The criteria for bioaccumulation in Annex D of the Stockholm Convention are given as follows:

- Evidence that the bioconcentration factor or bioaccumulation factor in aquatic species for the chemical is greater than 5,000 or, in the absence of such data, that the log Pow is greater than 5.
- Evidence that a chemical presents other reasons for concern, such as high bioaccumulation in other species, high toxicity or ecotoxicity.

• Monitoring data in biota indicating that the bioaccumulation potential of the chemical is sufficient to justify its consideration within the scope of the Convention.

Diquat is considered not bioaccumulative based on a fish BCF of 1.0 (Hamer et al. 1987).

Toxicity criterion

The criteria for toxicity in Annex D of the POPs convention are given as follows:

• Evidence of adverse effects to human health or to the environment that justifies consideration of the chemical within the scope of this Convention.

Or,

• Toxicity or ecotoxicity data that indicate the potential for damage to human health or to the environment.

The lowest aquatic long-term effect value of diquat is below 10 μ g/L (lowest NOEC is 1.1 μ g/L, Ducrot et al. 2010). Therefore, diquat is considered to meet the toxicity criterion.

Potential for long-range environmental transport

The criteria for long-range transport in Annex D of the Stockholm convention are given as follows:

- Measured levels of the chemical in locations distant from the sources of its release that are of potential concern.
- Monitoring data showing that long-range environmental transport, with the potential for transfer to a receiving environment, (via air, water or migratory species).

Or,

 Environmental fate properties and/or model results that demonstrate that the chemical has a potential for such transportation, with the potential for transfer to a receiving environment in locations distant from the sources of its release. For a chemical that migrates significantly through the air, its half-life in air should be greater than 2 days.

Diquat has low vapour pressure, and the modelled atmospheric half-life is <2 days (Hayes 2001); therefore it is unlikely to travel long distances through the air. There is no evidence to suggest diquat is being transported long distances in the environment.

Conclusion

Diquat does not fulfil the PBT criteria (not PBT) and has low potential for long-range transport. Therefore, diquat does not meet the criteria for POPs in Annex D of the Stockholm convention.

Acronyms and abbreviations

Shortened term	Full term
ac	active constituent
APVMA	Australian Pesticide and Veterinary Medicines Authority
AQ1	1-hydroxy- 3,4-dihydro-H-pyrido[1,2-a] pyrazine-2-carboxylic acid
AF	assessment factor
AR	applied radioactivity
BBCH	Biologische Bundesanstalt, Bundessortenamt und Chemische Industrie
BCF	bioconcentration factor
bw	body weight
CCPR	Codex Committee on Pesticide Residues
CI	confidence interval
cm	centimetre(s)
codex	Codex Alimentarius
d	day(s)
DAT	days after treatment
DDD	daily dietary dose
ds	dry soil or sediment
DT ₅₀	period required for 50 percent dissipation
EC _x	concentration causing X% effect (ErCX is used for growth rate; EbCX is used for biomass; EyC50 is used for yield)
ECHA	European Chemicals Agency
EFSA	European Food Safety Authority
ERX	rate causing X% effect
ExpE	exposure estimate
F1	first generation
g	gram(s)
GAP	Good Agricultural Practice

Shortened term	Full term
GIT	gastrointestinal tract
h	hour(s)
ha	hectare(s)
HC _x	hazardous concentration for X% of the species
HR _x	hazardous rate for X% of the species
HR	high residue
IPM	integrated pest management
JMPR	Joint FAO/WHO Meeting on Pesticide Residues
Kd or Kf	(Freundlich) adsorption constant
kg	kilogram(s)
Кр	sediment sorption coefficient
L	litre(s)
LC _X	lethal concentration to X% of the tested population
LD _X	lethal dose to X% of the tested population
LOC	level of concern
LR _x	lethal rate to X% of the tested population
m	metre(s)
max	maximum
mg	milligram(s)
mg/kg bw/day	milligrams per kilogram of bodyweight per day
mL	millilitre(s)
mm	millimetre(s)
mol	mole(s)
mPA	millipascal(s)
NEDI	National Estimated Daily Intake
NESTI	National Estimated Short Term Intake
NOAEL	No observable adverse effect level

