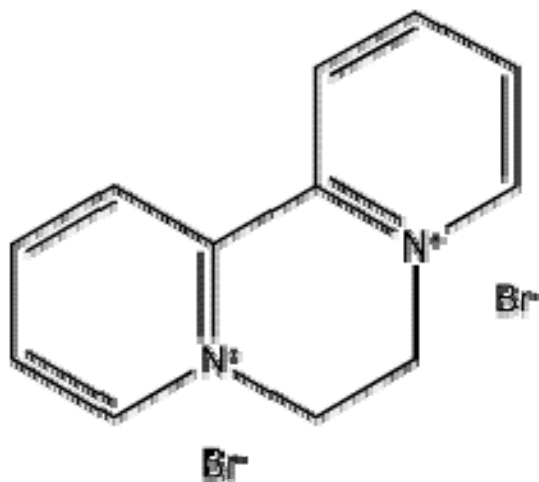


Risks of Diquat Dibromide Use to the Federally Threatened Delta Smelt (*Hypomesus transpacificus*)

Pesticide Effects Determinations

PC Code: 032201

CAS Number: 85-00-7



CAS Name: 6,7-dihydrodipyrido(1,2-a:2',1'-c)pyrazinediium dibromide

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List of Commonly Used Abbreviations and Nomenclature

µg/kg	Symbol for “micrograms per kilogram”
µg/L	Symbol for “micrograms per liter”
°C	Symbol for “degrees Celsius”
AAPCO	Association of American Pesticide Control Officials
a.i.	Active Ingredient
AIMS	Avian Monitoring Information System
Acc#	Accession Number
amu	Atomic Mass Unit
BCB	Bay Checkerspot Butterfly
BCF	Bioconcentration Factor
BEAD	Biological and Economic Analysis Division
bw	Body Weight
CAM	Chemical Application Method
CARB	California Air Resources Board
CAW	California Alameda Whipsnake
CBD	Center for Biological Diversity
CCR	California Clapper Rail
CDPR	California Department of Pesticide Regulation
CDPR-PUR	California Department of Pesticide Regulation Pesticide Use Reporting Database
CFWS	California Freshwater Shrimp
CI	Confidence Interval
CL	Confidence Limit
CTS	California Tiger Salamander
CTS-CC	California Tiger Salamander Central California Distinct Population Segment
CTS-SB	California Tiger Salamander Santa Barbara County Distinct Population Segment
CTS-SC	California Tiger Salamander Sonoma County Distinct Population Segment
DS	Delta Smelt
EC	Emulsifiable Concentrate
EC ₀₅	5% Effect Concentration
EC ₂₅	25% Effect Concentration
EC ₅₀	50% (or Median) Effect Concentration

ECOTOX	EPA managed database of Ecotoxicology data
EEC	Estimated Environmental Concentration
EFED	Environmental Fate and Effects Division
<i>e.g.</i>	Latin <i>exempli gratia</i> (“for example”)
EIM	Environmental Information Management System
EPI	Estimation Programs Interface
ESU	Evolutionarily significant unit
<i>et al.</i>	Latin <i>et alii</i> (“and others”)
<i>etc.</i>	Latin <i>et cetera</i> (“and the rest” or “and so forth”)
EUP	End Use Product
EXAMS	Exposure Analysis Modeling System
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
FQPA	Food Quality Protection Act
ft	Feet
GENEEC	Generic Estimated Exposure Concentration model
HPLC	High Pressure Liquid Chromatography
IC ₀₅	5% Inhibition Concentration
IC ₅₀	50% (or median) Inhibition Concentration
<i>i.e.</i>	Latin for <i>id est</i> (“that is”)
IECV1.1	Individual Effect Chance Model Version 1.1
KABAM	<u>K</u> _{OW} (based) <u>A</u> quatic <u>B</u> io <u>A</u> ccumulation <u>M</u> odel
kg	Kilogram(s)
kJ/mole	Kilojoules per mole
km	Kilometer(s)
K _{AW}	Air-water Partition Coefficient
K _d	Solid-water Distribution Coefficient
K _F	Freundlich Solid-Water Distribution Coefficient
K _{OC}	Organic-carbon Partition Coefficient
K _{OW}	Octanol–water Partition Coefficient
LAA	Likely to Adversely Affect
lb a.i./A	Pound(s) of active ingredient per acre
LC ₅₀	50% (or Median) Lethal Concentration
LD ₅₀	50% (or Median) Lethal Dose
LOAEC	Lowest Observable Adverse Effect Concentration
LOAEL	Lowest Observable Adverse Effect Level
LOC	Level of Concern

LOD	Level of Detection
LOEC	Lowest Observable Effect Concentration
LOQ	Level of Quantitation
m	Meter(s)
MA	May Affect
MATC	Maximum Acceptable Toxicant Concentration
m ² /day	Square Meters per Days
ME	Microencapsulated
mg	Milligram(s)
mg/kg	Milligrams per kilogram (equivalent to ppm)
mg/L	Milligrams per liter (equivalent to ppm)
mi	Mile(s)
mmHg	Millimeter of mercury
MRID	Master Record Identification Number
MW	Molecular Weight
n/a	Not applicable
NASS	National Agricultural Statistics Service
NAWQA	National Water Quality Assessment
NCOD	National Contaminant Occurrence Database
NE	No Effect
NLAA	Not Likely to Adversely Affect
NLCD	National Land Cover Dataset
NMFS	National Marine Fisheries Service
NOAA	National Oceanic and Atmospheric Administration
NOAEC	No Observable Adverse Effect Concentration
NOAEL	No Observable Adverse Effect Level
NOEC	No Observable Effect Concentration
NRCS	Natural Resources Conservation Service
OPP	Office of Pesticide Programs
OPPTS	Office of Prevention, Pesticides and Toxic Substances
ORD	Office of Research and Development
PCE	Primary Constituent Element
pH	Symbol for the negative logarithm of the hydrogen ion activity in an aqueous solution, dimensionless
pKa	Symbol for the negative logarithm of the acid dissociation constant, dimensionless

ppb	Parts per Billion (equivalent to µg/L or µg/kg)
ppm	Parts per Million (equivalent to mg/L or mg/kg)
PRD	Pesticide Re-Evaluation Division
PRZM	Pesticide Root Zone Model
ROW	Right of Way
RQ	Risk Quotient
SFGS	San Francisco Garter Snake
SJKF	San Joaquine Kit Fox
SLN	Special Local Need
SMHM	Salt Marsh Harvest Mouse
TG	Tidewater Goby
T-HERPS	Terrestrial Herpetofaunal Exposure Residue Program Simulation
T-REX	Terrestrial Residue Exposure Model
UCL	Upper Confidence Limit
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
VELB	Valley Elderberry Longhorn Beetle
WP	Wettable Powder
wt	Weight

1 Executive Summary

1.1 Purpose of Assessment

The purpose of this assessment is to evaluate potential direct and indirect effects on the Delta smelt (*Hypomesus transpacificus*, DS) arising from FIFRA regulatory actions regarding use of diquat dibromide on agricultural and non-agricultural sites. In addition, this assessment evaluates whether these actions can be expected to result in modification of designated critical habitat for the DS. This assessment was completed in accordance with the U.S. Fish and Wildlife Service (USFWS) and National Marine Fisheries Service (NMFS) *Endangered Species Consultation Handbook* (USFWS/NMFS, 1998), procedures outlined in the Agency's Overview Document (USEPA, 2004), and consistent with a suit in which diquat dibromide was alleged to be of concern to the DS (*Center for Biological Diversity (CBD) vs. EPA et al.* (Case No. 07-2794-JCS)).

