

**Australian Government** 

**Australian Pesticides and Veterinary Medicines Authority** 



# Diquat

Review Technical Report July 2024

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## <span id="page-9-0"></span>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*.

## <span id="page-9-1"></span>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.

## <span id="page-9-2"></span>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: [apvma.gov.au.](https://www.apvma.gov.au/)

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## <span id="page-10-0"></span>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.

## <span id="page-10-1"></span>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.

## <span id="page-11-0"></span>Product claims, use patterns and mode of action

Diquat is an active constituent in 67 products registered for use in Australia by the APVMA<sup>[1](#page-11-2)</sup>. These products can be divided into 2 groups based on the presence of paraquat as a second active constituent, as indicated in [Table](#page-11-1)  [1.](#page-11-1) These 2 groups can be further divided based on the concentration of diquat and paraquat.

#### <span id="page-11-1"></span>Table 1: Diquat product groups



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 Appendix A – [Summary of assessment outcomes.](#page-122-0)

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 [2](#page-11-3)2<sup>2</sup> 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

<span id="page-11-2"></span><sup>&</sup>lt;sup>1</sup> 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.

<span id="page-11-3"></span><sup>&</sup>lt;sup>2</sup> Mode of Action tables maintained by Croplife are available on the [CropLife website](https://www.croplife.org.au/resources/programs/resistance-management/) (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.

## <span id="page-13-0"></span>**Chemistry**

## <span id="page-13-1"></span>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](#page-13-2) and [Table 3.](#page-14-1) There are currently 12 active constituent approvals for diquat dibromide which are listed in [Table 4.](#page-16-2)



#### <span id="page-13-2"></span>Table 2: Nomenclature and structural formula of the active constituent diquat



#### <span id="page-14-1"></span>Table 3: Key physicochemical properties of the active constituent diquat dibromide

#### <span id="page-14-0"></span>Active constituent standards

The [Agricultural and Veterinary Chemicals Code \(Agricultural Active Constituents\) Standards 2022](https://www.legislation.gov.au/F2022L00137/latest/text) (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](https://openknowledge.fao.org/server/api/core/bitstreams/3acb5d0f-cd50-4daf-a5fd-33619288cfc9/content)  [\(FAO Specification for Diquat:](https://openknowledge.fao.org/server/api/core/bitstreams/3acb5d0f-cd50-4daf-a5fd-33619288cfc9/content) 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

#### <span id="page-15-0"></span>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](#page-16-2) 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.



#### <span id="page-16-2"></span>Table 4: Current active constituent approvals for diquat dibromide

## <span id="page-16-0"></span>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.](#page-17-0)

## <span id="page-16-1"></span>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).

![](_page_17_Picture_238.jpeg)

#### <span id="page-17-0"></span>Table 5: Currently registered chemical products containing diquat

![](_page_18_Picture_315.jpeg)

![](_page_19_Picture_320.jpeg)

![](_page_20_Picture_303.jpeg)

![](_page_21_Picture_173.jpeg)

## <span id="page-21-0"></span>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](#page-16-2) 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](#page-16-2) 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,](#page-17-0) would meet the safety criteria under section 5A of the Agvet Code from a chemistry and manufacture perspective.

## <span id="page-22-0"></span>**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.

## <span id="page-22-2"></span><span id="page-22-1"></span>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/cm<sup>2</sup>/h, indicating that human skin was the least permeable of tested skin (Scott and Corrigan, 1989).

### <span id="page-22-3"></span>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.

#### <span id="page-22-4"></span>Acute toxicity

The acute oral toxicity of diquat is moderate in rats and mice (lethal dose to 50% of sample ( $LD_{50}$ ) from 120– 231 mg/kg bw; Swan 1960, 1962; Duncan et al, 1985a; McCall and Robinson, 1990a), rabbits and guinea pigs  $(LD_{50}$  approximately 100 mg/kg bw; Swan, 1960; Clark and Hurst, 1970). In dogs and monkeys the  $LD_{50}$ s 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 ( $LC_{50} = 121$  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).