Shortened term	Full term
NOEC	no observed effect concentration
NOEL	no observable effect level
nm	nanometre(s)
OC	organic carbon
OECD	Organisation for Economic Co-operation and Development
Ра	pascals
РВТ	persistent – bioaccumulative – toxic
PEC	predicted environmental concentration
РНІ	preharvest interval
POP	persistent organic pollutant
Pow	octanol-water partition coefficient
PT	proportion of an animal's daily diet obtained in habitat treated with pesticide
RAL	regulatory acceptable level
RQ	risk quotient
SAC-WB	strong adsorption capacity – wheat bioassay
SDRAM	spray drift risk assessment manual
SSD	species sensitivity distribution
SL	soluble concentrate
STMR	Supervised Trials Median Residue
TOPPS	1,2,3,4-tetrahydro-1-oxo-2H-pyrido(1-2-a)-5-pyrazinium salt (R32245, CGA130327)
hâ	micrograms
USEPA	United States Environmental Protection Agency
UV	ultraviolet
VIS	visible
w/w	weight per weight

Glossary

Term	Description
active constituent	The substance that is primarily responsible for the effect produced by a chemical product
adsorption constant	A measure of the tendency of a chemical to bind to soils
acute exposure	Contact between a pesticide and a target occurring over a short time (e.g., less than a day)
acute toxicity	Adverse effects of finite duration occurring within a short time (up to 14 d) after administration of a single dose (or exposure to a given concentration) of a test substance or after multiple doses (exposures), usually within 24 h of a starting point (which may be exposure to the toxicant, or loss of reserve capacity, or developmental change, etc.)
adverse effect	Change in the morphology, physiology, growth, development, reproduction or life span of an organism, system, or subpopulation that results in impairment of the capacity to compensate for additional stress, or an increase in susceptibility to other influences
aged residue	Residues of a pesticide or its degradates in soil that have diffused into intra-particulate regions following application and have become less accessible to mass transfer and bioabsorption processes, although still amenable to solvent extraction
agricultural crop	Any terrestrial plant species grown commercially for food, fibre, foliage, fuel or medicinal production, with the exception of plants that are not part of a crop under management at the time of pesticide application (eg blackberries or volunteer grain plants that have escaped from a cropped area and become weeds in another area)
aquatic	Relating to water or sediment, as distinct from land or air
assessment factor	Reductive factor by which an observed or estimated endpoint of a pesticide is divided to arrive at a regulatory acceptable level
bioaccumulation	Progressive increase in the amount of a substance in an organism or part of an organism that occurs because the rate of intake exceeds the organism's ability to remove the substance from the body
bioconcentration	Uptake of a pesticide residue from an environmental matrix, usually through partitioning across body surfaces to a concentration in the organism that is usually higher than in the environmental matrix
bioconcentration factor	Ratio between the concentration of pesticide in an organism or tissue and the concentration in the environmental matrix (usually water) at apparent equilibrium during the uptake phase
bound residue	Residue associated with one or more classes of endogenous macromolecules that cannot be disassociated by extraction or digestion without alteration
cation	Monatomic or polyatomic species having one or more elementary charges of the proton
catchment	Landform that collects precipitation and retains it in an impoundment or drains it through a single outlet
chronic exposure	Continued or intermittent long-term contact between an agent and a target
chronic toxicity	Adverse effects following chronic exposure

Term	Description
concentration	Amount of a material, agent (e.g., pesticide) dissolved or contained in unit quantity in a given medium or system
dissipation	Loss of pesticide residues from an environmental compartment due to degradation and transfer to another environmental compartment
dissociation constant	The ratio of concentration of dissociated ions to the concentration of original acid
dose	Total amount of a pesticide or agent administered to, taken up or absorbed by an organism, system, or (sub-) population
dry weight basis	Pesticide residue concentration reported as if the residue were wholly contained in the dry matter of the sample
effect assessment	Combination of analysis and inference of possible consequences of the exposure to a pesticide based on knowledge of the dose–effect relationship associated with that agent in a specific target organism, system, or (sub-) population
endpoint	Measurable ecological or toxicological characteristic or parameter of the test system that is chosen as the most relevant assessment criterion
environmental fate	Destiny of a pesticide or chemical after release to the environment involving considerations such as transport through air, soil, or water, bioconcentration, degradation, etc.
environmental risk	Probability that an adverse effect on humans an environmental system/receptor will be observed for a given exposure to a pesticide based on the probability of that exposure and the sensitivity of the system/receptor
exposure	Concentration or amount of a particular substance that is taken in by an individual, population or ecosystem in a specific frequency over a certain amount of time
exposure assessment	Evaluation of the exposure of an organism, system, or (sub-) population to a pesticide or agent (and its derivatives)
exposure assessment	Evaluation of the exposure of an organism, system, or (sub-) population to a pesticide or agent (and its derivatives)
formulation	A combination of both active and inactive constituents to form the end use product
half-life	The time taken for the reactant concentration to fall to one-half its initial value
hazard	Inherent property of a pesticide having the potential to cause adverse effects when an organism, system, or (sub-) population is exposed to that agent or situation
Henry's law constant	A gas law that states the amount of gas absorbed by a given volume of liquid at a given temperature is directly proportional to the partial pressure of that gas in equilibrium with that liquid. As such it provides an indication of the preference of a chemical for air relative to water i.e. its volatility
herbicide	Pesticide used for the control of unwanted plants or weeds
hydrolysis	Chemical decomposition induced by water
indicator species	Species whose presence shows the occurrence of defined environmental conditions