The DS was listed as threatened on March 5, 1993 (58 FR 12854) by the USFWS (USFWS, 2007a). DS are mainly found in the Suisun Bay and the Sacramento-San Joaquin estuary near San Francisco Bay. During spawning DS move into freshwater. The PCEs for DSs are shallow fresh or brackish backwater sloughs for egg hatching and larval viability, suitable water with adequate river flow for larval and juvenile transport, suitable rearing habitat, and unrestricted access to suitable spawning habitat.

1.2 Scope of Assessment

1.2.1 Uses Assessed

Diquat dibromide is a member of a group of herbicides that are known as Cell Membrane Destroyers (<http://www.ces.purdue.edu/extmedia/ws/ws-23-w.html>, assessed 22 Nov 2010). Exposure to compounds in this group results in rapid disruption of cell membranes and very rapid kill of plant material. Formulation types registered include emulsifiable concentrate (EC), liquid (L) and Ready to Use (RTU). Currently, labeled uses of diquat dibromide include drainage system, lakes/ponds/reservoirs, streams/rivers/channeled water, swamps/marshes/wetland/stagnant water, forest trees, greenhouse, ornamental (non-flowering plants, woody shrubs and vine, ground cover, herbaceous plants, lawns and turf, non-flowering plants), shade tree, agricultural/farm structures/buildings and equipment, industrial/construction areas, commercial/industrial lawns, fencerows/hedgerows, paths/patios, paved areas (private roads/sidewalks), household/domestic dwellings outdoor premises, mulch, nursery stock, alfalfa, clover, canola, potato, acerola, date, dewberry, elderberry, fig, filbert (hazelnut), golf course turf, gooseberry, grapefruit, grapes, guava, huckleberry, almond, apple, apricot, artichoke, asparagus, avocado, blackberry, blueberry, boysenberry, cherry, jojoba, kiwi fruits, lemon, lime, loganberry, macadamia nut, mango, nectarine, olive, orange, papaya, passion fruit, peach, pear, pecan, persimmon, pistachio, plum, pomegranate, prune, tangerines, and walnut. All uses listed above are registered in California and considered as part of the federal action evaluated in this assessment.

Diquat dibromide [6,7-dihydrodipyrido (1,2-a:2'.1'-c) pyrazinediium dibromide] is the active ingredient. However, as a salt, diquat dibromide completely dissociates in water. Toxicity is assumed to be associated with the diquat cation. The ratio of molecular weights of 0.536 (184.2 g/mole for diquat cation and 344g/mole for diquat dibromide) is used to convert a.i. to cation of diquat dibromide. The labels report the content in both diquat dibromide and diquat cation. For example, both Reglone[®] and Reward[®] (EPA Reg.No. 100-1061 and 100-1091, respectively) labels indicate that the formulation contains "2 lbs. diquat cation per gal. as 3.73 lbs. salt per gal." For this assessment, application rates and toxicity will be listed in terms of the diquat cation.

1.2.2 Environmental Fate Properties of Diquat Dibromide

The primary route of environmental dissipation of diquat dibromide is strong adsorption to soil particles. Diquat dibromide does not hydrolyze or photodegrade in natural environments and is resistant to microbial degradation under aerobic and anaerobic conditions. When used as an aquatic herbicide, diquat dibromide is removed from the water column by adsorption to soil sediments, aquatic vegetation, and organic matter. Adsorbed diquat dibromide is persistent and immobile, and is not expected to be a ground-water contaminant.

1.2.3 Evaluation of Degradates and Stressors of Concern

There were no major degradates isolated from any of the environmental fate studies, except the aqueous photolysis study. The photolysis half-life of 74 days is observed in the aquatic environment without sediment. 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion appears to be the major photodegrade. However, in the natural aquatic environment with sediment, photolysis would not be considered as a means of diquat dibromide dissipation due to the high adsorption with the sediments; therefore, no further evaluation of degradates is needed.

1.3 Assessment Procedures

A description of routine procedures for evaluating risk to the San Francisco Bay Species is provided in Attachment I.

1.3.1 Exposure Assessment

1.3.1.a Aquatic Exposures

Tier-II aquatic exposure models are used to estimate high-end exposures of diquat dibromide in aquatic habitats resulting from runoff and spray drift from different uses. The models used to predict aquatic EECs are the Pesticide Root Zone Model coupled with the Exposure Analysis Model System (PRZM/EXAMS). Peak model-estimated environmental concentrations from different diquat dibromide uses range from 0.018 to 20.546 µg cation/L. Aquatic concentrations resulting from direct water applications are based on target concentrations found on labels (2500 µg cation/L for acute) and EFEDs Tier 1 rice model (0.557 µg cation/L for chronic). Available water monitoring data are very limited

1.3.1.b Terrestrial Exposures

For this assessment on the DS, assessed terrestrial organism risks were limited to terrestrial plants. The TerrPlant model is used to estimate diquat dibromide exposures to terrestrial-phase habitat, including plants inhabiting semi-aquatic and dry areas, resulting from uses involving foliar diquat dibromide applications. For terrestrial applications of diquat dibromide, exposure through both spray drift and runoff was estimated. For aquatic applications of diquat dibromide, only exposure through spray drift was estimated.

1.3.2 Toxicity Assessment

The assessment endpoints include direct toxic effects on survival, reproduction, and growth of individuals, as well as indirect effects, such as reduction of the food source and/or modification of habitat. Federally-designated critical habitat has been established for the DS. Primary constituent elements (PCEs) were used to evaluate whether diquat dibromide has the potential to modify designated critical habitat. The Agency evaluated registrant-submitted studies and data from the open literature (ECOTOX database) to characterize diquat dibromide toxicity. The most sensitive toxicity value available from acceptable or supplemental studies for each taxon relevant for estimating potential risks to the assessed species and/or their designated critical habitat was used.

Section 4 summarizes the ecotoxicity data available on diquat dibromide. Diquat dibromide is slightly toxic to freshwater fish, estuarine/marine fish, and freshwater invertebrates on an acute exposure basis. Diquat dibromide is practically non-toxic to estuarine/marine invertebrates. The chronic NOAEC for freshwater fish is 0.122 mg cation/L. NOAECs for other aquatic taxa were estimated using the Acute to Chronic Ratio (ACR) approach. Aquatic vascular and non-vascular plants were sensitive to diquat dibromide. Diquat dibromide did not impact survival and growth in the seedling emergence studies. Monocots and dicots were more sensitive to diquat dibromide during the stages of growth evaluated in the vegetative vigor studies.

1.3.3 Measures of Risk

Acute and chronic risk quotients (RQs) are compared to the Agency's Levels of Concern (LOCs) to identify instances where diquat dibromide use has the potential to adversely affect the assessed species or adversely modify their designated critical habitat. When RQs for a particular type of effect are below LOCs, the pesticide is considered to have "no effect" on the species and its designated critical habitat. Where RQs exceed LOCs, a potential to cause adverse effects or habitat modification is identified, leading to a conclusion of "may affect". If diquat dibromide use "may affect" the assessed species, and/or may cause effects to designated critical habitat, the best available additional information is considered to refine the potential for exposure and effects, and distinguish actions that are Not Likely to Adversely Affect (NLAA) from those that are Likely to Adversely Affect (LAA).

1.4 Summary of Conclusions

Based on the best available information, the Agency makes a May Affect, and Likely to Adversely Affect determination for DS from the use of diquat dibromide. Additionally, the Agency has determined that there is the potential for modification of DS designated critical habitat from the use of the chemical. A summary of the risk conclusions and effects determinations for each listed species assessed here and their designated critical habitat is presented in **Error! Reference source not found.** and **Table 1-2**. Use-specific determinations are provided in **Table 1-3** and **Table 1-4**. Further information on the results of the effects determination is included as part of the Risk Description in **Section 5.2**. Given the LAA determination for the DS and potential modification of designated critical habitat for DS, a description of the baseline status and cumulative effects for DS is provided in Attachment II.

