DIQUAT DIBROMIDE

MITIGATION PROPOSAL FOR REDUCTION OF HUMAN EXPOSURE

BY

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ABSTRACT

Diquat dibromide is used for desiccation of seed crops and potatoes, and for weed control of non-crop terrestrial and aquatic areas. The absorbed daily dosages for various work tasks were estimated in the exposure assessment document for diquat dibromide and range from 0.03 to 7.8 ug/kg/day. Based on the adjusted Estimated-No-Effect-Level (ENEL) of 33 ug/kg/day for developmental toxicity in rabbits, some of the work tasks require additional mitigation measures to reduce exposure below the target level of 0.33 ug/kg/day. The mitigation measures proposed in this document reduce the estimated exposure below the target level for all work tasks, except for aerial flaggers and applicators using backpack application equipment.

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Introduction

Current Exposure Levels and Risk:
All registered diquat dibromide-containing products are liquid. Diquat dibromide (diquat) is used for desiccation of seed crops and potatoes, and for weed control of non-crop terrestrial (such as right-of-way) and aquatic areas. It is also used in gardening and landscaping. The current exposure levels for workers involved in the handling of diquat were estimated in the exposure assessment document for diquat (Formoli, 1995). The exposure levels for various occupational and non-occupational tasks, expressed as absorbed daily dosages (ADD), range from 0.03 to 7.8 ug/kg/day. The estimates of exposure for handlers of aerial and ground applications were based on surrogate exposure data from paraquat applications (Meier, 1995; Chester *et al*., 1989; Chester and Ward, 1981). The estimates of exposure of aquatic use handlers were based on an actual diquat worker exposure study (Wojeck *et al*., 1983). The estimates of exposure for handlers of right-of-way applications were based on surrogate data from glyphosate (Edmiston *et al*., 1995). Using current toxicity data and estimates of exposure, the calculated margins of safety (MOS) for some of the occupational and non-occupational tasks were less than the value conventionally recommended to protect humans from the toxic effects as shown in Table 1 which summarizes the draft risk characterization document for diquat (Cochran *et al*., 1994).

Current Mitigation Measures:
The worker protection statements on the labels require workers handling diquat to wear the following personal protective equipment (PPE):

- Coveralls over short-sleeved shirt and short pants.
- Waterproof gloves.
- Chemical resistant footwear and socks.
- Protective eyewear.
- Chemical resistant headgear for overhead exposure.
- Chemical resistant apron when cleaning equipment, mixing, or loading.

According to the federal worker protection standards (WPS) for agricultural pesticides [40 CFR 170.240(d)(4-6)], when using closed systems mixing/loading, enclosed cabs, or enclosed cockpits, the PPE requirements for mixer/loaders may be reduced to work clothing

(long-sleeved shirt and long pants) plus chemical resistant apron and gloves, and for applicators may be reduced to work clothing. The labels of the ready-to-use products and those that require dilution for home garden and landscape uses do not have a specific protective clothing statement. These mitigation measures do not reduce estimated exposure for some work tasks to a level that would produce MOS of greater than 100. Unless otherwise specified, the estimates of exposure (ADD) before the proposed mitigation measures in Table 1 are for workers handling diquat at the highest rate of application allowed and wearing clothing consisting of short-sleeved shirt and short pants, coveralls, waterproof gloves, chemical resistant footwear and socks, protective eyewear, and chemical resistant headgear. The reentry interval to treated terrestrial areas is 24 hours. Entry into treated aquatic areas is prohibited while treatment is in progress. The reentry to treated water for swimming is 24 hours.

Table 1: Estimated Diquat ADD and MOS Prior to Proposed Mitigation Measures

Work Task or Activity	Use	ADD[a] (ug/kg/day)	MOS[b]
Mixer/loader/applicator (ground boom)[c]	Ground	0.3	110
Applicator (Knapsack)*	Ground	2.4	14
Pilot[d]	Aerial	0.3	110
Flagger*	Aerial	2.8	12
Mixer/loader[e] *	Aerial/Ground	7.8	4
Applicator (ready-to-use)[d]	Garden/Landscape	0.4	83
Mixer/loader/applicator (hand wand)[f] *	Right-of-way	0.4	83
Mixer (injection)	Aquatic	0.06	550
Applicator (injection)	Aquatic	0.03	1100
Applicator (handgun)*	Aquatic	0.5	66
Boat Driver (handgun)	Aquatic	0.1	330
Swimmer (theoretical)[g]	Aquatic	1.3	26
Swimmer (based on actual data)[g]	Aquatic	0.2	165
Bystander (50 meters)*	Aerial	0.5	66

a - From Formoli, 1995. Except as noted, the ADD values are estimated based on the product label highest rate of application and clothing consisting of short-sleeved shirt and short pants, coveralls, waterproof gloves, chemical resistant footwear and socks, protective eyewear, and chemical resistant headgear. The ADD for the bystanders is from inhalation route for two hours of exposure/day.