#### <span id="page-23-0"></span>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).

#### <span id="page-23-1"></span>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 LD $_{50}$ .

#### 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.

#### <span id="page-24-0"></span>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).

#### <span id="page-24-1"></span>**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).

#### <span id="page-24-2"></span>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).

#### <span id="page-25-0"></span>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.

#### <span id="page-25-1"></span>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.

## <span id="page-27-0"></span>Health-based guidance values

#### <span id="page-27-1"></span>Table 6: Points of departure for human health risk assessment

![](_page_27_Picture_296.jpeg)

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\)](#page-27-2) for diquat will be retained.

#### <span id="page-27-2"></span>Table 7: Acceptable daily intake for diquat

![](_page_27_Picture_297.jpeg)

![](_page_28_Picture_181.jpeg)

#### <span id="page-28-2"></span>Table 8: Acute reference dose for diquat

## <span id="page-28-0"></span>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.

## <span id="page-28-1"></span>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.

## <span id="page-29-0"></span>Worker health and safety

The risks associated with the use of products containing diquat have been assessed in accordance with the [APVMA Human Health Risk Assessment Manual,](https://www.apvma.gov.au/registrations-and-permits/data-guidelines/risk-assessment-manuals/human-health) and a summary of the evaluation is presented.

### <span id="page-29-1"></span>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\)](#page-29-2).

![](_page_29_Picture_149.jpeg)

<span id="page-29-2"></span>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 ≥ 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.

#### <span id="page-30-0"></span>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](#page-30-2) 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

<span id="page-30-2"></span>[Table 10](#page-30-2) and [Table 11](#page-32-1) 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.

![](_page_30_Picture_159.jpeg)

#### <span id="page-30-1"></span>Table 10: Risk assessment outcomes for liquid diquat products

<span id="page-30-3"></span><sup>&</sup>lt;sup>3</sup> 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.

![](_page_31_Picture_292.jpeg)

![](_page_32_Picture_262.jpeg)

#### <span id="page-32-1"></span>Table 11: Risk assessment outcomes for liquid paraquat plus diquat products

#### <span id="page-32-0"></span>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

<span id="page-32-2"></span><sup>4</sup> 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 reentry 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 reentry 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.

## <span id="page-33-1"></span><span id="page-33-0"></span>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.

#### <span id="page-33-2"></span>**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.

### <span id="page-34-0"></span>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.

### <span id="page-34-1"></span>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 and face shield or 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.

### <span id="page-34-2"></span>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.

### <span id="page-34-3"></span>Re-entry statements for diquat and paraquat combination products

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

## <span id="page-35-0"></span>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.

## <span id="page-35-1"></span>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 monpyridone 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.

## <span id="page-35-3"></span><span id="page-35-2"></span>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 –18ºC for a period of 6–8 months (Bullock, 1980). In another study diquat residues were measured periodically in coffee beans and bananas frozen at –18ºC 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 –20ºC (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 [Residue related aspects of trade\)](#page-69-0).

# 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 guidanc[e](#page-37-0)<sup>5</sup> 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 [Vegetable crops\)](#page-43-0).

<span id="page-37-0"></span><sup>5</sup> APVMA [crop group guidance,](https://www.apvma.gov.au/crop-groups) 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.



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



# 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:



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 [Vegetable cropsVegetable crops,](#page-43-0) 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 subtropical 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.

# <span id="page-43-0"></span>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

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[\)](#page-44-0) and spring onion (from the green onion subgroup)<sup>6</sup>. 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 0.2 mg/kg

Although the high residue (HR) was observed at 6–7 days after application at 0.8 kg ac/ha (1×), 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

<span id="page-44-0"></span><sup>&</sup>lt;sup>6</sup> [Crop group 009, Bulb vegetables,](https://www.apvma.gov.au/crop-groups/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 cro[p](#page-45-0) group<sup>7</sup> 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:



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

<span id="page-45-0"></span><sup>7</sup> [Crop group 010: Brassica \(cole or cabbage\) vegetables, Head cabbages, Flowerhead cabbages](https://www.apvma.gov.au/crop-groups/brassica-head-flowerhead) , 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 subgroup<sup>8</sup>[\)](#page-46-0).