Table 1-1. Effects Determination Summary for Effects of Diquat Dibromide on the DS

Species	Effects Determination	Basis for Determination
Delta Smelt <i>(Hypomesus transpacificus)</i>	May Affect, Likely to Adversely Affect (LAA)	Potential for Direct Effects
		<i>Aquatic-phase (Eggs, Larvae, and Adults):</i> Acute RQs exceeded the LOC for direct water applications. No chronic LOCs were exceeded. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater fish). In addition, several fish incidents were reported in EIIS. For some incidents, it was unclear if mortality was due toxicity of diquat dibromide or if mortality was a result of reduced dissolved oxygen from the high rate of plant mortality after diquat dibromide application.
		Potential for Indirect Effects
		<i>Aquatic prey items, aquatic habitat, cover and/or primary productivity</i> Freshwater invertebrates: Acute RQs exceeded the LOC for 11 of 21 scenarios; chronic RQs exceeded the LOC for 8 of 21 scenarios. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater invertebrates). Likelihood of an individual effect for other scenarios with LOC exceedences ranged from 1 in 20 to 1 in 5E+7. Estuarine/marine invertebrates: Acute LOC was exceeded for the two direct water applications; chronic LOC was not exceeded. Non-vascular plants: LOC was exceeded for nursery scenario and direct water applications. According to the 1999-2008 CA PUR data, the some of the highest diquat dibromide usage categories were landscape maintenance and nurseries in California. Direct application to water was also reported with moderate usage. Vascular plants: Acute RQs exceeded the LOC for 18 of 21 scenarios
		<i>Riparian habitat</i> For monocots, the LOC was only exceeded for aerial applications, residential applications, and direct water applications for exposure to spray drift alone. For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone. All RQ exceedences were based on vegetative vigor endpoints, as greenhouse toxicity tests indicated that diquat dibromide has a minimal effect on seedling emergence of the tested species. Multiple lines of evidence, including incidents of plant damage, support the conclusion of risk to plants.

Table 1-2. Effects Determination Summary for the Critical Habitat Impact Analysis

Designated Critical Habitat for:	Effects Determination	Basis for Determination
Delta Smelt (<i>Hypomesus transpacificus</i>)	Habitat Modification	Freshwater fish: Acute RQs exceeded the LOC for direct water applications. No chronic LOCs were exceeded. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater fish). In addition, several fish incidents were reported in EIS. For some incidents, it was unclear if mortality was due toxicity of diquat dibromide or if mortality was a result of reduced dissolved oxygen from the high rate of plant mortality after diquat dibromide application. Freshwater invertebrates: Acute RQs exceeded the LOC for 11 of 21 scenarios; chronic RQs exceeded the LOC for 8 of 21 scenarios. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater invertebrates). Likelihood of an individual effect for other scenarios with LOC exceedences ranged from 1 in 20 to 1 in 5E+7. Estuarine/marine invertebrates: Acute LOC was exceeded for the two direct water applications; chronic LOC was not exceeded. Non-vascular plants: LOC was exceeded for nursery scenario and direct water applications. According to the 1999-2008 CA PUR data, the some of the highest diquat dibromide usage categories were landscape maintenance and nurseries in California. Direct application to water was also reported with moderate usage. Vascular plants: Acute RQs exceeded the LOC for 18 of 21 scenarios Terrestrial plants: For monocots, the LOC was only exceeded for aerial applications, residential applications, and direct water applications for exposure to spray drift alone. For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone. All RQ exceedences were based on vegetative vigor endpoints, as greenhouse toxicity tests indicated that diquat dibromide has a minimal effect on seedling emergence of the tested species.

Table 1-3. Use Specific Summary of the Potential for Adverse Effects to Aquatic Taxa

Uses	Potential for Effects to Identified Taxa Found in the Aquatic Environment:							
	DS (direct effects) ¹		Freshwater Invertebrates ²		Estuarine/Marine Invertebrates ²		Non-Vascular Plants ²	Vascular Plants ²
	Acute	Chronic	Acute	Chronic	Acute	Chronic		
Alfalfa, Clover, Jojoba (aerial and ground)	No	No	No	No	No	No	No	Yes
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	No	No	Yes	No	No	No	No	Yes
Avocado	No	No	Yes	Yes	No	No	No	Yes
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon Tangerine	No	No	No	No	No	No	No	No
Forestry	No	No	Yes	Yes	No	No	No	Yes
Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears. Peaches, Plums,	No	No	No	No	No	No	No	Yes

Prune, Pomegranate								
Grapes, Kiwi Fruits	No	No	Yes	No	No	No	No	Yes
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	No	No	Yes	Yes	No	No	Yes	Yes
Olive	No	No	No	No	No	No	No	Yes
Potatoes (aerial and ground)	No	No	No	No	No	No	No	Yes
	No	No	No	No	No	No	No	Yes
Household/Domestic Dwellings Outdoor Premises, Paved Areas	No	No	No	No	No	No	No	No
Right of Way Areas (including Roadsides, CRP acreage)	No	No	No	No	No	No	No	No
Artichokes, Asparagus	No	No	Yes	Yes	No	No	No	Yes
Recreation Area Turf, Golf Course	No	No	No	No	No	No	No	Yes
Canola (aerial and ground)	No	No	Yes	Yes	No	No	No	Yes
	No	No	Yes	Yes	No	No	No	Yes
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	No	No	Yes	Yes	No	No	No	Yes
Aquatic Food Use	Yes	No	Yes	No	Yes	No	Yes	Yes
Aquatic Non-Food Use	Yes	No	Yes	Yes	Yes	No	Yes	Yes
1 A yes in this column indicates a potential for direct effects to DS.								
2 A yes in this column indicates a potential for indirect effects to DS.								

Table 1-4. Use Specific Summary of the Potential for Adverse Effects to Terrestrial Taxa

Uses	Potential for Effects to Identified Taxa Found in the Terrestrial Environment:	
	Dicots ¹	Monocots ¹
Aerial Applications		
Alfalfa, Clover, Jojoba	Yes	Yes
Potatoes	Yes	Yes
Canola	Yes	Yes
Ground Applications		
Alfalfa, Clover, Jojoba	Yes	No
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	Yes	No
Avocado	Yes	No
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon, Tangerine	Yes	No
Forestry	Yes	No
Acerola, Apples, Apricots, Cherries, Fig,	Yes	No

Uses	Potential for Effects to Identified Taxa Found in the Terrestrial Environment:	
	Dicots ¹	Monocots ¹
Nectarines, Pears, Peaches, Plums, Prune, Pomegranate		
Grapes, Kiwi Fruits	Yes	No
Olive	Yes	No
Potatoes	Yes	No
Artichokes, Asparagus	Yes	No
Recreation Area Turf, Golf Course	Yes	No
Canola	Yes	No
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	Yes	No
Right of Way Areas (including Roadsides, CRP acreage)	Yes	No
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	Yes	No
Household/Domestic Dwellings Outdoor Premises, Paved Areas	Yes	Yes
Direct Water (food use)	Yes	Yes
Direct Water (non-food)	Yes	Yes
1- A yes in this column indicates a potential for indirect effects to DS.		

Based on the conclusions of this assessment, a formal consultation with the U. S. Fish and Wildlife Service under Section 7 of the Endangered Species Act should be initiated.

