



Val Dolcini  
Director

## MEMORANDUM

Jared Blumenfeld  
Secretary for  
Environmental Protection

TO: Karen Morrison  
Assistant Director  
Pesticide Programs Division

**HSM-19005**

FROM: Susan McCarthy, M.S. *(original signed by S. McCarthy)*  
Environmental Program Manager II  
Chief, Worker Health and Safety Branch  
(916) 324-4116

DATE: December 16, 2019

SUBJECT: COMPLETION OF DIQUAT DIBROMIDE MITIGATION FOR SWIMMER EXPOSURE

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The diquat dibromide mitigation memorandum (Stefanova-Wilbur and Wroblicky, 2019) describes the findings of the Worker Health and Safety (WHS) Branch in regards to the need for mitigation of swimmer exposures for diquat.

Diquat dibromide [6,7-dihydrodipyrido (1,2-a:2',1,-c) pyrazinedium dibromide, hereafter diquat] is a non-selective herbicide, algicide, desiccant and defoliant. Diquat is used in both commercial and residential settings, and the target areas are terrestrial as well as aquatic. On average, about 190,000 lbs diquat active ingredient (AI) were sold annually in California between 2008 and 2017 (DPR, 2018a, 2019a). The annual use for commercial and agricultural applications averaged about 77,000 pounds AI for the same period (DPR, 2016, 2018b, 2019b). Six percent of this amount was applied to aquatic areas. The aquatic uses are for algae and aquatic weed control, and include lakes, ponds, residential backyards, and similar settings. Diquat is applied to these sites primarily by manual equipment.

The Department of Pesticide Regulation's (DPR) risk characterization document (RCD) for pesticide products containing diquat was finalized in 1994 (Cochran *et al.*, 1994). A subsequent Addendum was published in 1997 (Cochran *et al.*, 1997). The re-entry interval (REI) for swimming, used in the risk assessments, was 1 day as listed on diquat labels at the time. Neither the RCD nor the Addendum found exposures of concern for people swimming in diquat-treated waters. A Notice of Completion of Risk Assessment was issued in 1997 (Cortez, 1997).

In 1995, the United States Environmental Protection Agency (U.S. EPA) published the Reregistration Eligibility Decision for diquat (U.S. EPA, 1995). Following the mitigation measures included in this document, and the submission of new toxicological data to U.S. EPA, the registrant requested label revisions. In 2002, U.S. EPA modified the language for both occupational and residential uses on the product labels. The REI of 4 days for non-occupational use "other than aquatic and spot treatment" was set to "when sprays are dry" (U.S. EPA, 2002).

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Following these modifications, most of the current product labels either do not have language for a swimming REI, or list an REI of 0 days. The U.S. EPA's revised exposure assessment in support of the registration review of diquat stated REI=0 days, and established that the Margins of Exposure (MOE) as a measure of risk for swimmer exposures were orders of magnitude above the levels of concern (LOC) (U.S. EPA, 2016).

The memorandum by Stefanova-Wilbur and Wroblicky also determined that the removal of the swimming REI from the product labels would not significantly affect the swimmer risks, as the MOEs will remain well over the LOC (Stefanova-Wilbur and Wroblicky, 2019).

Given DPR's findings, the low use of diquat as an algicide and aquatic herbicide, and the historical absence of swimmer illnesses associated with diquat; there are no exposures of significant health concern for the swimmer scenario.

Thus, WHS finds that there is no need for further mitigation action with respect to potential swimmer exposures to diquat. Your approval of this conclusion is requested.

Attachment

cc: Shelley DuTeaux, Chief, Human Health Assessment Branch  
Eric Kwok, Senior Toxicologist, Human Health Assessment Branch  
Svetlana Koshlukova, Senior Toxicologist, Human Health Assessment Branch  
Kevin Solari, Environmental Program Manager I, WHS Branch

APPROVAL

(original signed by K. Morrison)  
Karen Morrison, Assistant Director

December 23, 2019  
Date

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Val Dolcini  
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## MEMORANDUM

Jared Blumenfeld  
Secretary for  
Environmental Protection

TO: Susan McCarthy, M.S.  
Environmental Program Manager II  
Chief, Worker Health and Safety Branch

VIA: Kevin Solari  
Environmental Program Manager I  
Worker Health and Safety Branch

*(original signed by K. Solari)*

FROM: Miglena Stefanova-Wilbur, Ph.D.  
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*(original signed by M. Wilbur)*

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Environmental Scientist  
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(916) 445-4322

*(original signed by G. Wroblicky)*

DATE: December 10, 2019

SUBJECT: COMPLETION OF DIQUAT DIBROMIDE MITIGATION FOR SWIMMER EXPOSURE

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### Overview

Based on the facts outlined in this memorandum, the Worker Health and Safety Branch has determined that no additional mitigation measures are needed for swimmer risks associated with aquatic uses of the active ingredient (AI) diquat dibromide [6, 7-dihydrodipyrido (1,2-a:2',1,-c) pyrazinediium dibromide, hereafter diquat]. This determination is based on previous Department of Pesticide Regulation (DPR) mitigation efforts, label changes made by the United States Environmental Protection Agency (U.S. EPA) in 2002, and of most recent U.S. EPA risk assessment and registration review of diquat.

Diquat is a non-selective contact herbicide, algicide, pre-harvest desiccant, post-harvest defoliant, and plant growth regulator (U.S. EPA, 2016). According to U.S. EPA, diquat is considered Toxicity Category II and III for oral, dermal and inhalation toxicity. It is an eye irritant (Toxicity Category II) but not a skin irritant (Toxicity Category IV) or skin sensitizer. Severe cases of exposure may lead to death, usually following accidental or intentional ingestion. Diquat is “not likely to be carcinogenic to humans” (U.S. EPA, 2016).

Registered diquat-containing products in California are predominantly liquid, formulated as either a soluble concentrate or ready-to-use liquid. The signal word on diquat product labels can be either “Warning” or “Caution”, depending on the product.

## Diquat Use

The annual sale of products containing diquat in California for the years 2008-2017 ranged from 150,000 to 300,000 pounds AI, averaging 190,000 pounds AI per year (DPR, 2018a; DPR, 2019a). Diquat use data acquired from DPR’s Pesticide Use Reporting (PUR) program indicate that, on average, approximately 41% of this (77,300 pounds AI) was used for commercial and agricultural applications. The annual use rate for these applications has been steady, ranging between 60,000 and 97,000 pounds AI annually (DPR, 2016; DPR, 2018b; DPR, 2019b). In 2017, (the last year for which PUR data is available), 76,800 pounds of AI were used for commercial and agricultural applications, representing 0.04% of all reported pesticide AIs (183.4 million pounds) and 0.3% of all herbicides (25.7 million pounds)<sup>1</sup>.

The total diquat use reported in California for the years 2008-2017 was 773,335 pounds (DPR, 2016; DPR, 2018b; DPR, 2019b). Of this amount, 6.2% was applied in aquatic areas.