b - Based on the adjusted Estimated-No-Effect-Level (ENEL) of 33 ug/kg/day for developmental toxicity for acute exposure (Cochran *et al*., 1994).

c) Long-sleeved shirt, long pants, headgear, footwear, and eyewear.

d) Long-sleeved shirt, long pants, and footwear.

e) The application rate and clothing protection were not provided.

f) Work clothing, Tyvek coveralls, gloves, and footwear were worn during mixing/loading/application.

g) No clothing.

* - Require additional mitigation.

Mitigation Adequacy for Various Work Tasks

The adjusted ENEL for developmental toxicity (delayed ossification and fetal malformations) in rabbits and the adjusted No Observed Effect Level (NOEL) for cataracts in dogs were determined to be 33 ug/kg/day and 50 ug/kg/day, respectively (Cochran *et al*., 1994). The risk assessment is being driven by the acute ENEL for developmental toxicity (see Table 1). If the acute ENEL has adequate MOS following proposed mitigation measures, chronic risk is not an issue. With a MOS of 100 fold, which is conventionally recommended to protect humans from toxic effects, the target level of mitigation for exposure reduction is 0.33 ug/kg/day for developmental toxicity. Additional mitigation measures are proposed for tasks with estimated exposure above the target levels.

Exposures Requiring Additional Mitigation:

1. Workers:
   Based on the target level for developmental toxicity, all work tasks asterisked in Table 1 require additional mitigation for acute exposure.

2. Residents:
   Drift from aerial applications is a non-occupational situation requiring additional mitigation for acute exposure.

Exposure not Requiring Further Mitigation:

The estimated exposure to mixer/loader/applicators using a ground rig and spray booms, pilots, applicators and mixers using aquatic injection equipment, and boat drivers of handgun spraying for aquatic application during a workday are below the target level and do not require further mitigation. The theoretical estimate of the ADD for a swimmer is above the target level, however, the estimate of the ADD for a swimmer based on actual aquatic dissipation data from the maximum application rate (Fujie, 1988) suggest that the exposure is below the target level. No further exposure reduction measure is required for a swimmer. The estimate of exposure to applicators using ready-to-use formulations is slightly above the target level. The estimate of exposure to an applicator using ready-to-use formulations in Table 1 was for a worker applying ready-to-use formulations of diquat without gloves for a standard seven hours of actual work in a day. Almost all of the estimated exposure was to hands. Title 3, California Code of Regulations, Section 6738(c) requires chemical resistant gloves for this type of pesticide applications. Gloves will reduce the estimated exposure of workers applying ready-to-use formulations to negligible levels. In addition, a worker will not spend an entire seven hours of actual work applying ready-to-use formulations of diquat. Home residents may spend even less time than workers applying. Considering the level of conservatism in the estimate of exposure and the small difference between the estimate of exposure and the target level, no mitigation is recommended for applicators or home residents using ready-to-use formulations.

Mitigation Options

Administrative Controls:

- Currently there is no buffer zone for diquat aerial applications. Diquat can drift during aerial applications. The diquat drift pattern is expected to be similar to that of paraquat. The estimate of exposure to a bystander 50 meters away from an aerial application is slightly above the target level (MOS=66). This estimate of exposure is above the target level because it was increased by 2.5 fold to adjust for maximum application rate allowed on the product label. The assumptions that aerial applications are all made at the highest application rate and a 2.5 fold increase in the application rate results in 2.5 fold increase in exposure could overestimate exposure to bystanders. **Therefore, further mitigation may not be warranted. However, to be conservative, a 1/8 mile (200 meters) buffer zone for aerial application could be imposed to insure that the public and bystanders are not exposed to diquat above the target level.**
- The estimated exposure to flaggers wearing all the required PPE is above the target level. **No reasonable and practical mitigation measures e.g., requiring flaggers wearing work clothing to be in an enclosed cab, will reduce their exposure to or below the target level. It is recommended that human flaggers are not used.**

Engineering Controls:

- The estimate of exposure for mixer/loaders of aerial applications is based on an actual diquat biomonitoring study conducted in Germany (Sawinsky and Pasztor, 1977). The exposure to mixer/loaders of ground applications was conservatively estimated from the exposure data for mixer/loaders of diquat during aerial application. The diquat study did not describe the PPE worn by the workers. A closed mixing/loading system was not required for diquat; it was not common in Europe and was probably not used during this study. When using a closed mixing/loading system, the PPE requirement for a diquat mixer/loader is reduced to work clothing, chemical resistant apron, and chemical resistant gloves. **A closed mixing/loading system in conjunction with work clothing, chemical resistant apron, and chemical resistant gloves will reduce the estimated mixer/loader exposure to the target level.**
- The estimate of exposure to workers mixing/loading/applying diquat using backpack sprayers is above the target level. **No reasonable and practical exposure reduction measures will reduce the exposure to applicators using backpack sprayers to the target level.** A worker exposure study monitoring workers using hand-held, backpack, or portable power sprayers has shown that the estimated daily dermal exposure to workers using backpack sprayers was approximately 50 fold higher than those using hand-held equipment (Merricks, 1988).

Personal Protective Equipment (PPE):

- The estimate of exposure to rights-of-way mixer/loader/applicators, such as Caltrans workers using vehicle-mounted tanks attached via long hoses to hand wands, is slightly above the target level. The workers wore Tyvek coveralls over work clothing, gloves,

eyewear, hard hats, and footwear during mixing/loading and application. This PPE is almost identical to the PPE requirements in the current product label for applicators of noncrop uses, except a chemical resistant apron is also required by the label when cleaning equipment, mixing, or loading. **A closed mixing/loading system (as recommended in the engineering control section) and a chemical resistant apron during mixing/loading will further reduce the estimated exposure of a mixer/loader/applicator that is already close to the target level.**

- The estimate of exposure to applicators of aquatic applications using handgun equipment is slightly above the target level (MOS=66). This estimate of exposure is above the target level because it was increased by four fold to adjust for maximum application rate allowed on the product label. The assumptions that aquatic applications are always made at the highest application rate and a four-fold increase in the application rate results in four fold increase in exposure could overestimate exposure to these workers. **Therefore, mitigation measures in addition to those listed in the product label may not be warranted. However, to be conservative, chemical resistant full body protective clothing over short-sleeved shirt and short pants could be required to reduce the estimated ADD of applicators of aquatic applications using handgun equipment to the target level.**

Voluntary Cancellation of Specific Uses:

- The estimate of exposure to workers mixing/loading/applying diquat using backpack sprayers is above the target level. **No reasonable and practical exposure reduction measures will reduce the estimated exposure to applicators using backpack sprayers to the target level. The use of backpack sprayers should be prohibited.**

Mitigation Proposal

Adopt a regulation or suggest labeling requiring:

- Prohibition of use of backpack equipment.
- An 1/8 mile buffer zone for aerial applications, as a conservative option. However, mitigation may not be warranted because the estimate of exposure is conservative and slightly above the target level (MOS=66).
- No human flaggers for aerial applications.
- Closed mixing/loading system.
- Applicators of aquatic applications using handgun equipment to wear chemical resistant full body protective clothing over short-sleeved shirt and short pants, as a conservative option. However, mitigation may not be warranted because the estimate of exposure is conservative and slightly above the target level (MOS=66).

Estimate of Exposure Following Proposed Mitigation

By Work Task/Mitigation Option:

The estimates of exposure for handlers of right-of-way applications were based on surrogate data from glyphosate (Edmiston *et al*., 1995). Hand exposure contribution to the total exposure was 45%, despite wearing gloves. In addition to glyphosate, five other herbicides were also monitored in this study (Edmiston *et al*., 1995). The exposure of workers was the highest during glyphosate handling, indicating that the estimate of exposure for workers handling diquat may be an extreme case scenario. The current product label requires handlers for noncrop uses to wear coveralls (over short-sleeved shirt and short pants), waterproof gloves, chemical resistant footwear, protective eyewear, and chemical resistant headgear. A chemical resistant apron is required during mixing/loading and cleaning of equipment. While the protection provided by a closed mixing/loading system (as recommended in the engineering control section) and a chemical resistant apron during mixing/loading can not be quantified for a mixer/loader/applicator, it will further reduce the estimated exposure of a mixer/loader/applicator that is already close to the target level. Edmiston *et al*., 1995 noted several factors that possibly add to dermal exposure (particularly to hands) such as handling a spray hose without gloves, raising the nozzle to reach difficult spots, and walking into the recently treated area instead of backing away from the spray mist. The investigators concluded that exposure reduction may be possible by ensuring that workers are wearing gloves during handling (clean or new gloves each day as required in California Regulations), washing and removing their gloves and washing their hands before entering the truck, and keeping the wand height at a low level to avoid spray mist. These use safety recommendations should further reduce exposure to the target level.