When evaluating the significance of this risk assessment's direct/indirect and adverse habitat modification effects determinations, it is important to note that pesticide exposures and predicted risks to the species and its resources (*i.e.*, food and habitat) are not expected to be uniform across the action area. In fact, given the assumptions of drift and downstream transport (*i.e.*, attenuation with distance), pesticide exposure and associated risks to the species and its resources are expected to decrease with increasing distance away from the treated field or site of application. Evaluation of the implication of this non-uniform distribution of risk to the species would require information and assessment techniques that are not currently available. Examples of such information and methodology required for this type of analysis would include the following:

- Enhanced information on the density and distribution of DS life stages within the action area and/or applicable designated critical habitat. This information would allow for quantitative extrapolation of the present risk assessment's predictions of individual effects to the proportion of the population extant within geographical areas where those effects are predicted. Furthermore, such population information would allow for a more comprehensive evaluation of the significance of potential resource impairment to individuals of the assessed species.
- Quantitative information on prey base requirements for the assessed species. While existing information provides a preliminary picture of the types of food sources utilized by the assessed species, it does not establish minimal requirements to sustain healthy individuals at varying life stages. Such

information could be used to establish biologically relevant thresholds of effects on the prey base, and ultimately establish geographical limits to those effects. This information could be used together with the density data discussed above to characterize the likelihood of adverse effects to individuals.

- Information on population responses of prey base organisms to the pesticide. Currently, methodologies are limited to predicting exposures and likely levels of direct mortality, growth or reproductive impairment immediately following exposure to the pesticide. The degree to which repeated exposure events and the inherent demographic characteristics of the prey population play into the extent to which prey resources may recover is not predictable. An enhanced understanding of long-term prey responses to pesticide exposure would allow for a more refined determination of the magnitude and duration of resource impairment, and together with the information described above, a more complete prediction of effects to individual species and potential modification to critical habitat.

2 Problem Formulation

Problem formulation provides a strategic framework for the risk assessment. By identifying the important components of the problem, it focuses the assessment on the most relevant life history stages, habitat components, chemical properties, exposure routes, and endpoints. The structure of this risk assessment is based on guidance contained in U.S. EPA's *Guidance for Ecological Risk Assessment* (USEPA, 1998), the Services' *Endangered Species Consultation Handbook* (USFWS/NMFS, 1998) and is consistent with procedures and methodology outlined in the Overview Document (USEPA, 2004) and reviewed by the U.S. Fish and Wildlife Service and National Marine Fisheries Service (USFWS/NMFS/NOAA, 2004).

2.1 Purpose

The purpose of this endangered species assessment is to evaluate potential direct and indirect effects on individuals of the delta smelt (DS) arising from FIFRA regulatory actions regarding use of diquat dibromide on food and non-food crops in both aquatic and terrestrial environments, indoor greenhouses, outdoor residential areas, and forests. This ecological risk assessment has been prepared consistent with a settlement agreement in the case *Center for Biological Diversity (CBD) vs. EPA et al.* (Case No. 07-2794-JCS). The settlement was entered in Federal District Court for the Northern District of California on May 17, 2010.

In this assessment, direct and indirect effects to the DS and potential modification to its designated critical habitat are evaluated in accordance with the methods described in the Agency's Overview Document (USEPA, 2004).

The DS was listed as threatened on March 5, 1993 (58 FR 12854) by the USFWS (USFWS, 2007a). DS are mainly found in the Suisun Bay and the Sacramento-San Joaquin estuary near San Francisco Bay. During spawning DS move into freshwater. The PCEs for DSs are shallow fresh or brackish backwater sloughs for egg hatching and larval viability, suitable water with adequate river flow for larval and juvenile transport, suitable rearing habitat, and unrestricted access to suitable spawning habitat.

In accordance with the Overview Document, provisions of the ESA, and the Services' *Endangered Species Consultation Handbook*, the assessment of effects associated with registrations of diquat dibromide is based on an action area. The action area is the area directly or indirectly affected by the federal action, as indicated by the exceedance of the Agency's Levels of Concern (LOCs). It is acknowledged that the action area for a national-level FIFRA regulatory decision associated with a use of diquat dibromide may potentially involve numerous areas throughout the United States and its Territories. However, for the purposes of this assessment, attention will be focused on relevant sections of the action area including those geographic areas associated with locations of the DS and their designated critical habitat within the state of California. As part of the "effects determination," one of the following three conclusions will be reached separately for each of the assessed species regarding the potential use of diquat dibromide in accordance with current labels:

- "No effect";
- "May affect, but not likely to adversely affect"; or
- "May affect and likely to adversely affect".

Additionally, for habitat and PCEs, a "No Effect" or a "Habitat Modification" determination is made.

A description of routine procedures for evaluating risk to the San Francisco Bay Species are provided in Attachment I.

2.2 Scope

The end result of the EPA pesticide registration process (*i.e.*, the FIFRA regulatory action) is an approved product label. The label is a legal document that stipulates how and where a given pesticide may be used. Product labels (also known as end-use labels) describe the formulation type (*e.g.*, liquid or granular), acceptable methods of application, approved use sites, and any restrictions on how applications may be conducted. Thus, the use or potential use of diquat dibromide in accordance with the approved product labels for California is "the action" relevant to this ecological risk assessment.

Registered formulation types include emulsifiable concentrate (EC), liquid (L) and Ready to Use (RTU). The application methods are categorized into three types:

- Desiccation – applied from ground or air for complete coverage of aerial portions of plant;
- Aquatic Weed Control – for submerged weeds, water treatments may be applied by injecting diquat dibromide below the water surface or by pouring it directly from the container into the water while moving slowly over the water surface in a boat. It is to be distributed evenly over infested areas. For floating weeds it is to be applied by thoroughly wetting foliage;
- Non-crop weed control – applied in a manner to obtain full coverage and thorough weed contact to the point of run-off.

Although current registrations of diquat dibromide allow for use nationwide, this ecological risk assessment and effects determination addresses currently registered uses of diquat dibromide in portions of the action area that are reasonably assumed to be biologically relevant to the DS and its designated critical habitat. Further discussion of the action area for the DS and its critical habitat is provided in **Section 2.7**.

2.2.1 Evaluation of Degradates

There were no major or minor degradates isolated from any of the environmental fate studies, except the aqueous photolysis study. The photolysis half-life of 74 days is observed in the aquatic environment without sediment. 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion appears to be the major photodegrade. However, in the natural aquatic environment with sediment, photolysis would not be considered as a means of diquat dibromide dissipation due to the high adsorption with the sediments; therefore, no further evaluation of degradates is needed.

2.2.2 Evaluation of Mixtures

The Agency does not routinely include, in its risk assessments, an evaluation of mixtures of active ingredients, either those mixtures of multiple active ingredients in product formulations or those in the applicator's tank. In the case of the product formulations of active ingredients (that is, a registered product containing more than one active ingredient), each active ingredient is subject to an individual risk assessment for regulatory decision regarding the active ingredient on a particular use site. If effects data are available for a formulated product containing more than one active ingredient, they may be used qualitatively or quantitatively in accordance with the Agency's Overview Document and the Services' Evaluation Memorandum (USEPA, 2004; USFWS/NMFS/NOAA, 2004).

Diquat dibromide currently has 35 registered products that contain multiple active ingredients. Analysis of the available open literature and acute oral mammalian LD₅₀ data for multiple active ingredient products relative to the single active ingredient is provided in Appendix A. The results of this analysis show that an assessment based on the toxicity of the single active ingredient of diquat dibromide is appropriate. A qualitative examination of acute toxicity data (*e.g.*, LD₅₀) trends, with associated confidence intervals, across the range of percent active ingredient, show no discernable trends in potency that would suggest synergistic (*i.e.*, more than additive) or antagonistic (*i.e.*, less than additive) interactions.