Diquat labels allow for both ground and aerial applications to terrestrial and aquatic environments. PUR records show that diquat is applied primarily by ground equipment. The aquatic uses are as a general herbicide and algicide in ponds, lakes, reservoirs, residential backyards, and similar settings. For control of aquatic weeds, applications are made using hand-held equipment – handgun spray or subsurface injection (Formoli, 1993). Aerial applications to aquatic sites are practically nil; of the 11,141 pounds diquat AI applied aerially between 2008 and 2017, only 10 pounds were reportedly used in aquatic areas (DPR, 2016; DPR, 2018b; DPR, 2019b).

## Regulatory History – Department of Pesticide Regulation (DPR)

In 1994, DPR completed a risk characterization document (RCD) for pesticide products registered in California containing diquat as an active ingredient (Cochran *et al.*, 1994). This document, and the subsequent Addendum to the RCD (Cochran *et al.*, 1997), found no risks for residential exposures from swimming in diquat-treated water. The risks were calculated with the assumption of REI=1 day, as required by the registered product labels at that time. The RCD Addendum also concluded that the Margins of Exposure (MOEs) for all occupational and non-

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<sup>1</sup>[ftp://transfer.cdpr.ca.gov/pub/outgoing/pur/data/2017\\_PUR\\_report\\_textfiles/fig1\\_lbs\\_ai\\_types/fig1\\_lbs\\_ai\\_types.txt](ftp://transfer.cdpr.ca.gov/pub/outgoing/pur/data/2017_PUR_report_textfiles/fig1_lbs_ai_types/fig1_lbs_ai_types.txt), accessed August 8, 2019.

occupational exposures were greater than the Level of Concern (LOC) of 100 (Cochran *et al.*, 1997). DPR issued a Notice of Completion of Risk Assessment in April 1997 (Cortez, 1997).

## Regulatory History – U.S. EPA

In 1995, U.S. EPA prompted label revisions for diquat products based on its Reregistration Eligibility Decision for Diquat Dibromide (U.S. EPA, 1995). These revisions included both Worker Protection Standard (WPS)-covered uses and residential treatments. U.S. EPA retained the 1-day reentry interval (REI) for swimming in diquat-treated aquatic sites. After the submission of additional dermal toxicity and dermal absorption data by Syngenta, the registrant requested modifications to the existing labels. In 2002, U.S. EPA reduced some requirements for personal protective equipment and the REI for workers. The REI for “non-WPS uses other than aquatic and spot treatment” was reduced from 4 days to “when sprays are dry” (U.S. EPA, 2002).

In August 2016, U.S. EPA issued a revised human health exposure assessment in support of the registration review of diquat where the REI for swimming was listed as 0 days (U.S. EPA, 2016, p.61). For residential post-application (reentry) exposures in aquatic environments (swimming in ponds, lakes and reservoirs), U.S. EPA found dermal, inhalation and incidental ingestion MOEs above the LOC (U.S. EPA, 2016).

## Swimmer Exposure

Following the label changes from 2002 (U.S. EPA, 2002), some currently registered product labels either explicitly stipulate a 0 (zero) day REI for swimming in diquat-treated ponds, lakes, etc., or the swimming REI has been removed from the labels altogether. Although, it should be noted that some currently registered product labels continue to list an REI of 1 day for such treatments. This memorandum discusses how these changes may affect the risk for swimmer exposure to diquat in California.

DPR’s RCD Addendum (Cochran *et al.*, 1997) found MOEs well above the LOC for adults swimming in water previously treated with diquat products at the 1-day REI listed on the then-active labels. The MOE equaled 1,076 as a worst case (Table 2) (Cochran *et al.*, 1997) using the theoretical water concentration of 0.75 parts per million (ppm) at the 1-day REI, at an application rate of 4 lbs AI/acre-foot, and a dissipation half-life of 1 day (Formoli, 1993).

The swimmer exposure estimate used by Formoli (1993) was obtained by a method significantly different from the model published by U.S. EPA after the completion of DPR’s risk assessment (U.S. EPA, 2003; U.S. EPA, 2015a). In order to evaluate the swimmer risk associated with the removal of the REI from some labels, the swimmer exposure in this memorandum was estimated using the following information:

- theoretical diquat concentrations in water on the day of application, as the REI is 0 days on some current labels (1.5 mg/L = 1.5 ppm) (Formoli, 1993),

- assumption of no chemical decay, and
- two algorithms:
  - the method used in the Exposure Assessment Document (EAD) (Formoli, 1993) and
  - the SWIMODEL developed by U.S. EPA (U.S. EPA, 2003; U.S. EPA, 2015a).

Dermal and ingestion routes of exposure were included in both estimates. Inhalation exposure was not evaluated because of:

- 1) the low volatility of diquat (vapor pressure  $\ll 0.01$  mPa (Tomlin, 2009) approximately equivalent to  $\ll 7.5 \times 10^{-8}$  mm Hg)<sup>2</sup>, and
- 2) the U.S. EPA recommendation not to include the inhalation exposure route for swimming outdoors (U.S. EPA, 2003).

The following equations were used to calculate the dermal and incidental oral exposure with the SWIMODEL (U.S. EPA, 2003; U.S. EPA, 2015a):

- $Dose_{dermal} = [ET \times SA \times K_p \times C_w \times (1 \text{ L}/1,000 \text{ cm}^3)] / BW$ , where
  - $K_p = 10^{\log K_p}$  and  $\log K_p = -2.72 + 0.71 \times \log(K_{ow}) - 0.0061 \times MW$
- $Dose_{oral} = (ET \times IR \times C_w) / BW$

The inputs used for the swimmer exposure estimates in the SWIMODEL are listed in Table 1.

**Table 1. Inputs Recommended by SWIMODEL (U.S. EPA, 2003; U.S. EPA, 2015a) and Used by DPR for Estimating Swimmer Exposure to Diquat**

Input	Value	Remark/Reference
ET = Exposure time (hours)	1 hour	Default value (U.S. EPA, 2015a)
SA = Surface area of skin (cm <sup>2</sup> )	19,500 cm <sup>2</sup> (adults), 10,800 cm <sup>2</sup> (child, 6-11 yrs)	Default value (U.S. EPA, 2015a)
K <sub>p</sub> = Permeability coefficient (cm/hour)	8.22 x 10 <sup>-9</sup> cm/hr	Chemical-specific. Calculated from LogK <sub>p</sub> (see equation in text)
LogK <sub>ow</sub> = Octanol/water partition coefficient (unitless)	-4.6	Chemical-specific (Tomlin, 2009)
MW = Molecular weight	344.1	Chemical-specific (U.S. EPA, 2015b)
C <sub>w</sub> = Concentration in water (mg/L)	1.5 mg/L = 1.5 ppm	Chemical-specific. Theoretical concentration on the day of application (Formoli, 1993)
IR = Ingestion rate (L/hr)	0.025 L/hr (adult), 0.05 L/hr ((child)	Default value (U.S. EPA, 2003)
BW = Body weight (kg)	80 kg (adult), 32 kg (child, 6-11 yrs)	Default value (U.S. EPA, 2015a)

<sup>2</sup> Conversion mPa to mmHg: <http://www.advindsys.com/PressureConversionTable.htm>, accessed June 15, 2018.