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.

<span id="page-46-0"></span><sup>8</sup> [Crop group 13: Leafy vegetables \(including Brassica leafy vegetables\),](https://www.apvma.gov.au/crop-groups/leafy-vegetables) 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, 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 postemergence (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 [s](#page-48-0)ubgroup (Subgroup 016B, Tuberous and corm vegetables<sup>9</sup>) 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 preharvest 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 (1x 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

<span id="page-48-0"></span><sup>&</sup>lt;sup>9</sup> [Crop group 016: Root and tuber vegetables,](https://www.apvma.gov.au/crop-groups/root-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:



#### 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 group<sup>[10](#page-49-0)</sup> 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

<span id="page-49-0"></span><sup>&</sup>lt;sup>10</sup> [Crop group 017: Stalk and stem vegetables,](https://www.apvma.gov.au/crop-groups/stalk-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 guidelines<sup>[11](#page-52-0)</sup>) 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

<span id="page-52-0"></span><sup>&</sup>lt;sup>11</sup> [Crop group 020: Cereal grains,](https://www.apvma.gov.au/crop-groups/cereal-grains) 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:



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 25). The MRLs recommended above for wheat and 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 \*0.05 mg/kg

## **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

# **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, 0.06, 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 1 mg/kg

#### 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 preharvest 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 5 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 ≥ 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 ≥ LOQ (0.02 mg/kg) were found in any poppy seed sample from either Tasmanian trial at any 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, 1966; Anon., 1972; Earl and Anderson, 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.](#page-63-0)



#### <span id="page-63-0"></span>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](#page-64-0) and [Table 15](#page-65-0) using the OECD Feed Calculator and the relevant HR or Supervised Trials Median Residue (STMR).



#### <span id="page-64-0"></span>Table 14: Calculation of poultry broiler dietary burden of diquat

<span id="page-64-1"></span><sup>&</sup>lt;sup>12</sup> See [crop groups,](https://www.apvma.gov.au/crop-groups) available on the APVMA website.



#### <span id="page-65-0"></span>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](#page-67-0) and [Table 17](#page-67-1) 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.



# <span id="page-67-0"></span>Table 16: Calculation of beef cattle dietary burden of diquat

<span id="page-67-1"></span>Table 17: Calculation of dairy cattle dietary burden of diquat



<span id="page-67-2"></span><sup>13</sup> See *crop groups*, available on the APVMA website.

<span id="page-67-3"></span><sup>&</sup>lt;sup>14</sup> See *crop groups*, available on the APVMA website.



# 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 ¼, ½, ¾ 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.

# <span id="page-69-0"></span>Residue related aspects of trade

The overseas MRLs presented in [Table 18](#page-70-0) are established for commodities considered to be major export commodities.



#### <span id="page-70-0"></span>Table 18: International MRLs for Australian major export commodities (December 2023)

<span id="page-70-1"></span><sup>15</sup> Food and Agriculture Organization of the United Nations (FAO), 2023. *[Codex Alimentarius, International Food Standards](https://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/)*, FAO website, accessed December 2023.

<span id="page-70-2"></span><sup>16</sup> European Commission (EC), *[EU Pesticides Database](https://food.ec.europa.eu/plants/pesticides/eu-pesticides-database_en)*, EC website, accessed December 2023.

<span id="page-70-3"></span><sup>17</sup> Japanese Food Chemistry Research Foundation (JFCRPF), 2023. *[Table of MRLs for Agricultural Chemicals,](http://db.ffcr.or.jp/front/)* JFCRPF website, accessed December 2023.