2.3 Previous Assessments

Recent risk assessments available in the docket which serve as the basis for this ecological risk assessment include the following:

- Ecological Risk Assessment for Diquat Dibromide for use on Canola, 2010 (DPBarcode D372017)
- Report of the Food Quality Protection Act (FQPA) Tolerance Reassessment Progress and Risk Management Decision (TRED), 2002 (http://www.epa.gov/oppsrrd1/REDs/diquat_tred.pdf).

- Reregistration Eligibility Document (RED) Diquat Dibromide, 1995 (<http://www.epa.gov/oppsrrd1/REDs/0288.pdf>).

The most recent 2010 EFED risk assessment for a new use on canola concluded that there were no acute or chronic LOC exceedances for freshwater and estuarine fish, including listed species. The freshwater and estuarine invertebrate acute LOC is exceeded for listed species, but not for non-listed species. The Agency's LOC is exceeded for aquatic vascular plants including listed species. There is no LOC exceedance for unicellular aquatic plants. Diquat dibromide residues on mammalian and avian food items exceed the Agency's LOC for acute and chronic risk (including listed species) on dose-based and dietary basis. Diquat dibromide is practically non-toxic to honey bees. Diquat dibromide residues on non-target terrestrial plants (including listed species) exceed the Agency's LOC by spray drift only. No potential risk to terrestrial plants from runoff is expected.

2.4 Environmental Fate Properties

The active ingredient, diquat dibromide, is a salt and completely dissociates in water. Toxicity is assumed to be associated with the diquat cation. The ratio of molecular weights of 0.536 (184.2 g/mole for diquat cation and 344g/mole for diquat dibromide) is used to convert a.i. to cation of diquat dibromide. For this assessment, environmental fate will be discussed in terms of the diquat cation.

Table 2-1 lists the physical-chemical properties of diquat dibromide. **Table 2-2** lists the other environmental fate properties of diquat dibromide, along with the major degradate detected in the submitted environmental fate and transport studies. No minor degradates were isolated from any of the environmental fate studies. Brief summaries of the environmental fate studies follow the tables.

Table 2-1. Physical-chemical Properties of Diquat Dibromide

Property	Parent Compound	
	Value and units	MRID or Source
Molecular Weight	344.05 g/mole	Footprint @ http://sitem.herts.ac.uk/aeru/footprint/en// , accessed on April 21, 2010
Chemical Formula	C ₁₂ H ₁₂ Br ₂ N ₂	Footprint @ http://sitem.herts.ac.uk/aeru/footprint/en// , accessed on April 21, 2010
Density/ Relative Density/ Bulk Density	1.25 g/cm ³	http://www.chemblink.com/products/85-00-7.htm
Vapor Pressure	<1x 10 ⁻⁷ Torr @ 20°C	MRID# 40245101
Henry's Law Constant	< 1.4x10 ⁻¹³ atm-m ³ /mole @ 20°C	Estimated from water solubility and vapor pressure
Water Solubility	700 g/L @ 20°C	MRID# 00136329,40302701
Log (Octanol – water partition coefficient) (Log K _{OW})	3.81 @ 20°C	Footprint @ http://sitem.herts.ac.uk/aeru/footprint/en// , accessed on April 21, 2010

Table 2-2. Summary of Diquat Dibromide Environmental Fate Properties

Study	Value and unit	Major ⁰ Degradate	MRID # or Citation	Study Classification, Comment
Abiotic Hydrolysis	Half-life ¹ = stable		00154101	Acceptable
Aqueous Photolysis	Half-life ¹ = 74 days, pH 7	1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-iumion (as 12% of applied)	40418801	Acceptable
Soil Photolysis	Half-life ¹ = stable		40246101	Acceptable
Aerobic Soil Metabolism	Half-life ¹ = stable		40972301	Acceptable
Anaerobic Soil Metabolism	Half-life ¹ = stable		40972302	Acceptable
Aerobic Aquatic Metabolism	Half-life ¹ = stable		40927601	Acceptable
Anaerobic Aquatic Metabolism	Half-life ¹ = stable		40972302	Acceptable
Solid-water distribution coefficient (K _d)	K _d = 4895 L/kg, lowest non-sand K _d , K _d = 5839 L/kg, average		40348601	Acceptable
Terrestrial Field Dissipation	Dissipation Half-life ^{1,2} = stable		42060301 42060302	Acceptable
Aquatic Field Dissipation	Dissipation Half-life ^{1,2} = 1-2 days,		40971403	Acceptable
Bioconcentration Factor (BCF)	Steady State BCF= 1.03X L/kg whole fish; ≤ 2.5X L/kg viscera (non-edible fish portion)		40326901	Acceptable
⁰ No major degradates isolated from any of the environmental fate studies, except the aqueous photolysis study. ¹ Half-lives were calculated using the single-first order equation and nonlinear regression, unless otherwise specified. ² The value may reflect both dissipation and degradation processes.				

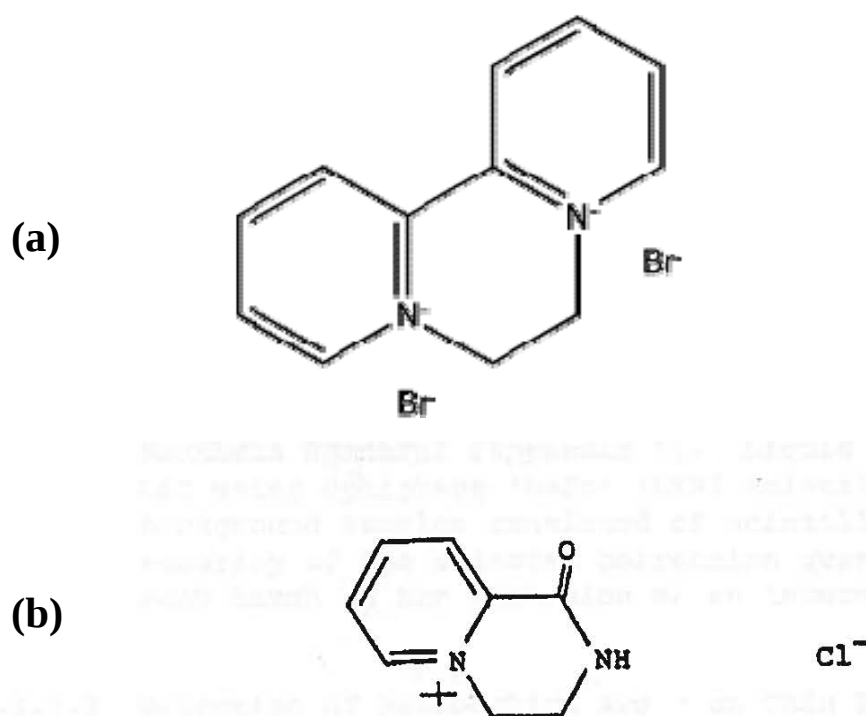


Figure 2-1. Structures of (a) diquat dibromide and (b) the major degradate, 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion, as the chloride salt.

Hydrolysis

Diquat cation was stable to hydrolysis in water at all pHs (tested at pH 5, 7, and 9).

Photolysis

The aqueous photolysis study shows a half-life of 74 days in the aquatic environment without sediment. 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion (**Figure 2-1**) appears to be the major photodegradate. However, in the aquatic environment with sediment (i.e., natural aquatic environment) photolysis would not be considered as a means of diquat cation dissipation.

[¹⁴C]Diquat cation did not photodegrade on loam soil irradiated with a xenon arc lamp at 20.5 - 29.1 °C for 107.42 hours (equivalent to approximately 32 days of natural sunlight). Diquat cation was the only compound identified in the extracts.