The human health risk using the SWIMODEL algorithm was determined as:

$$\text{MOE} = \text{PoD} / [(\text{Dose}_{\text{dermal}} + \text{Dose}_{\text{oral}})]$$

where the toxicological point of departure (PoD) is the oral No-Observed-Adverse-Effect-Level (NOAEL) of 3 mg/kg/day (U.S. EPA, 2016). On the other hand, the algorithm used by DPR in the RCD Addendum utilized the dermal NOAEL of 100 mg/kg/day as a PoD (Cochran *et al.*, 1997). The swimmer risk estimates generated by DPR and U.S. EPA are summarized in Table 2.

**Table 2. Risk Estimates for Persons Swimming in Diquat-Treated Ponds and Lakes (Target MOE=10<sup>2</sup>)**

Age group	Algorithm	DPR		U.S. EPA (2016) <sup>c</sup>
		MOE before label changes (Cochran <i>et al.</i> , 1997) <sup>a</sup>	MOE after 2002 label changes <sup>b</sup>	
Swimmer adult	Diquat EAD/RCD <sup>d</sup> (Formoli, 1993; Cochran <i>et al.</i> , 1997)	1.1x10 <sup>3</sup>	0.5x10 <sup>3</sup>	N/A <sup>f</sup>
	SWIMODEL (U.S. EPA, 2003; U.S. EPA, 2015a) <sup>e</sup>	N/A	6.4x10 <sup>3</sup>	4.2x10 <sup>8</sup>
Swimmer child	SWIMODEL (U.S. EPA, 2003; U.S. EPA, 2015a) <sup>e</sup>	N/A	1.3x10 <sup>3</sup>	1.0x10 <sup>8</sup>

<sup>a</sup> Theoretical water concentration = 0.75 mg/L at REI = 1 day (Formoli, 1993). This estimate is more conservative than the point estimate measured post-application in aquatic dissipation study (Formoli, 1993).  
<sup>b</sup> Theoretical water concentration = 1.5 mg/L at REI = 0 day (Formoli, 1993).  
<sup>c</sup> Water concentration not specified. See text.  
<sup>d</sup> PoD = dermal NOAEL = 100 mg/kg/day (Cochran *et al.*, 1997).  
<sup>e</sup> PoD = oral NOAEL = 3 mg/kg/day (U.S. EPA, 2016).  
<sup>f</sup> N/A = Not applicable.

DPR used conservative assumptions in the swimmer exposure estimates. The theoretical water concentration used by DPR in both algorithms (Table 1) was 1.5 mg/L as assumed by Formoli (1993). This concentration is higher than the point estimate measured post-application in a diquat aquatic dissipation study (Formoli, 1993). In his exposure calculations, Formoli (1993) based this value on the maximum application rate (4 lbs AI/acre) at a non-specified depth. For comparison, U.S. EPA also assumed the maximum label application rate, but at a depth of 4 feet, representative of water bodies where people would swim (e.g., lakes, ponds) (U.S. EPA, 2016). The U.S. EPA document did not list a specific value for the water concentration of diquat used in the exposure assessment. DPR's calculations show that an application rate of 4 lbs AI/acre at a 4-foot depth is equivalent to 0.37 mg/L diquat. Another conservative assumption U.S. EPA made was the age group representative of children – 3-6 years old. DPR on the other hand, used the SWIMODEL-default child age of 6-11 years in calculating the risk estimate (Table 2).

As seen from Table 2, the estimates obtained by two independent algorithms and both DPR and U.S. EPA yield four-digit MOEs for persons swimming in diquat-treated waters when the exposure occurs on the day of diquat application (REI=0 days, according to some current diquat labels).

A query of DPR's Pesticide Illness Surveillance Program (PISP) database did not identify any swimmer illnesses related to the aquatic uses of diquat since the implementation of the PISP program in 1992 and up to 2016, the latest year with available PISP data (DPR, 2019c).

## Conclusions

Given the findings in this memorandum, the use of diquat products on aquatic sites does not pose any health impacts of concern to people swimming in treated waters (ponds, lakes, reservoirs, etc.). Consequently, no further mitigation is warranted for the swimmer exposure scenario.

## Acknowledgements

The contribution of Diana Le (DPR) to the collection and analysis of diquat product labels is appreciated. Drs. Lisa Ross (DPR, retired) and Michael Zeiss (DPR, retired) made valuable comments to the earlier versions of this manuscript.

## Attachment

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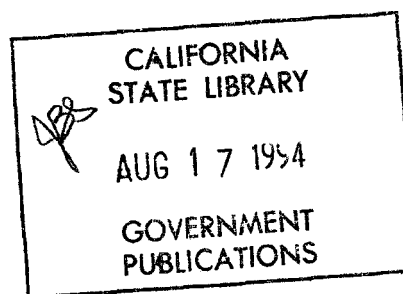
ATTACHMENT I

ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA  
TO THE PESTICIDE PRODUCTS THAT CONTAIN

DIQUAT DIBROMIDE

BY

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HS-1662, May 14, 1993



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ABSTRACT

Diquat dibromide is a non-selective, contact herbicide that is used in California mainly for desiccation of seed crops. It is also used for landscape maintenance, rights-of-way, and aquatic weed control. A total of 44 illnesses and injuries associated with the use of diquat dibromide were reported in California from 1984 through 1989. Most of these incidents occurred due to lack of required protective clothing and/or inadequate training. Prolonged dermal exposure to diquat dibromide can cause severe skin damage. Systemically absorbed diquat dibromide does not selectively accumulate in lung tissues. Diquat dibromide is excreted rapidly from the human body, primarily in urine, following an intravenous injection. Its dermal absorption rate is estimated at 1.4% in 24 hours in humans. Diquat dibromide exposure monitoring studies and surrogate data were used to estimate workers' absorbed daily dosages.

This report was prepared as Appendix B to the risk characterization document for diquat dibromide. The risk assessment is being conducted because of chronic, and developmental toxicities observed in toxicity testing in laboratory rats and rabbits.

## APPENDIX B

Department of Pesticide Regulation  
Worker Health and Safety Branch

Human Exposure Assessment

Diquat Dibromide

May 14, 1993

### CHEMICAL/PHYSICAL PROPERTIES

Diquat dibromide is the common name of 6,7-dihydrodipyrido (1,2-a: 2',1'-c) pyrazinediium dibromide. Its chemical formula is  $C_{12}H_{12}Br_2N_2$  with a molecular weight of 344.1 daltons. It is completely soluble in water, but insoluble in non-polar organic solvents. The solids melt at 300 °C. The technical material is available only as a liquid. Diquat dibromide is stable in neutral or acidic solutions, but unstable in alkaline solutions and is corrosive to metals. Diquat dibromide is a non-flammable, non-volatile product. Traces of ethylene dibromide are present in the technical material as manufacturing impurities. The word "diquat" used hereafter refers to diquat dibromide.