<span id="page-70-4"></span><sup>18</sup> Ministry of Food and Drug Safety Korea, 2023. *[MRLs in Pesticides](https://residue.foodsafetykorea.go.kr/prd/progress)*, accessed December 2023.

<span id="page-70-5"></span><sup>19</sup> Laws & Regulations Database of the Republic of China (Taiwan),2023. *[Standards for Pesticide Residue Limits in Foods](https://www.fda.gov.tw/ENG/law.aspx?cid=16)*, accessed December 2023.

<span id="page-70-6"></span><sup>20</sup> Electronic Code of Federal Regulations (eCFR), 2023. *[USA Electronic Code of Federal Regulations,](https://www.ecfr.gov/current/title-40/chapter-I/subchapter-E/part-180)* eCFR website, accessed December 2023.




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 Japan<sup>[21](#page-73-0)</sup> 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:

<span id="page-73-0"></span><sup>21</sup> Japanese Food Chemistry Research Foundation (JFCRPF), 2023. *[Table of MRLs for Agricultural Chemicals,](http://db.ffcr.or.jp/front/)* 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](#page-76-0) and [Table 20](#page-79-0) 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.



#### <span id="page-76-0"></span>Table 19: Amendments to Table 1 of the MRL Standard







#### <span id="page-79-0"></span>Table 20: Amendments to Table 4 of the MRL Standard



# 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](#page-80-0) an[d](#page-81-0) 

[Table 22.](#page-81-0) These uses are within the application rate range indicated on currently approved labels.

<span id="page-80-0"></span>



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



### 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:



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 0.07 mg/kg

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.

### 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 3× 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 contact the control of the contr

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 preemergence 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 contained by the contact of the 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:



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](#page-88-0) an[d Table 24: Revised amendments to Table 4](#page-89-0) of the MRL Standard



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.



### <span id="page-88-0"></span>Table 23: Revised amendments to Table 1 of the MRL Standard



### <span id="page-89-0"></span>Table 24: Revised amendments to Table 4 of the MRL Standard



# 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.](#page-90-0) Environmental risks were determined according to contemporary methodology outlined in the [APVMA Risk](https://apvma.gov.au/node/46416)  [Assessment Manual –](https://apvma.gov.au/node/46416) Environment. All endpoints are expressed in terms of the diquat cation as the active constituent.



#### <span id="page-90-0"></span>Table 25: Environmental risk assessment scenarios for diquat



<span id="page-91-0"></span><sup>22</sup> Spot spray also possible in duboisia



# Fate and behaviour in the environment

Diquat has low volatility and high solubility in water. Its octanol-water partition coefficient [\(Table 3\)](#page-14-0) 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.  $DT_{50}$  values for beetles sampled at the 3 sites were 3.2, 1.5 and 1.8 days (mean DT<sub>50</sub> 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 DT<sub>50</sub> values for insects captured in pitfall traps at 4 of the sites were 1.6, 3.9, 1.6 and 1.9 days (mean  $DT_{50}$  2.3 days). DT<sub>50</sub> 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. DT<sub>50</sub> 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 DT<sub>50</sub> 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  $DT_{50}$  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, ≤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

<span id="page-92-0"></span> $23$  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 x 10<sup>6</sup> cm<sup>-3</sup> (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.](#page-93-0) A full listing of endpoints is provided i[n Appendix B.](#page-131-0)



### <span id="page-93-0"></span>Table 26: Key regulatory endpoints for environmental exposure assessment

# Effects on non-target species

Diquat has moderate toxicity to mammals (LD<sub>50</sub> 120 mg ac/kg bw, *Rattus norvegicus*) and high toxicity to birds (geomean LD<sub>50</sub> 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<sup>50</sup> 750 µg ac/L, *Stizosterdion vitreum*) and aquatic invertebrates (lowest LC<sup>50</sup> 420 µg ac/L, Stizosterdion vitreum), and high toxicity to sediment dwellers (LC<sup>50</sup> 84 µg ac/L, *Hyallella azteca*), algae (lowest ErC<sup>50</sup> 1.2 µg ac/L, *Navicula pelliculosa*) and aquatic plants (EC<sup>50</sup> 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 (ER $_{50}$  3.5 g ac/ha) and water injection (ER $_{50}$  3.1 µg 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<sup>50</sup> 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 [\(Table 27\)](#page-96-0). After considering the exposure periods for each of the aquatic