Microbial Degradation

Diquat dibromide at approximately 3 µg/g did not degrade in an aerobic sandy loam soil incubated at 25 °C in the dark for 9 months.

[¹⁴C]Diquat cation did not degrade when incubated under anaerobic aquatic conditions for 9 months at 25°C. After 9 months, one unidentified degradate comprised approximately 5 percent

of the applied radioactivity. Throughout the study 89 to 100 percent of the diquat cation residues were associated with the soil sediment portion of the system. No anaerobic aquatic half-life could be calculated.

[¹⁴C]Diquat cation did not degrade when incubated under aerobic aquatic conditions for 31 days at 25 °C. Between 95 to 99 percent of the diquat cation residues were associated with the soil sediment portion of the system. No aerobic aquatic half-life could be calculated.

Volatility

Diquat cation has a vapor pressure of $<1 \times 10^{-7}$ Torr @ 20°C; therefore, volatility is not expected to be a route of dissipation. There was no evidence of volatility in any study submitted to satisfy environmental fate requirements.

Mobility

Diquat cation is immobile with Freundlich K_{ads} values of 15 in sand sediment, 36-42 in two sand soils, and Freundlich K_{ads} values of 1882 – 10740 in sandy loam, sandy clay loam, and loam soils.

Field Dissipation

Diquat cation did not degrade for 3 years after application to two plots in New York; concentrations of diquat cation ranged from 0.01 to 0.32 ppm in the upper 15-cm soil depth. The two plots were planted to potatoes; the potato vegetation from the clay loam soil plot was removed prior to application to represent bare ground application, the other plot was on a loam soil and diquat dibromide was sprayed on the vegetation. There were two applications of diquat dibromide (2 lb ai/gal SC/L) at 0.25 lb diquat cation/A/application (total 0.5 lb cation/A). In general, there was no pattern of leaching; diquat cation was recovered at 0.01-0.03 ppm from individual soil cores from the 15- to 22.5-cm soil depth.

Diquat cation did not degrade for 3 years after application to two plots of loam soil in Idaho; concentrations of diquat cation ranged from 0.01 to 0.13 ppm in the upper 35-cm soil depth. Application was made to bare ground and to potato vegetation. The plots were cultivated to 35 cm, and in subsequent years, they were cropped to a rotation of sugarbeets, wheat and potatoes. There were two applications of diquat dibromide (2 lb ai/gal SC/L) at 0.25 lb diquat cation/A/application (total 0.5 lb cation/A). There were no residues recovered from below 35 cm.

Diquat cation dissipated with half-lives of 1-2 days from Florida pondwater that was treated four times at 4 lb ai/A/application at approximately monthly intervals with diquat dibromide (Ortho Diquat Herbicide-HA). Diquat cation was removed from the water column by adsorbing to sediment. The diquat cation concentrations in the sediment were variable ranging to a maximum of 1.2 ppm in the 0- to 5-cm depth with no discernible pattern of decline. In the aquatic dissipation study, the sites chosen were both near Gainesville, FL. Although the pond sites were treated under the same climatic conditions, the sediments were of different textures; one was sandy clay loam and the other was a sand sediment. The findings from these two sites were in agreement with findings from field dissipation studies conducted under a variety of climatic conditions and also were comparable to predictions from laboratory results.

2.4.1 Environmental Transport Mechanisms

The primary route of environmental dissipation of diquat dibromide is disassociation to the diquat cation and then strong adsorption to soil particles. Diquat cation does not hydrolyze or photodegrade in natural environments and is resistant to microbial degradation under aerobic and anaerobic conditions. When used as an aquatic herbicide, diquat dibromide is removed from the water column by adsorption to soil sediments, aquatic vegetation, and organic matter. Adsorbed diquat dibromide is persistent and immobile, and is not expected to be a ground-water contaminant.

Reinert and Rodgers (1987) studied various sediment types and found that unbound, biologically available diquat dibromide can be biodegraded by bacteria in the laboratory. However, because of the rapid adsorption of diquat dibromide to sediments in the environment, which may render it unavailable to biodegradation, the opportunity for microbial decomposition is not very great.

2.4.2 Mechanism of Action

Diquat dibromide is a member of a group of herbicides that are known as Cell Membrane Destroyers (<http://www.ces.purdue.edu/extmedia/ws/ws-23-w.html>). Exposure to compounds in this group results in rapid disruption of cell membranes and very rapid kill. More specifically, diquat dibromide, along with paraquat dichloride, is in the smaller class of bipyridyliums. The bipyridyliums penetrate into the cytoplasm and cause the formation of peroxides and free electrons which destroy the cell membranes almost immediately. Rapid destruction of cell membranes prevents translocation to other regions of the plant. Severe injury is evident hours after application, first as water-soaked areas which later turn yellow or brown. Maximum kill is attained in a week or less. Partial coverage of a plant with spray results in spotting and/or partial shoot kill. New growth on surviving plants will be normal in appearance.

The bipyridyliums are foliar applied, strongly cationic, relatively toxic herbicides that are used postemergence only. Extremely strong binding to clay prevents activity for weed control or leaching in the soil. Only shoot kill can be expected. Liquids with suspended colloids (muddy water, slurry fertilizers) can cause inactivation.

2.4.3 Use Characterization

Diquat dibromide is used as a nonselective contact herbicide for noncrop weed control, aquatic weed control, and as a plant regulator and desiccant for agricultural seed crops. Analysis of labeled use information is the critical first step in evaluating the federal action. The current labels for diquat dibromide represent the FIFRA regulatory action; therefore, labeled use and application rates specified on the label form the basis of this assessment. The assessment of use information is critical to the development of the action area and selection of appropriate modeling scenarios and inputs.

Table 2-3 presents the uses and corresponding application rates and methods of application considered in this assessment. For aquatic uses, labels (*e.g.*, Reward, EPA Reg No. 100-1091)

specify the treatment of only $\frac{1}{3}$ to $\frac{1}{2}$ of the water body area at one time and to wait 14 days between treatments.

Table 2-3. Diquat Dibromide Uses Assessed for California

Use (App. Method)	Form.	Maximum Single App. Rate	Maximum* App. Rate per Year	Maximum* Number of App. per Year
Aquatic Food Crop				
Agricultural Drainage System (boat)	L	1.865 lb a.i./ac-ft	See table notes	See table notes
Lakes/Ponds/Reservoirs (with human or wildlife use) (boat, aircraft)	L	1.865 lb a.i./ac-ft	See table notes	See table notes
Aquatic Non-Food Industrial				
Drainage System (Sprayer)	L	4 lb a.i./ac-ft	See table notes	See table notes
Lakes/Ponds/Reservoirs (with human or wildlife use) (Injection equipment, Helicopter, Sprayer)	L	1.865 lb a.i./ac-ft	See table notes	See table notes
Aquatic Non-Food Outdoor				
Streams/Rivers/Channeled Water (Aircraft)	L	1.865 lb a.i./ac-ft	See table notes	See table notes
Swamps/Marshes/Wetland/Stagnant Water (Sprayer)	L	4 lb a.i./ac-ft	See table notes	See table notes
Forestry				
Forest Trees (Softwoods, Conifers) (Ground)	L	0.9325 lb a.i./ac	See table notes	2**
Indoor Non-Food				
Greenhouse – Empty (Sprayer)	L	1.865 lb a.i./ac	See table notes	2
Outdoor Residential				
Ornamental Non-Flowering Plants, Ornamental Woody Shrubs and Vine (Sprayer)	EC	0.482 lb a.i./ac	See table notes	2
Household/Domestic Dwellings Outdoor Premises (Sprayer)	EC	0.457 lb a.i./ac	See table notes	2
Mulch, Ornamental and/or Shade Tree (Sprayer)	RTU	0.758 lb a.i./ac	See table notes	2
Terrestrial + Greenhouse Non-Food Crop				
Nursery Stock (Sprayer)	L	1.865 lb a.i./ac	See table notes	2
Terrestrial Food Crop				
Alfalfa (Aircraft, Ground)	L	0.933 lb a.i./ac	See table notes	1***
Clover (Aircraft, Ground)	L	0.933 lb a.i./ac	See table notes	1***