### U.S. EPA STATUS

In June 1986, the United States Environmental Protection Agency (U.S. EPA) issued a reregistration standard based on its assessment of the available data on diquat. The standard identified numerous data gaps, and therefore made conclusions that were subject to change. It concluded that (a) until additional required chronic toxicity data were made available and evaluated, diquat was not considered to cause oncogenic, teratogenic or reproductive effects; (b) the presence of ethylene dibromide as an impurity would not pose a significant risk to human health with the current uses of diquat; and (c) diquat appeared to be acutely toxic through dermal exposure. Consequently the U.S. EPA identified the missing data to be developed and determined certain label restrictions and revisions including a restricted use classification, signal word revision, dermal exposure precaution, crop rotation restriction, reentry interval and protective clothing requirements. As certain data were developed and reviewed, the U.S. EPA changed its position on some label restrictions, including restricted use classification, signal word change, and protective clothing requirements.

### USAGE

Diquat is a non-selective, contact herbicide that is used for desiccation of certain seed crops and potatoes. It is also used for non-crop and aquatic weed control. As of April 24, 1992, there were 36 products registered in California that contain diquat. The majority of these products are labeled for non-crop uses, mainly for industrial, home garden, right-of-ways, landscape maintenance and aquatic weed control. There are three agricultural products for use as desiccants on seed crops (alfalfa, clover, grain, and soybeans) and potatoes. Based on the pesticide use reports for 1990, a total of 105,650 lb. of diquat were used in California mostly on alfalfa (48% of the total use), rights-of-way (25%) and landscape maintenance (10%) (DPR, 1991). Aquatic use accounted only for approximately one percent of the total use. Diquat can be used by aerial or ground equipment for agricultural uses. Diquat applications to alfalfa are mainly by air. Diquat right-of-way applications are mostly made by the California Department of Transportation, and county and city employees using vehicle-mounted application equipment. Aquatic application is done by ground equipment.

## FORMULATION

All diquat products in California are liquid. The products for agricultural uses are 35.3% diquat formulations containing 2.0 lb. active ingredient (a.i. cation)/gal. The products for manufacturing uses are also 35.3% formulations. Other formulations are mostly 0.3% to 5.0% diquat. The rate of application is 0.25 to 0.5 lb. a.i. (cation) per acre for agricultural uses, 2.0 to 4.0 lb. a.i. (cation) per surface acre for aquatic uses and 0.5 to 1.0 lb a.i. (cation) in 100 gal. of water for non-crop terrestrial uses.

## LABEL PRECAUTIONS

Products with 35.3% diquat have the toxicity category II signal word of "warning" for their acute oral, dermal and inhalation toxicities. Formulations with lower than 35.3% diquat are either toxicity category II or III. Hazards of ingestion, inhalation and dermal contact have been indicated on these product labels. A statement of practical treatment is given for accidental exposures. The product labels require workers handling concentrated material to wear face shield or goggles, protective clothing, rubber gloves, rubber apron and shoe coverings impermeable to diquat. Waterproof footwear and clothing are required during spraying except for aquatic subsurface uses. 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. The use of treated water for domestic purposes, animal consumption, spraying and irrigation is prohibited for 14 days after application. Some product labels for home garden uses warn users to keep children and pets out of the treated area until spray mist has completely dried.

## WORKER ILLNESSES

A total of 44 illnesses and injuries associated with the use of diquat alone or in combination with other pesticides have been reported in California from 1984 through 1989 (Edmiston, 1990 and 1992). The incidents included eye injuries (16 cases), skin injuries (12 cases), eye/skin injuries (two cases) and systemic illnesses (13 cases). There was also one suicidal death from ingestion of diquat in 1989. Illnesses and injuries due to diquat alone accounted for 32 incidents (including three non-occupational), and four required hospitalization ranging from three to 19 days. The longest disability incurred was 74 days which resulted from a prolonged and extensive skin exposure, requiring skin grafting. Most of the worker illnesses and injuries were due to lack of required protective clothing and equipment, or/and inadequate training. Symptoms such as nausea, dyspnea, and dizziness have been reported. Skin or/and eye injuries such as rashes, burns, conjunctivitis as well as loss of toe nails were observed. Most of the incidents occurred to the pesticide applicators. Other incidents occurred during mixing/loading, foliar contact and incidental activities during handling.

## DERMAL TOXICITY

Data collected in 1966 on the handling of diquat indicate incidents of human skin discoloration and nose bleeding (Summary Report, 1966). These data were presented without further details. Severe skin burns as a result of prolonged and extensive exposure to diquat have also been reported (Manoguerra, 1990). Systemically absorbed diquat does not selectively accumulate in lung tissue and pulmonary injury by diquat is less prominent than by paraquat. Diquat has severe toxic effects on the central nervous system (Morgan, 1989). Damage and discoloration of fingernails caused by frequent exposure to concentrated solutions of diquat were also reported. Rashes, blisters and transient skin discoloration were reported as a result of exposure to the concentrated commercial preparation. Accidental ingestion of a small amount of diquat by a person caused diarrhea and oral ulceration (FAO, 1971). Breathing spray mist can cause nasal, throat and respiratory tract irritation (MIB, 1981). Diquat did not cause skin sensitization in guinea pigs tested with formulated products (Thompson, 1985 and Robbins, 1987).

## METABOLISM

Male albino Wistar rats were administered  $^{14}\text{C}$ -diquat by stomach tube (1.8 uCi, 45 mg/kg) or by subcutaneous injection (5.6 uCi, 10 mg/kg) and kept in metabolism cages for four days (Mills, 1976). Urine and feces were collected daily and analyzed collectively from groups of five rats using a liquid scintillation spectrometer. Rats that were given a single oral dose excreted 6.3% and 89.3% of the administered radioactivity in the urine and feces, respectively, within four days, mainly as diquat. Urine contained 5.1% diquat, and 0.2% diquat monopyridone and 0.1% diquat dipyrindone (diquat metabolites). Feces contained 57% diquat and 4.1% monopyridone. Rats that received a subcutaneous injection excreted 87.1% and 4.8% of the administered radioactivity in urine and feces, respectively, within four days, mainly as diquat.