endpoints and the water  $DT_{50}$  of 0.50 days under field conditions, an HC<sub>5</sub> of 2.1 µg ac/L was derived, which is lower than the lowest EC<sub>50</sub> value. In addition, the lower limit HC5 is more than one third of the median HC<sub>5</sub>. 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 µg 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<sub>50</sub> 105 µg ac/bee, *Apis mellifera*) and moderate toxicity by oral exposure (LD<sub>50</sub> 22 µg ac/bee, *Apis mellifera*). The RAL for spray drift assessment is 17,500 g ac/ha based on the contact LD<sub>50</sub> 105 µg ac/bee and a conversion factor of LOC 0.4 / ExpE 2.4  $*$  1000 as per the APVMA's Spray [drift risk assessment manual](https://apvma.gov.au/node/51826) (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 LR<sub>50</sub> 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 (LR<sub>50</sub> 4.1 g ac/ha, *Typhlodromus pyri*). However, toxicity to the parasitic wasp was reduced (LR<sub>50</sub> 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 (LC<sup>50</sup> 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 (ER<sub>50</sub> 15 g ac/ha, *Brassica oleracea*). Under field conditions, a natural stand of yellow nutsedge was the most sensitive based on visual injury

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

Noting dicots are more sensitive than monocots, an SSD analysis was performed on the post-emergent ER<sub>50</sub> values for the 10 dicotyledonous species [\(Table 28\)](#page-97-0). An HR<sup>5</sup> of 12 g ac/ha was derived, which is lower than the lowest ER<sub>50</sub> value. As such, 12 g ac/ha was set as the RAL for the protection of vegetation areas.

The 3-hour  $EC_{50}$  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 µg 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.



#### <span id="page-96-0"></span>Table 27: Toxicity endpoints for aquatic primary producers used in SSD analysis

Endpoints from [Table 61](#page-138-0) 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)/DT<sub>50</sub> 0.5 days)))  $*$  (exposure days  $*$  $ln(2)/DT_{50}$  0.5 days)

# <span id="page-97-0"></span>Table 28: Post-emergent toxicity endpoints for dicots used in SSD analysis based on data from laboratory and field studies



### <span id="page-97-1"></span>Table 29: 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  $*$   $(-ln(2)/DT_{50}$  0.5 days)))  $*$  (exposure days  $* ln(2)/DT_{50}$  0.5 days)

# 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 [Appendix B.](#page-131-0) Acceptable risks of diquat could only be concluded for general weed control in hops, lucerne, fallow (full disturbance only), and sugarcane [\(Table 30\)](#page-99-0). 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.](#page-99-0)

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.



### <span id="page-99-0"></span>Table 30: Summary of risk assessment outcomes for terrestrial vertebrates



<span id="page-100-0"></span> $24$  Spot spray acceptable in duboisia up to maximum rate of 368 g ac/ha

<span id="page-100-1"></span><sup>&</sup>lt;sup>25</sup> 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](#page-97-1) 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 [\(Table 31\)](#page-102-0). 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 waterways<sup>[26](#page-101-0)</sup> considered the lowest RAL values of 2.1  $\mu$ 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 [\(Table 33\)](#page-103-0). For sand soils containing ≤10% soil, the maximum supported annual peak soil concentration is 3.3 mg ac/kg dry soil<sup>[27](#page-101-1)</sup> 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.