Term	Description
integrated pest management	Use of pest and environmental information in conjunction with available pest control technologies to prevent unacceptable levels of pest damage by the most economical means and with the least possible hazard to persons, property, and the environment
larva	Recently hatched insect, fish, or other organism that has different physical characteristics than those seen in the adult, requiring metamorphosis to reach the adult body structure
median effective concentration	Statistically derived concentration of a pesticide in an environmental medium expected to produce a certain effect in 50 % of the test organisms in a given population under defined conditions
median lethal concentration	Statistically derived concentration of a substance in an environmental medium expected to kill 50 % of test organisms in a given population under defined conditions
metabolite	Any intermediate or product resulting from metabolism
mineralisation	Conversion of an element from an organic form to an inorganic form. Mineralisation of pesticides most commonly refers to the microbial degradation to carbon dioxide as a terminal metabolite
mode of action	Biochemical effect that occurs at the lowest dose or concentration or is the earliest among a number of biochemical effects that could, understandably, lead to the death of the pest
no observed effect level	Greatest concentration or amount of a substance, found by experiment or observation, which causes no detectable adverse alteration of morphology, functional capacity, growth, development, or life span of the target organism under defined conditions of exposure
non-selective herbicide	Herbicide that is generally toxic to all plants treated
non-target species	Organisms that are not the intended targets of a particular use of a pesticide
partition coefficient	log Pow is the logarithm (base-10) of the partition coefficient between n-octanol and water
persistence	Residence time of a chemical species (pesticide and/or metabolites) subjected to degradation or physical removal in a soil, crop, animal, or other defined environmental compartment
photolysis	Chemical decomposition induced by light or other radiant energy
regulatory acceptable level	Criterion or standard that is considered safe or without appreciable risk
runoff	Portion of the wet precipitation on the land that ultimately reaches streams and, eventually, the sea
soil incorporation	Application of a pesticide to soil by mixing or injection into the soil body
solubility in water	The mass of a given substance (the solute) that can dissolve in a given volume of water
soluble concentrate	A liquid homogenous preparation to be applied as a true solution of the active constituent after dilution with water

Term	Description
strong adsorption capacity – wheat bioassay	A system of calibration by laboratory bioassay for the capacity of the soil to deactivate diquat by adsorption
terrestrial	Relating to land, as distinct from water or air
translocation	Movement of a substance within the test system or organism
vapour pressure	The pressure at which a liquid is in equilibrium with its vapour at a given temperature. It is a measure of the tendency of a material to vaporise. The higher the vapour pressure the greater the potential
volatile	Any substance which evaporates quickly
watercourse	A river, creek or other natural watercourse (whether modified or not) in which water is contained or flows (whether permanently or from time to time); and includes:
	a dam or reservoir that collects water flowing in a watercourse
	a lake or 'wetland' through which water flows
	a channel into which the water of a watercourse has been diverted
	part of a watercourse
	an estuary through which water flows.
wetland	An area of land where water covers the soil—all year or just at certain times of the year. They include:
	swamps, marshes
	billabongs, lakes, lagoons
	saltmarshes, mudflats
	mangroves, coral reefs
	bogs, fens, and peatlands.
	A 'wetland' may be natural or artificial and its water may be static or flowing, fresh, brackish or saline.

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177 Diquat Review Technical Report

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