Tissue distribution of diquat was studied in male and female albino Wistar rats (Litchfield, 1973). Rats were fed diquat (250 ppm diquat cation) in their diet. A group of 10 rats were sacrificed at two, four, and eight weeks. The brain, lungs, liver, kidneys, hind leg muscles, stomach, small and large intestines were analyzed for diquat using colorimetric determination. Recovery of diquat injected into the tissue was 90 - 95%. Diquat presence in tissues was measurable in two weeks. No sex differences were observed. Diquat tissue concentration was generally lower than that of paraquat, particularly in lungs. No diquat was detected in tissues (MDL of 0.05 ug/g) within one week of return to a normal diet.

Male mice were subcutaneously injected with 0.2 mL  $^{14}\text{C}$ -diquat, 50 mg cation/kg. Two mice were killed by exposure to diethyl-ether at 10 minutes, one hour, 24 hours, and 72 hours after the injection (Litchfield, 1973). Whole body autoradiography showed that radioactivity was distributed throughout most tissues at 10 minutes. Radioactivity level declined in most tissues but intestinal epithelium and urine radioactivity increased at one hour. At 24 hours, radioactivity was observed only in the small and large intestines and bladder. At 72 hours, radioactivity was observed only in stomach and intestinal contents.

A British Saana goat was administered a single oral dose of 145 mg/kg diquat ion (Griggs, 1970). Milk and excreta were collected daily. Samples were analyzed by scintillation counting using a Packard Tricarb spectrometer. Approximately 96% of the radioactive dose was recovered in feces (94%), urine (2%), and milk (traces) within seven days, mainly as diquat.

A single oral dose (20 or 5 mg/kg) of  $^{14}\text{C}$ -diquat was given to a cow (Stevens, 1966). Only traces (0.001 to 0.015%) of the administered dose was found in milk and 2.6% in urine in seven days. Tissues and organs of a 120-Kg calf slaughtered 24 hours after dosing with 1.38 g of ethylene bridged-labeled  $^{14}\text{C}$ -diquat were analyzed. The kidney and liver contained 0.66 ppm and 0.21 ppm diquat residues, respectively. Other tissues and organs contained <0.05 ppm diquat residues.

In order to determine the extent of human elimination of diquat in urine, a dose of one uCi  $^{14}\text{C}$ -diquat was administered intravenously (iv) to six male human volunteers (Feldmann, 1974). Urine samples were collected for five days at four-hour intervals followed by a 12-hour interval in the first day and every 24 hours for the remaining four days. Samples were analyzed by wet ashing 5 mL of the urine and trapping all of the carbon as carbon dioxide ( $\text{CO}_2$ ) in ethanolamine. The trapped  $\text{CO}_2$  was diluted and counted with a scintillation counter. Total urinary elimination was measured at  $61.2 \pm 16.0\%$  of the administered dose in five days. Approximately 90% of the excreted dose was eliminated in the first 24 hours following administration.

## DERMAL ABSORPTION

### In Vitro:

Dermal absorption of diquat has been studied in vitro in humans and animals, using glass diffusion cells (Corrigan, 1989(a)). Human abdominal or rat dorsal whole skin was taken post mortem and mounted in the diffusion cell between the donor and receptor chambers. Different dilutions of diquat (1 mg/mL, 5 mg/mL, and 50 mg/mL) were applied to the skin at the rate of 0.1 mL/cm<sup>2</sup>.  $^{14}\text{C}$ -diquat was diluted in these solutions to a final activity of about 4 uCi/mL. A Betamatic II liquid scintillation spectrometer was used for analysis. A measured



volume of 0.9% saline was placed into the receptor chamber. Samples of 50 uL were taken from the receptor chamber at different time intervals. A lag time of about two hours for rat skin and 15 hours for human skin was observed until initial absorption. The initial period of increasing absorption was followed by a steady state. A steady state absorption rate was calculated for each dilution as shown in Table 1.

Table 1

In Vitro Dermal Absorption of Diquat  
In Human and in Rat

# of reps.	Dilution mg/mL	Application Rate (mg/cm <sup>2</sup> )	Dermal Absorption Rate		
			ug/cm <sup>2</sup> /hr	ug/cm <sup>2</sup> /24 hrs	%/24 hrs
<u>Human:</u>					
7	1	0.1	0.06	1.44	1.44
8	5	0.5	0.18	4.32	0.86
7	50	5.0	0.98	23.54	0.47
<u>Rat:</u>					
6	1	0.1	0.23	5.54	5.52
5	5	0.5	1.01	24.24	4.85
5	50	5.0	9.55	229.20	4.58

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Similar in vitro dermal absorption studies with human skin, using different dilutions of diquat, have resulted in dermal absorption rates that ranged from 0.18 to 1.4% (Corrigan, 1989(b), Scott, 1985).

In Vivo:

Dermal absorption of diquat was studied in rats (Brorby, 1988). <sup>14</sup>C- labeled diquat was dissolved in water and applied (0.05 mg, 0.5 mg, and 5.0 mg) to the shaved dorsal trunk of rats. Urine, feces, and volatiles were collected following the dermal treatment. Approximately 2.5%, 3.6%, and 3.4% of the applied dose were systemically absorbed in 24 hours in rats treated with 0.05 mg, 0.5 mg, and 5.0 mg of <sup>14</sup>C-labeled diquat, respectively.

Human dermal absorption of diquat was also studied in vivo (Feldmann, 1974). <sup>14</sup>C-diquat was applied to the ventral forearm of six normal male human volunteers at four ug/cm<sup>2</sup>. This is equivalent to a thin film of 0.25% diquat solution. The dose was dissolved in a small amount of acetone and applied to the skin. The acetone was evaporated by gentle blowing during application. The application sites remained unoccluded. The volunteers were advised not to wash their forearms for 24 hours. Urine samples were collected for five days at three four-hour intervals followed by a 12-hour interval during the first day and every 24 hours for the remaining four days. Samples were analyzed by wet ashing 5 mL of the urine and trapping all of the carbon as carbon dioxide (CO<sub>2</sub>) in ethanolamine. The trapped CO<sub>2</sub> was diluted and counted with a scintillation counter. The results were corrected for incomplete urinary excretion of diquat. Only 0.3 ± 0.1% of the administered dose was recovered in five days.

In evaluating the parameters affecting dermal absorption, it was noted that occluding the application site increased diquat dermal absorption by 3.5 fold to 1.4% (Wester, 1985). Damaged skin absorbed 9.5 fold more diquat (3.8%) than non-occluded normal skin of human volunteers. A dermal absorption of 1.4% will be used in calculating diquat absorbed daily dosages for regulatory purposes.

## WORKER EXPOSURE

### Aquatic Use

Workers were monitored during normal applications of diquat for aquatic weed control (Wojeck, 1983). Each worker wore a long- or short-sleeved shirt, long trousers, socks and heavy shoes or boots. Two application methods were used.

For control of water hyacinths and other floating vegetation, diquat was applied from an airboat by two workers, an applicator using hand-operated spray equipment and a driver. Diquat (35.3% a.i.) was used at a rate of 1 qt. formulated product per acre (final spray mixture of 1.76% diquat). Another aquatic herbicide, Komeen<sup>R</sup> (2 qt./acre) was also used as a tank mix with diquat.