<span id="page-101-0"></span><sup>&</sup>lt;sup>26</sup> See Appendix B, Attachments 1 and 2 of<https://apvma.gov.au/node/46416>

<span id="page-101-1"></span><sup>27</sup> Back-calculated from 2480 g ac/ha and soil depth of 5-cm (2480/750)

### <span id="page-102-0"></span>Table 31: Assessment of risks to non-target aquatic species for aquatic use situations



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\)](#page-97-1)

<span id="page-102-1"></span> $RQ =$  risk quotient = PEC / RAL, where acceptable  $RQ \le 1$ 

#### Table 32: Soil exposure estimates





Risk assessment scenarios as described in [Table 25;](#page-90-0) 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.

### <span id="page-103-0"></span>Table 33: Assessment of runoff risks to aquatic species for terrestrial use situations



<span id="page-103-1"></span><sup>28</sup> Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard



Worst-case scenario based on 1 $\times$  800 g ac/ha applied annually for 20 years with no interception and indicated soil DT  $_{50}$ 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\)](#page-102-1)

Soil DT<sub>50</sub> and Kf from [Table 55](#page-131-1)

Rainfall P value is default for Tier 1

Runoff Q value = (((-0.000196\*(rain^3))+(0.0232\*(rain^2)))+(-0.00520\*rain)); runoff curve for worst-case Australian soil profile  $Cr<sub>soil surface</sub> = EXP(-3<sup>*</sup>ln(2)/DT<sub>50soil</sub>)<sup>*</sup>(1/(1+Kf))$ 

Slope factor  $F = (0.02153 \times \text{slope} + 0.001423 \times \text{slope}^2)$ , where default screening level slope is 8%

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

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\)](#page-93-0)

RAL = regulatory acceptable level (from [Table 29\)](#page-97-1)

 $RQ =$  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.



#### 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\)](#page-97-1)

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.



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

RAL = regulatory acceptable level (from [Table 29\)](#page-97-1)

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

### 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 [\(Table 36\)](#page-107-0), and no protection statements are therefore required.



#### <span id="page-107-0"></span>Table 36: Screening level assessment of risks to soil organisms (worst-case scenario)

Worst-case scenario based on 1 $\times$  800 g ac/ha applied annually for 20 years with no interception and soil DT<sub>50</sub> 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\)](#page-97-1)

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

### Non-target terrestrial plants

As indicated in [Table 29,](#page-97-1) 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.






### <span id="page-108-0"></span>Effects on non-target species

A representative combination product containing 115 g/L diquat and 135 g/L paraquat had moderate toxicity to rats (LD<sup>50</sup> 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](#page-142-0) through to [Table 73](#page-148-0) in [Appendix B](#page-131-0) for all predicted combination toxicity values for non-target species. For further details on the estimation method, please refer to the [APVMA Risk Assessment Manual –](https://www.apvma.gov.au/registrations-and-permits/data-guidelines/risk-assessment-manuals/environment) Environment.

Based on available data, the diquat/paraquat combination products were predicted to have high toxicity to mammals (geomean LD<sub>50</sub> 76 mg acs/kg bw, 4 mammal species) and birds (geomean LD<sub>50</sub> 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<sub>50</sub>) 1.7 mg acs/L for most sensitive species) and aquatic invertebrates (lowest LC<sup>50</sup> 0.15 mg acs/L, *Hyalella azteca*), and high toxicity to primary producers (geomean E<sub>r</sub>C<sub>50</sub> 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<sup>50</sup> 26 µg acs/bee, *Apis mellifera*) and oral exposure (LD<sup>50</sup> 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](https://apvma.gov.au/node/51826) (SDRAM).

Based on the available data, the  $LR_{50}$  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 ER<sub>50</sub> 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 ER<sub>50</sub> values for 7 non-target terrestrial plant species. An HR<sub>5</sub> of 18 g acs/ha was derived [\(Table 38\)](#page-109-0), which is lower than the lowest ER<sub>50</sub> 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,](#page-110-0) 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.