Use (App. Method)	Form.	Maximum Single App. Rate	Maximum* App. Rate per Year	Maximum* Number of App. per Year
Canola (Aircraft, Ground)	L	0.933 lb a.i./ac	See table notes	1
Terrestrial Food + Feed Crop				
Potato, White/Irish (Aircraft, Ground)	L	0.933 lb a.i./ac	See table notes	1****
Terrestrial Non-Food + Outdoor Residential				
Ornamental Ground Cover	RTU	2.054 lb a.i./ac	See table notes	2
Fencerows/Hedgerows, Mulch, Ornamental and/or Shade Tree, Ornamental Herbaceous Plants, Ornamental Lawns and Turf, Ornamental Non-Flowering Plants, Ornamental Woody Shrubs and Vines, Paths/Patios, Paved Areas (Private Roads/Sidewalks) (Hose-end Sprayer, Sprayer)	EC	2.091 lb a.i./ac	See table notes	2
Terrestrial Non-Food Crop				
****Acerola (West Indies Cherry), Cranberry, Date, Dewberry, Elderberry, Fig, Filbert (Hazelnut), Ginseng (Medical), Gooseberry, Grapefruit, Grapes, Guava, Huckleberry, Almond, Apple, Apricot, Artichoke, Asparagus, Avocado, Banana, Blackberry, Blueberry, Boysenberry, Cherry, Jojoba, Kiwi Fruits, Lemon, Lime, Loganberry, Macadamia Nut (Bushnut), Mango, Nectarine, Olive, Orange, Papaya, Passion Fruit (Granadilla), Peach, Pear, Pecan, Persimmon, Pistachio, Plantain, Plum, Pomegranate, Prune, Tangerines, Walnut (English/Black) (Ground Sprayer)	L	0.933 lb a.i./ac	See table notes	2**

Use (App. Method)	Form.	Maximum Single App. Rate	Maximum* App. Rate per Year	Maximum* Number of App. per Year
Golf Course Turf, Agricultural/Farm Structures/Buildings and Equipment, Commercial/Industrial Lawns, Greenhouse-In Use, Industrial/Construction Areas (Outdoor), Commercial/Industrial Lawns, Nonagricultural Rights-Of-Way/Fencerows/Hedgerows, Nonagricultural Uncultivated Areas/Soils, Recreation Area Lawns, Nonagricultural Rights-Of-Way/Fencerows/Hedgerows, Nonagricultural Uncultivated Areas/Soils (Ground Sprayer)	L	1.865 lb a.i./ac	See table notes	2
Ornamental Grasses (product Container)	RTU	2.054 lb a.i./ac	See table notes	2
Nonagricultural Outdoor Buildings/Structures (Sprayer)	EC	2.091 lb a.i./ac	See table notes	2
Abbreviations: App. = applications; Form. = formulation; L – Liquid, EC – Emulsified Concentrated, RTU – Ready To Use. *These two columns are all N.S. (non-specified) according to the LUIS (Label Use Information System) report. For aquatic use directions: treat only $\frac{1}{3}$ to $\frac{1}{2}$ of the water body area at one time and wait 14 days between treatments. **For Tree, Vine, Small Fruit, Vegetable Crops Nonbearing Uses, apply during site preparation prior to planting and up to 1 year of harvest. Retreatment may be necessary for complete control of grasses and older established weeds. For Non-crop or Non-planted Areas on Farms uses, apply for full coverage and thorough weed contact. Retreatment may be necessary to control grasses and established weeds. A treatment interval of 30 days is assumed for these uses. ***For alfalfa, clover and potato uses, diquat dibromide is intended as pre-harvest desiccation broadcast, so only 1 application allowed. **** All uses listed here are non-bearing plants/trees or fruit cannot be harvested for food use for at least one year after application of diquat dibromide (per label language).				

According to the United States Geological Survey's (USGS) national pesticide usage data (based on information from 1999 to 2004), an average of 194,518 lbs of diquat dibromide is applied nationally to agricultural use sites in the U.S. (non-agricultural uses are not included) (**Figure 2-2**).

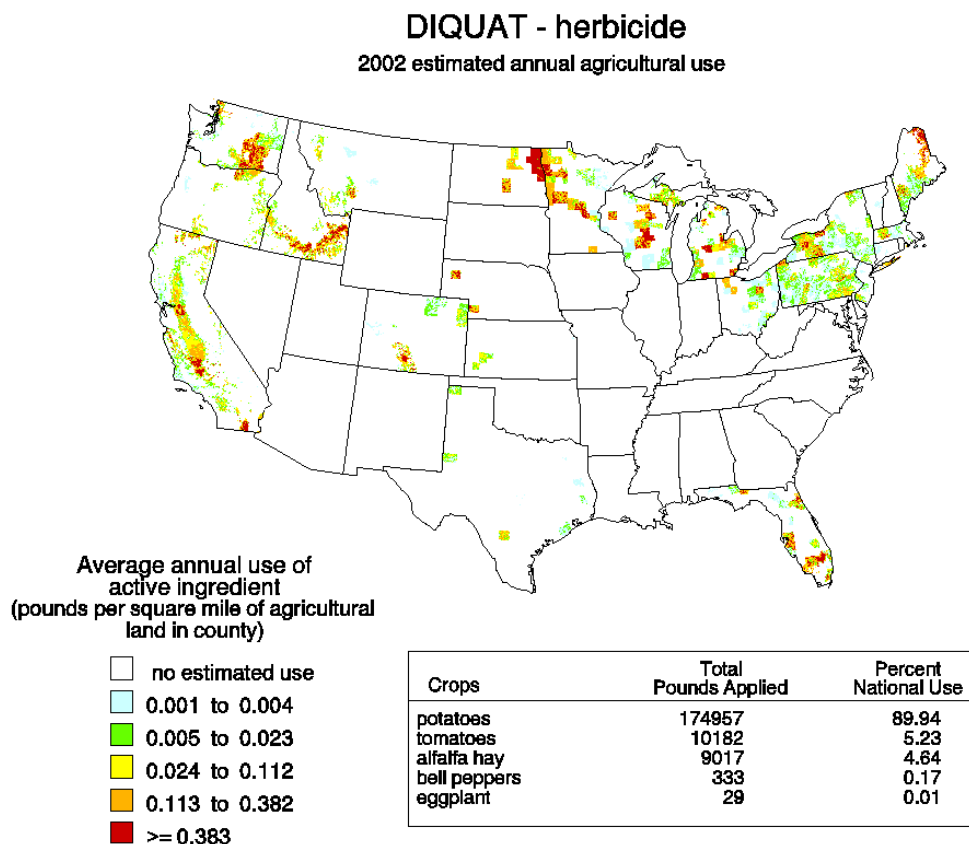


Figure 2-2. 2002 Estimated Annual Agricultural Use Map for Diquat Dibromide.
(from http://water.usgs.gov/nawqa/pnsp/usage/maps/show_map.php?year=02&map=m1950)¹

The Agency's Biological and Economic Analysis Division (BEAD) provides an analysis of both national- and county-level usage information (County-Level Usage for Aluminum Phosphide, Magnesium Phosphide, Diquat Dibromide, Zinc Phosphide, and Metam Sodium in California in Support of a San Francisco Bay Endangered Species Assessment, October 6, 2010) using state-level usage data obtained from USDA-NASS², Doane (www.doane.com; the full dataset is not provided due to its proprietary nature) and the California's Department of Pesticide Regulation Pesticide Use Reporting (CDPR PUR) database³. CDPR PUR is considered a more

¹ The pesticide use maps available from this site show the average annual pesticide use intensity expressed as average weight (in pounds) of a pesticide applied to each square mile of agricultural land in a county. The area of each map is based on state-level estimates of pesticide use rates for individual crops that were compiled by the CropLife Foundation, Crop Protection Research Institute based on information collected during 1999 through 2004 and on 2002 Census of Agriculture county crop acreage. The maps do not represent a specific year, but rather show typical use patterns over the five year period 1999 through 2004.