For control of hydrilla, diquat was injected into the water at a rate of 2 gal. formulated product per acre (final spray mixture of 4.41% diquat), using an invert system. The crew for this method consisted of a gloved mixer who prepared the tank mix on the shore and an applicator who drove the airboat and injected the diquat into the water. The applicator also assisted in pumping the spray mixture to the tank on the boat.

Workers applied diquat two to five hours/day, four days a week. There were three handgun spray crews and one invert system crew. The workers were monitored three times over a three-month period. Potential dermal exposure of workers was monitored by placing dermal alpha-cellulose pads at 10 locations on the body outside of the clothing. Hand exposure was estimated from two consecutive hand rinses with 100 mL water or from patches that were cut from palms and backs of cotton sampling gloves worn by each worker. Anderson air samplers with polyurethane foam plugs were used to collect air samples near the breathing zone of workers. Urine samples were also collected, once prior to the monitoring and then each day during the monitoring study.

Diquat recoveries from cotton gloves and alpha-cellulose pads were 94% and 93%, respectively. The recovery from foam plugs was 80%. Samples were analyzed using a Beckman DK-2A spectrophotometer. Urine samples were analyzed separately. Diquat in urine ranged from 0.007 to 0.047 ppm. Respiratory exposure was reported <0.1% of the total body exposure. Workers' potential dermal exposure was estimated from residues found on the alpha-cellulose pads and cotton gloves or hand rinses. Potential dermal exposure in Table 2 was calculated according to the body regions and surface areas described in the U.S. EPA Guidelines, Subdivision U. Gloves as a medium to assess hand exposure typically overestimate that exposure by up to nine fold (Smith, 1991).

Table 2

## Estimate of Mixer/Loaders and Applicators' Exposure to Diquat During Application of Aquatic Weed

	Handgun Application (0.5 lb. a.i./acre)		Invert Application (4.0 lb. a.i./acre)	
	Applicator	Boat Driver	Applicator	Mixer
n	9	9	3	3
Body Exposure:	ug/hr	ug/hr	ug/hr	ug/hr
Head & Neck	34.2	7.8	27.1	7.8
Hand	393.6	123.0	73.8	90.2
Rest of Body	1,429	118.1	256.3	384.1
Potential Daily Dermal Exposure (ug/person/day)	14,850	1,991	2,858	3,857
Daily Dermal Exposure (ug/person/day)	4,565	1,141	1,012	1,091
Absorbed Daily Dosage (ug/kg/day)	3.6*	0.9*	0.2	0.2

Based on: Non-detected samples at half of MDL, MDL = 0.01 ug/cm<sup>2</sup>, 8-hour workday, body weight of 70 kg, and dermal absorption of 1.4%.

\* - Corrected for the highest label rate (2 lb. a.i./acre) for floating weeds.

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#### Terrestrial Crop and Non-Crop Uses

Diquat worker exposure data are very limited. In the absence of worker exposure data for diquat, paraquat worker exposure data would be a suitable surrogate. Paraquat is also a bipyridylum herbicide that has chemical and physical properties and use patterns similar to that of diquat. The application equipment is also similar for these two products, except a closed mixing and loading system is required when handling paraquat. A closed mixing and loading system is not a requirement for handling diquat. The exposure to a mixer/loader during ground application can be conservatively estimated from the exposure data for mixer/loaders of diquat during aerial application.

Only one worker exposure study of terrestrial use of diquat was available. This study was published in the open literature in German (Sawinsky, 1977). A summary is available in English. The study monitored workers' exposure during aerial application of diquat. It did not describe the rate of application or the type of protective clothing and equipment worn by the workers. Air samples taken from the cockpit contained a mean value of 4.5 ug/m<sup>3</sup> diquat and residue samples taken from pilots' clothing contained a mean value of 61.5 ug/100 cm<sup>2</sup> diquat during the four hours of monitoring. No residues were detected in the cockpit air when the air filter and ventilation were in operation. Clothing samples of the mixer and the loader contained 3500 ug/100 cm<sup>2</sup> and 8700 ug/100 cm<sup>2</sup> diquat, respectively, during the monitoring period. Urine samples were taken only from the ground crew. Urinary diquat residues ranged from non-detectable levels to 30 ug/100 mL sample. The mixer's and the loader's mean urinary diquat were 6.3 ug/100 mL and 19.6 ug/100 mL, respectively. Workers' dermal exposure can not be estimated from residues on clothing samples since it was not clear whether sufficient number of samples

were taken from various parts of the clothing. The mixer and the loader exposures were estimated from residues found in their urine, corrected for incomplete diquat urinary excretion (Feldmann, 1974) and 1400 mL daily urinary output (Guyton, 1969). The mixer and the loader Absorbed Daily Dosages were 4.1 ug/kg/day and 12.8 ug/kg/day, respectively, assuming that all the protective clothing and equipment described in the U.S. product label were worn.

A worker exposure study of paraquat during an aerial application to cotton was conducted in the San Joaquin Valley in 1979 to estimate the exposure of pilots, mixer/loaders, and flaggers (Chester, 1981). This study was used as a surrogate to estimate the exposure of pilots and flaggers to diquat during aerial application. Mixer/loaders' exposure can not be estimated from this study since a closed mixing/loading system was used.

One pint of Ortho Paraquat CL containing 1.4 lb. a.i./gallon was used in 10 gallons of water with one pint of X-77 (as an adjuvant) and three to four lb. of Tumble Leaf<sup>R</sup> (sodium chlorate) as a defoliant per acre on the first trial. Only Ortho Paraquat CL and X-77 were used in the second trial. A total of 1200 acres of cotton were sprayed using a Thrush Commander aircraft. Mixing and loading were done using a closed system. The pilots' clothing consisted of open necked short-sleeved shirt, T-shirt, long trousers, boots and hat. Flaggers wore protective cotton coveralls over normal clothing. Dermal exposure pads consisting of polythene-backed 100 cm<sup>2</sup> Whatman 542 filter papers were attached to the skin or clothing with adhesive tape at various locations. Hand exposure of the pilots and the flaggers was evaluated using bleached cotton gloves. Penetration through normal work clothing and protective clothing was evaluated by using white cotton T-shirts and by placing cotton Tubigrips (elasticized tubular support bandages) on the left leg (ankle to top of thigh) of each individual. Air samples from the breathing zones of workers were collected using personal air samplers to determine respiratory exposure. Body parts surface area and total dermal exposure were calculated according to methods described in subdivision U of the EPA Applicator Exposure Guideline. Respiratory exposure was calculated using the instrument sampling rates and duration of exposure. The instrument sampling rate (three liters/minute) was corrected for human breathing rate (29 liters/minute) during light work (EPA Worker Exposure Guideline, Subdivision U). Dermal and inhalation exposure of these workers to paraquat was used to estimate diquat exposure in Table 3.