<span id="page-109-0"></span>Table 38: Diquat/paraquat combination products – Predicted toxicity endpoints for non-target terrestrial plants (post-emergent exposure) used in SSD analysis

Group	<b>Exposure</b>	<b>Endpoint</b>	<b>AF</b>	<b>RAL</b>
Mammals	Acute	$LD_{50}$ 76 mg acs/kg bw	10	7.6 mg acs/kg bw
<b>Birds</b>	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	$0.66 \mu g$ 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	$LR_{50}$ 5.6 g acs/ha	$\mathbf{1}$	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		
<b>Terrestrial plants</b>	Post-emergent	HR <sub>5</sub> 18 gacs/ha	1	18 g acs/ha

<span id="page-110-0"></span>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  $*(-In(2)/DT<sub>50</sub> 7.0 \text{ days}))$ )  $*(exposure days * In(2)/DT<sub>50</sub> 7.0 \text{ days}))$ 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 [\(Table 40\)](#page-112-0). 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 ≥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 [Effects on non-target species](#page-108-0) section, 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. Risks of spray drift are addressed separately, as needed.

### <span id="page-112-0"></span>Table 40: Diquat/paraquat combination products: crop groups for terrestrial vertebrate assessment



Risk assessment scenarios as described in [Table 37;](#page-107-0) seasonal exposure rates based on indicated application rate, frequency and  $DT_{50}$ 

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



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](#page-110-0)

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



### Table 43: Screening level assessment of risks of combination products containing 115 g/L diquat and 135 g/L paraquat 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 39](#page-110-0)

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

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



RAL = regulatory acceptable level from [Table 39](#page-110-0)

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

### Recommendations

Uses supported from the viewpoint of environmental safety are listed in [Table 45](#page-114-0) with the required protection statements and restraints. Uses that are not supported from the viewpoint of environmental safety are listed in [Table 46.](#page-115-0) These recommendations include consideration of the environmental risks of the diquat/paraquat combination products, as needed.

### <span id="page-114-0"></span>Table 45: Supported uses of diquat from the viewpoint of environmental safety



#### 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

### <span id="page-115-0"></span>Table 46: Uses of diquat not supported from the viewpoint of environmental safety





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 [APVMA Spray Drift Policy,](https://apvma.gov.au/node/10796) July 2019 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,](#page-117-0) which is the maximum amount of spray drift exposure that is not expected to cause undue harm to sensitive areas.



#### <span id="page-117-0"></span>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.](#page-117-1)

<span id="page-117-1"></span>



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.



#### 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.



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

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



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









## <span id="page-131-0"></span>Appendix B – Listing of environmental endpoints





### Table 55: Diquat – fate and behaviour in soil







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







### Table 57: Diquat – fate and behaviour in air



### Table 58: Diquat – monitoring data





### Table 59: Diquat – effects on terrestrial vertebrates



### Table 60: Diquat – laboratory studies on aquatic species



<span id="page-136-0"></span><sup>&</sup>lt;sup>29</sup> All toxicity values are reported in terms of the active constituent, which is defined as the diquat cation





### Table 61: Diquat – microcosm studies on aquatic species



### Table 62: Diquat – effects on bees





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

### Table 64: Diquat – laboratory studies on soil organisms





### Table 65: Diquat – field studies on soil organisms



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







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

### <span id="page-142-0"></span>Table 68: Diquat/paraquat combination products: short-term effects on terrestrial vertebrates

Group	<b>Species</b>	$0.46$ diquat <sup>30</sup>	$0.54$ paraguat <sup>31</sup>	1.00 combination <sup>32</sup>
Mammals	Rattus norvegicus	$LD_{50}$ 120 mg ac/kg bw Rittenhouse 1979	$LD_{50}$ 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
				<b>MDR 0.97</b>

<span id="page-142-1"></span> $30$  All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

<span id="page-142-2"></span> $31$  All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

<span id="page-142-3"></span><sup>32</sup> Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity



Geomean  $LD_{50}$  42 mg acs/kg bw (2 bird species)


#### Table 69: Diquat/paraquat combination products: short-term effects on aquatic species<sup>[33](#page-144-0)</sup>

<span id="page-144-0"></span><sup>33</sup> All 'measured' endpoints 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)/DT<sub>50</sub> 7.0 days))) (exposure days  $*$  $ln(2)/DT_{50}$  7.0 days). The more conservative water DT<sub>50</sub> 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.