Based on the estimate of ADD that is not adjusted for maximum application rate for applicators using handgun equipment for aquatic applications, no further mitigation is required. Based on the estimate of ADD that is adjusted (four fold increase) for maximum application rate, chemical resistant full body protective clothing will reduce the exposure to applicators of aquatic applications using handgun equipment to 0.25 ug/kg/day, as shown in Table 2.

Table 2: Exposure Reduction Achieved from Proposed Mitigation Measures for Applicators Using Handgun Equipment for Aquatic Applications

Mitigation	Head & Neck (ug/day)	Hand (ug/day)	Rest of Body (ug/day)	Total (ug/day)	ADD* (ug/kg/day)	ADD** (ug/kg/day)
Label[a]	29.9	351.7	304.9	686.2	0.13	0.5
Proposed[b]	15.0	175.9	152.5	343.1	0.06	0.25

* - Dermal absorption of 1.4% (Formoli, 1995), negligible inhalation exposure, and body weight of 75.9 kg (Thongsinthusak, *et al*., 1993).

** - Corrected for application rate of 2 lb a.i./surface acre.

a - Coveralls (over short-sleeved shirt and short pants), waterproof gloves, chemical resistant footwear and socks, protective eyewear, and chemical resistant headgear, providing 90% protection.

b - Chemical resistant full-body protective clothing (over short-sleeved shirt and short pants) providing 95% protection (Thongsinthusak *et al*., 1991), protective eyewear, and footwear.

The study that was conducted in Germany to monitor the exposure of mixer/loaders of diquat during aerial applications did not describe the PPE worn by the mixer/loaders. It was assumed that the mixer/loaders wore work clothing and gloves. A closed mixing/loading system provides 95% dermal and respiratory protection (Thongsinthusak *et al*., 1991) and reduces the mixer/loader estimated exposure from 7.8 ug/kg/day to 0.4 ug/kg/day. Since the estimate of exposure to diquat mixer/loaders was derived from a urine monitoring study, the dermal protection provided by a chemical resistant apron can not be accurately calculated. However, the protection provided by an apron assures further reduction in mixer/loader exposure, and therefore, further increases the MOS.

General Populace Risk:

Based on the estimate of exposure that is not adjusted (corrected) for maximum application rate for bystanders, no further mitigation is required. Based on the estimate of exposure that is adjusted (2.5 fold increase) for maximum application rate, the ADD of 0.5 ug/kg/day for a bystander at 50 meters distance from an aerial application site will be reduced to 0.39 ug/kg/day by imposing a 1/8-mile buffer zone. The residue concentration (y) at 200 meters (x) was calculated from log linear correlation of paraquat residues observed at various downwind distances in a study conducted by Chester and Ward, 1981, as shown in Table 3.

A summary of the estimated exposures following proposed mitigation and the safety factors obtained following proposed mitigation measures is presented in Table 4. The levels of protection provided by various PPE and engineering control measures are listed in Table 5.

Table 3: Estimates of Diquat Exposure to Bystanders Based on Paraquat Downwind Drift Residue Study

Distance meter	Observed (ug/m^3)	Observed (ug/m^3)	Average (ug/m^3)	Calculated[a] (ug/m^3)	Corrected[b] (ug/m^3)	ADD[c] (ug/kg/day)
	trial I	trial II				
50	6.40	16.66	11.53	8.60	21.50	0.48
100	2.68	12.91	7.80	8.00	20.00	0.44
200	**2.10**			**7.00[d]**	**17.50**	**0.39**
400	0.81	5.85	3.33	5.35	13.37	0.30
800	3.44	4.03	3.74	3.13	7.83	0.17
1600	1.70	0.47	1.09	1.07	2.68	0.06

a - from log linear correlation [ln y=2.214-0.0013x] where x is distance and y is the calculated residues in the air, r^2=0.895

b - corrected for 0.5 lb a.i.(from 0.2 lb/acre) and based on the previous column of calculated values.

c - inhalation rate of 0.84 m^3/hour for light activity, body weight of 75.9 kg (Thongsinthusak, *et al*., 1993), and two hours of exposure daily.

d - interpolated from the curve fitted to the other data.