Table 3  
Diquat Aerial Application Crew Estimated  
Exposure Using Paraquat Data as Surrogate

<u>Trial I</u>				
Work Title Sex	Flagger 1 Female (ug/dav)	Flagger 2 Female (ug/dav)	Pilot 1 Male (ug/dav)	Pilot 2 Male (ug/dav)
Head,Face,Neck	7,877	431.5	14.9	14.9
Hand	2,256	163.2	460.8	249.6
Body	2,464	344.9	531.4	276.0
Daily Dermal Exposure	12,600	940.0	1,007	540.0
Absorbed Daily Dermal Dosage	176.4	13.1	14.1	7.6
Daily Resp. Exp.	202.2	0.4	0.7	0.7
ADD (ug/kg/dav)	5.0	0.2	0.2	0.1
ADD Adjusted for 1/2 lb. a.i./acre (ug/kg/dav)	14.5	0.7	0.6	0.3

<u>Trial II</u>				
Work Title Sex	Flagger 1 Female (ug/dav)	Flagger 2 Female (ug/dav)	Pilot 1 Male (ug/dav)	Pilot 2 Male (ug/dav)
Head,Face,Neck	16,260	752.6	19.8	19.8
Hand	3,392	123.5	1,344	185.6
Body	1,544	1,016	592.0	361.6
Daily Dermal Exposure	21,190	1,892	1,956	567.0
Absorbed Daily Dermal Dosage	296.7	26.5	27.4	7.9
Daily Resp. Exp.	0.5	25.3	0.9	5.6
ADD (ug/kg/dav)	5.4	0.7	0.4	0.2
ADD Adjusted for 1/2 lb. a.i./acre (ug/kg/dav)	15.5	2.0	1.1	0.4

Note: Clothing penetration of 5% for upper arms and forearms was assumed based on chest and back pad ratio to the T-shirt for flaggers. Upper arms and forearms of pilots assumed 100 percent dermal exposure since they wore short-sleeved shirts. Respiratory uptake of 50% (Raabe, 1988) and dermal absorption rate of 1.4% (see dermal absorption section of this document). An eight-hour work day, and body weights of 54.8 kg for females and 70 kg for males were assumed.

### Ground Applicator Exposure

Diquat ground applicators' exposure was estimated using a study conducted in Florida where applicators were monitored for dermal and respiratory exposure to paraquat during post-harvest treatment of tomatoes (Wojeck, 1983). Ortho Paraquat CI (29.1% a.i.) was applied by enclosed cab tractors, normal clearance tractors without cabs, or by high-clearance tractors without cabs. Applicators on high-clearance tractors sat about two feet above the horizontal boom, while applicators on normal clearance sat one foot above the horizontal boom. The rate of application was 0.5 lb. of a.i. per acre. Applicators wore long- or short-sleeved shirts, long trousers, socks, and heavy shoes or boots.

Dermal alpha-cellulose pads (100 cm<sup>2</sup>) were attached to various parts of the body outside of workers' clothing. Hand exposure was estimated from two consecutive hand washes in water, or from areas cut from the palm and back of a pair of cotton sampling gloves. Respiratory exposure was measured by using Willson "Dustite" respirators fitted with 16-ply gauze backed with filter pads. Workers wore the dermal exposure pads, gloves, and respirators during the entire spray operation. Dermal exposure was calculated based on surface areas for regions of the body as outlined in the EPA Worker Exposure Guideline, Subdivision U. The results are shown in Table 4.

Table 4  
Diquat Ground Boom Applicator Exposure Estimated  
from Paraquat Boom Application on Tomatoes.

Tractor type	Applicators on normal clearance <u>without cab</u>	Applicators on normal clearance <u>enclosed cab</u>	Applicators on high clearance <u>without cab</u>
lb. a.i./acre	0.5	0.5	0.5
No. of replications	4	2	2
<u>Body Region</u>	<u>(mg/dav)</u>	<u>(mg/dav)</u>	<u>(mg/dav)</u>
Head, Face, Neck	99.9	3.36	0.16
Hand	303.8	22.08	12.88
Body	131.5	18.48	14.72
Daily Dermal Exposure	535.2	43.92	27.76
Respiratory Exp.	0.6	0.08	0.16
Absorbed Daily Dermal Dosage	7.5	0.61	0.39
Absorbed Daily Dosage (ADD)	<u>(ug/kg/dav)</u> 111.0	<u>(ug/kg/dav)</u> 9.4	<u>(ug/kg/dav)</u> 6.7

- Assumptions: Clothing protection of 90%, dermal absorption rate of 1.4%, and inhalation uptake of 50%.

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### Home Garden and Landscape Use

No human exposure data are available for home garden or landscape uses of diquat. A human exposure study of paraquat during garden and yard application was used as surrogate to estimate the exposure of garden and landscape workers applying diquat (Staiff, 1975). A 0.44% paraquat pressurized product was applied by volunteers as spot treatment to control weeds in gardens and yards. Applicators' potential dermal exposure was monitored by attaching alpha-cellulose pads to various parts of the body or clothing. Hand exposure was measured by rinsing hands in water. Respiratory exposure was measured by using filter pads (not specified) in the respirators

worn by workers. A total of 15 exposure situations were studied. The volunteers wore no gloves or hats. Almost all exposure was on the hands. Only traces ( $<1.0 \text{ ug/cm}^2$ ) of paraquat were found on the lower legs. Respiratory exposure values were below the detection limit except for one sample containing  $0.8 \text{ ug}$  paraquat. Dermal exposure was calculated based on residues on the hands. Dermal exposure ranged from  $0.01 \text{ mg/hr}$  to  $0.57 \text{ mg/hr}$  with a mean of  $0.29 \text{ mg/hr}$ . Diquat garden and landscape workers' absorbed daily dosage (ADD) was estimated to range from  $0.01$  to  $0.8 \text{ ug/kg/7-hour workday}$ , with a mean of  $0.4 \text{ ug/kg/7-hour workday}$ .

The exposure of applicators using hand-held equipment such as knapsack sprayers was estimated based on the exposure values of workers who applied 2, 4-D (Abbott, 1987). Workers ( $n=2$ ) loaded premixed 2, 4-D into knapsack tanks and then applied the herbicide using the knapsack sprayers. Dermal exposure was measured by obtaining clothing samples from representative body parts. Gloves were used to measure hand exposure. The mean dermal exposure during loading from a total of eight replicates was  $32.4 \text{ mg/lb. a.i.}$ , assuming the workers wore long-sleeved shirts and long pants. The mean dermal exposure during application from a total of 12 replicates was  $30.2 \text{ mg/lb. a.i.}$ , assuming the workers wore long-sleeved shirts and long pants. The absorbed daily dosage for a worker loading and applying  $1 \text{ lb. a.i.}$  diquat in a day was calculated to be  $12.5 \text{ ug/kg/day}$ , assuming 90% clothing protection to the covered body areas, 1.4% dermal absorption and negligible inhalation exposure.