<span id="page-144-1"></span><sup>&</sup>lt;sup>34</sup> All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent 0

<span id="page-144-2"></span> $35$  All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent 0

<span id="page-144-3"></span><sup>36</sup> 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

<span id="page-144-4"></span><sup>37</sup> Where toxicity data are not available, the endpoint for the most sensitive species was selected to predict combination toxicity





Primary producers Geomean EC<sub>50</sub> 0.0066 mg acs/L (5 species, excl. *S.costatum*)

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

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



<span id="page-146-0"></span> $38$  All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

<span id="page-146-1"></span> $39$  All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

<span id="page-146-2"></span><sup>40</sup> Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity



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

<span id="page-147-0"></span><sup>&</sup>lt;sup>41</sup> All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

<span id="page-147-1"></span><sup>&</sup>lt;sup>42</sup> All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

<span id="page-147-2"></span><sup>43</sup> Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity



### 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)



<span id="page-148-0"></span><sup>&</sup>lt;sup>44</sup> All formulations contain 115 g/L diquat, which comprises  $46\%$  of the total active constituent

<span id="page-148-1"></span><sup>&</sup>lt;sup>45</sup> All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

<span id="page-148-2"></span><sup>46</sup> Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity

<span id="page-148-3"></span><sup>47</sup> All formulations contain 115 g/L diquat, which comprises 46% of the total active constituent

<span id="page-148-4"></span><sup>48</sup> All formulations contain 135 g/L paraquat, which comprises 54% of the total active constituent

<span id="page-148-5"></span><sup>49</sup> Refer to **APVMA Risk Assessment Manual – Environment** for calculation method to predict combination toxicity



<span id="page-149-0"></span><sup>50</sup> Where toxicity data are not available, the endpoint for the most sensitive species was selected to predict combination toxicity



## 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.](#page-151-0) 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](#page-153-0); acute risks to birds are summarised in [Table 76](#page-156-0).



#### <span id="page-151-0"></span>Table 74: Seasonal exposure estimates for diquat in animal food items





Risk assessment scenarios as described in [Table 25;](#page-90-0) seasonal exposure rates based on indicated application rate, frequency, and  $DT_{50}$ 

### <span id="page-153-0"></span>Table 75: Acute risks of diquat to wild mammals (RAL 12 mg/kg bw)



<span id="page-153-1"></span><sup>&</sup>lt;sup>51</sup> Assuming a maximum of 40% of an orchard is treated, each application is equivalent to 110 g ac/ha across the entire orchard





Crop groups as indicated in [Table 74;](#page-151-0) generic focal species and shortcut values for indicated crop groups from EFSA (2009)

<span id="page-155-0"></span><sup>52</sup> Only screening level scenario is presented as the assessment passes at this level

Seasonal exposure rates selected from [Table 74](#page-151-0) 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

<span id="page-156-0"></span>RQ = risk quotient = DDD/RAL, where acceptable RQ ≤1

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





<span id="page-157-0"></span><sup>53</sup> No avian focal species have been identified for ground directed application in vineyards; therefore, a 'bare soil' scenario was considered

<span id="page-157-1"></span><sup>&</sup>lt;sup>54</sup> Only screening level scenario is presented as the assessment passes at this level



Crop groups as indicated in [Table 74;](#page-151-0) generic focal species and shortcut values for indicated crop groups from EFSA (2009) Seasonal exposure rates selected from [Table 74](#page-151-0) 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 LD<sub>50</sub> 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 ≤1

<span id="page-158-0"></span><sup>55</sup> 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  $DT_{50}$  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 DT<sub>50</sub> 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 µg/L (lowest NOEC is 1.1 µg/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







# **Glossary**









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