Expectations of Implemented Mitigation Proposal: Exposure Appraisal

The mitigation proposals are expected to reduce the estimated exposure to workers and the general populace for potential adverse health effects to the levels shown in Table 4.

There are several conservative factors that are used to estimate occupational exposure to pesticides and to calculate the absorbed doses. These factors are operating in the human exposure assessment and because they are multiplicative, result in overestimates of exposure values. For example, it is a common practice in exposure studies to observe the exposure that occurs during several replicates of the work task and then normalize it to an eight-hour workday. This normalization assumes the worker performs the work task continuously for eight hours. In reality, field conditions, breakdowns, and weather changes can shorten workdays or reduce the acreage that can be treated during an eight-hour workday. Normalizing daily exposure from less than a full day of exposure monitoring can significantly over estimate the exposure that occurs during one workday (Spencer *et al*., 1995; Franklin *et al*., 1981). As a result, the ADD calculated from this exposure will over estimate the daily dosage.

A standard practice used in the exposure assessment is to estimate the exposure based on the maximum label rate for a particular crop or use. In reality pesticides are usually applied at less than the maximum label rates. A review of the application work orders for one year of a Central Coast pest control operator serving vegetable row crop growers indicated the following mean percentages of the maximum label rates of various pesticides were applied: insecticides-82%, fungicides-68% and herbicides-58% (Haskell, 1994).

The dermal exposure that occurs while handling a pesticide is often monitored with dermal dosimetry (gauze patches or T-shirts) worn on top of or underneath the worker's clothing. In compliance with EPA guidelines, when residues are not detectable on the samples, the value is assumed to be one-half the minimum detectable level (MDL). If the analytical method is not very sensitive, this default calculation can cause a significant over estimate of the dermal exposure.

Dosage is expressed as a single static value both in worker exposure and animal toxicology studies. The rate of dermal absorption is always lower than the rate of oral absorption in animals used for toxicology testing. Adverse effects occur only when plasma levels exceed a critical level. However, dermal acquisition occurs over the entire workday, and because the dermal absorption rate is lower than oral, plasma levels for the same total absorbed dosage will not be nearly as high for a dermal versus oral exposure. A dermal dose acquired over the entire workday produces peak plasma levels much lower than the bolus oral feeding dosage acquired by animals in seconds to minutes. Because effect is highly dependent on plasma level, treating an eight-hour dermal acquisition as though it were a bolus (i.e., summing the entire dermal dose) is very conservative. The net effect of assuming instantaneous dermal dose acquisition and absorption is an overestimate of peak plasma concentration compared to the oral route by several fold for the same absorbed dose (Auton *et al*., 1993).

The inherent overestimation of exposure values in the exposure assessment process may translate to an overprotection following the mitigation measures.

Table 4: Summary of Proposed Mitigation Measures, Estimates of ADDs, and Associated MOSs Following Proposed Mitigation

Work Task	Use	Proposed Mitigation Measure*	ADD After Mitigation (ug/kg/day)	MOS** (fold)
Applicator (backpack)	Ground	Not possible	N/A	N/A
Flagger	Aerial	No human flaggers	N/A	N/A
Mixer/loader	Aerial/Ground	Closed system mixing/loading	0.4	83>[a]
Mixer/loader/applicator (hand wand)	Right-of-way	Closed system mixing/loading	0.4	83>[b]
Applicator (handgun)	Aquatic	Rainsuit[c]	0.25	132
Bystander (50 meters)	Aerial	1/8 mile buffer zone	0.39	85

* - In addition to PPE required by the product label.

** - Based on the ENEL of 33 ug/kg/day for developmental toxicity for acute exposure (Cochran *et al*., 1994).

a - Chemical resistant apron worn during mixing/loading will further reduce exposure and result in a MOS greater than 83.

b - Closed mixing/loading and apron during mixing/loading operation will further reduce exposure and result in a MOS greater than 83.

c - Substituting coveralls with a rainsuit (chemical resistant full-body protective clothing).

N/A - Not applicable

Table 5: Percent Protection Provided by PPE and Engineering Control Measures (Thongsinthusak *et al*., 1991)

PPE or Engineering Control	Percent Protection	Area of Protection	Route
Coveralls	90	Body except head, feet, and hands	dermal
Chemical resistant gloves	90	Hands	dermal
Rainsuit	95	Total body except face	dermal
Headgear and eyewear[a]	90	Covered areas	dermal
Closed system mixing/loading	95	Total	dermal and respiratory

a - Not included in the reference.

Representative Current Labels

See Appendix I

(Appendix I available on request. See address on cover of document.)

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