#### Right-of-Way Use

Diquat right-of-way application is mostly made by California Department of Transportation, county, and city employees using truck-mounted boom sprayers with enclosed cabs. These vehicle-mounted sprayers function similar to a high-clearance enclosed cab tractors. A conservative estimate of diquat exposure of right-of-way applicators can be made based on the estimated exposure for applicators using high-clearance open cab tractors.

#### Drift

A diquat drift monitoring study, performed in Davis, California, showed residues on the fallout sheet and the air samples at downwind collection stations as far as 1,600 meters from the application site (Akersson, 1986). Diquat was sprayed from a height of five feet using a Weatherly 210 type aircraft at a speed of 100 to 110 miles/hour. The air sampling data were not defined adequately to estimate bystander's inhalation exposure to diquat, but the similarity of drift pattern between diquat and paraquat was evident. Paraquat drift data indicated air residues of  $16.7 \text{ ug/m}^3$  and  $0.5 \text{ ug/m}^3$  at 50 meters and 1600 meters respectively downwind of an aerial application at a rate of  $0.18 \text{ lb. a.i./acre}$  (Chester et al. 1981). Using paraquat drift data, bystander's ADDs at 50 meters and 1600 meters downwind from an aerial application ( $0.5 \text{ lb. a.i./acre}$ ) of diquat were estimated to be  $4.6 \text{ ug/kg/day}$  and  $0.1 \text{ ug/kg/day}$ , respectively.

#### Aquatic Dissipation

Aquatic dissipation of diquat was studied at two locations in Florida. Diquat was used at a rate of  $4 \text{ lb. a.i./acre}$  as surface treatment (Fujie, 1988). Four applications were made at each location at 30-day intervals. The ponds had no or very little outflow. Water samples were taken from top, middle and bottom of the pond. Water and sediment samples were taken prior to the first application and continued for about 30 days after each application. After the fourth application, sediment sampling continued for 180 days. Sample analysis indicated that diquat was distributed in all depths one day after application. Diquat dissipated rapidly from the water at both locations. Diquat concentration in water eight hours after the application ranged from  $0.06$  to  $0.12 \text{ ug/mL}$ . The concentration dropped to a range of  $0.02$  to  $0.09 \text{ ug/mL}$  24 hours after the application and to a range of  $<0.004$  to  $0.02 \text{ ug/mL}$  seven days after the application. The half-life at both sites ranged from 0.7 to 2.3 days ( $r = 0.96-0.99$ ) with an arithmetic mean of 1.2 days. Sediment data reflected high variability. Samples taken 180 days after the last application showed little or no degradation from the levels found at seven days after the last application, indicating strong binding of diquat to the clay.

Diquat exposure to a swimmer from treated water is estimated based on a maximum application rate of  $4 \text{ lb. a.i./acre foot}$  ( $1.5 \text{ ppm}$ ). Dermal and ingestion are the primary routes of exposure. The reentry interval to treated water for swimming is 24 hours. In most dermal absorption studies (both in vivo and in vitro) a volume of  $0.1 \text{ mL}$  is applied to a skin area of  $1 \text{ cm}^2$  as an ideal dermal exposure for a period of 24 hours (Corrigan, 1989a,b, Feldmann, 1974). This rate is equivalent to a thin film of the solution covering the skin area. Dermal exposure to diquat during swimming in treated water is comparable to the ideal  $0.1 \text{ mL/cm}^2$  dermal exposure accommodated

for dermal absorption studies. At this rate, the dermal exposure to a 70-kg human with a skin surface area of 21,110 cm<sup>2</sup> is 2,111 mL of treated water.

Two scenarios were used to estimate diquat exposure to a swimmer spending four hours a day in the treated water. The first scenario assumes the theoretical maximum concentration of 1.5 ppm reached immediately following diquat application and this initial concentration drops to 0.75 ppm at its half-life of 1.2 days after the application. The second scenario is based on the actual measured concentration of 0.09 ppm in the water that was observed in the above dissipation study 24 hours following the application. Absorbed daily dosages (ADD) from dermal and oral routes for the above two scenarios are shown in Table 5.

Table 5

Estimate of Diquat Exposure to Swimmers from Treated Water

Scenario #	Concentration at reentry ug/mL	Water volume available for dermal exposure mL/person	Dermal exposure ug/person	Oral exposure ug/person	ADD ug/kg/day
1	0.75	2111	1583	75	1.39
2	0.09	2111	190	9	0.17

Based on: Dermal absorption rate of 1.4%, ingestion of 100 mL of treated water, body weight of 70 kg and four hours of exposure/day.

Formoli, WH&S, 1993



Table 6

## Diquat Workers Estimated Lifetime Average Daily Dosage

<u>Work Task</u>	<u>Use</u>	ADD (ug/kg/day)	AADD* (ug/kg/day)	LADD** (ug/kg/day)
Applicator Normal clearance without cab	Ground	111.0	4.56	2.61
Applicator Normal clearance enclosed cab	Ground	9.4	0.39	0.22
Applicator High clearance without cab	Ground	6.7	0.27	0.16
Flagger	Aerial	8.2	0.22	0.13
Pilot	Aerial	0.6	0.02	0.01
Loader***	Aerial	12.8	0.35	0.20
Mixer***	Aerial	4.1	0.11	0.06
Applicator (Ready-to-use)****	Garden/Landscape	0.4	0.02	0.009
Applicator (Knapsack)****	Garden/Landscape	12.5	0.74	0.42
Applicator	Right-of-way	6.7	0.05	0.026
Applicator (handgun)	Aquatic	3.6	0.10	0.06
Boat Driver (handgun)	Aquatic	0.9	0.02	0.01
Applicator (injection)	Aquatic	0.2	0.005	0.003
Mixer (injection)	Aquatic	0.2	0.005	0.003
Swimmer	Aquatic	0.2-1.4	0.001-0.008	0.0006-0.004
Bystander(50 meters)	Aerial	4.6	0.13	0.072
Bystander(1600 meters)	Aerial	0.1	0.003	0.002

Except as noted, the ADD values are estimated based on the product label highest rate of application and an eight-hour workday. The ADD for the bystanders is from inhalation route only. Applicators wore long-sleeved shirts, long trousers and footwear. Pilots wore short-sleeved shirts, T-shirts, long trousers, boots, and hats. Flaggers wore normal clothing and coveralls.

\* Based on estimated diquat yearly exposure of 15 days for ground workers including garden/landscape, 10 days for aerial and aquatic workers (Ibarra, 1992; Mukai, 1992), 2.5 days for right-of-way workers (Haskell, 1993), and 2 days for swimmers.

\*\* A 40-year work period in a lifetime.

\*\*\* The application rate and clothing protection were not provided.

\*\*\*\* A seven-hour workday.

Formoli, WH&S, 1992

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