² United States Department of Agriculture (USDA), National Agricultural Statistics Service (NASS) Chemical Use Reports provide summary pesticide usage statistics for select agricultural use sites by chemical, crop and state. See http://www.pestmanagement.info/nass/app_usage.cfm.

³ The California Department of Pesticide Regulation's Pesticide Use Reporting database provides a census of pesticide applications in the state. See <http://www.cdpr.ca.gov/docs/pur/purmain.htm>.

comprehensive source of usage data than USDA-NASS or EPA proprietary databases, and thus the usage data reported for diquat dibromide by county in this California-specific assessment were generated using CDPR PUR data. Ten years (1999-2008) of usage data were included in this analysis. Data from CDPR PUR were obtained for every agricultural pesticide application made on every use site at the section level (approximately one square mile) of the public land survey system.⁴ BEAD summarized these data to the county level by site, pesticide, and unit treated. Calculating county-level usage involved summarizing across all applications made within a section and then across all sections within a county for each use site and for each pesticide. The county level usage data that were calculated include: average annual pounds applied, average annual area treated, and average and maximum application rate across all ten years.

A summary of diquat dibromide usage for all California use sites is provided below in **Table 2-4**. **Table 2-5** provides average annual usage of diquat dibromide by county in California. Based on average annual usage data, 67% of total annual diquat dibromide occurs in ten counties: Fresno, Imperial, Kings, Riverside, Orange, Los Angeles, Santa Barbara, Monterey, and San Diego counties.

Table 2-4. Summary of California Department of Pesticide Registration (CDPR) Pesticide Use Reporting (PUR) Data from 1999 to 2008 for Currently Registered Diquat Dibromide Uses¹

Site Name	Average Annual Applied (total lbs a.i.)	Average Application Rate (lbs a.i./A)	Maximum Application Rate(lbs a.i./A)
ALFALFA*	21239.22	0.9	0.93
ALMOND*	11.53	0.4	0.93
APPLE*	29.26	0.93	0.93
AVOCADO*	72.20	0.3	0.93
BOAT/PIER*	1.13	2.3	2.3 lbs a.i./acre-ft
CHERRY	6.71	0.9	0.9
CLOVER*	1348.55	0.9	0.93
DITCH BANK*	140.94	2.2	4.0
GRAPE*	71.89	0.7	0.93
GRAPE, WINE*	315.25	0.93	0.93
GRAPEFRUIT	0.01	0.1	0.2

⁴ Most pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and along roadside and railroad rights of way, and postharvest treatments of agricultural commodities are reported in the database. The primary exceptions to the reporting requirement are home-and-garden use and most industrial and institutional uses (<http://www.cdpr.ca.gov/docs/pur/purmain.htm>).

Site Name	Average Annual Applied (total lbs a.i.)	Average Application Rate (lbs a.i./A)	Maximum Application Rate(lbs a.i./A)
INDUSTRIAL SITE	1.26	0.3	0.8
LANDSCAPE MAINTENANCE*	15412.87	1.1	2.09
N-GRNHS FLOWER*	105.71	1.4	1.87
N-GRNHS PLANTS IN CONTAINERS*	545.65	1.87	1.87
N-GRNHS TRANSPLANTS*	4.11	1.87	1.87
N-OUTDR FLOWER*	449.66	1.7	2.06
N-OUTDR PLANTS IN CONTAINERS*	3009.36	1.8	2.06
N-OUTDR TRANSPLANTS*	313.10	1.1	2.06
OLIVE	10.71	0.9	0.9
ORANGE*	2.55	0.6	0.93
PEACH*	33.97	0.93	0.93
POMEGRANATE	8.30	0.3	0.3
POTATO*	6339.00	0.9	0.93
RASPBERRY	0.19	0.5	0.5
RECREATION AREA*	12.88	1.87	1.87
RIGHTS OF WAY**	18207.94	NA	NA
STRUCTURAL PEST CONTROL **	670.24	NA	NA
TANGELO	0.01	0.1	0.2
TANGERINE*	8.43	0.6	0.93
TURF/SOD*	16.81	0.8	0.93
UNCULTIVATED AG*	984.16	1.87	1.87
WALNUT*	0.47	0.93	0.93
WATER (INDUSTRIAL)*	95.91	4.0	4.0 lbs ai/acre-ft
WATER AREA*	3025.03	4.0	4.0 lbs ai/acre-ft

Site Name	Average Annual Applied (total lbs a.i.)	Average Application Rate (lbs a.i./A)	Maximum Application Rate(lbs a.i./A)
1- Based on data supplied by BEAD (County-Level Usage for Aluminum Phosphide, Magnesium Phosphide, Diquat Dibromide, Zinc Phosphide, and Metam Sodium in California in Support of a San Francisco Bay Endangered Species Assessment. BEAD, October 6, 2010). Non-registered and unknown uses listed in the BEAD memo were not provided in this table. * Maximum application rate in the CPUR data as provided by BEAD was higher than the labeled maximum use rate. These values were modified to reflect the maximum label rate. Values for the average application rate were also modified if they were higher than the highest label rate. The average annual applied rate and the average application rate may still reflect errors in the CPUR data base. These modifications were made since the action does not include use above legal labeled rates. ** NA – Not available. Data not provided by BEAD			

Table 2-5. Annual Average Diquat Dibromide Use by County from CDPR PUR Data - from 1999 to 2008 for Currently Registered Uses

County	Average Annual Use (lbs ai)*	Percent of Total Use
FRESNO	10,373	13.8%
IMPERIAL	7,349	9.8%
KINGS	5,780	7.7%
RIVERSIDE	5,462	7.2%
KERN	4,852	6.4%
ORANGE	4,243	5.6%
LOS ANGELES	3,770	5.0%
SANTA BARBARA	3,287	4.4%
MONTEREY	2,689	3.6%
SAN DIEGO	2,356	3.1%
SAN MATEO	2,293	3.0%
SAN JOAQUIN	2,150	2.9%
SACRAMENTO	2,138	2.8%
SAN LUIS OBISPO	2,134	2.8%
SAN BERNARDINO	1,860	2.5%
CONTRA COSTA	1,600	2.1%
VENTURA	1,374	1.8%
GLENN	1,229	1.6%
TULARE	1,048	1.4%
NEVADA	768	1.0%
SANTA CLARA	751	1.0%
MODOC	703	0.9%
ALAMEDA	696	0.9%
LAKE	645	0.9%
SISKIYOU	641	0.9%
SANTA CRUZ	587	0.8%
NAPA	547	0.7%
SONOMA	538	0.7%
PLACER	473	0.6%

County	Average Annual Use (lbs ai)*	Percent of Total Use
SOLANO	357	0.5%
STANISLAUS	354	0.5%
YOLO	289	0.4%
MARIN	228	0.3%
MERCED	197	0.3%
MADERA	166	0.2%
BUTTE	157	0.2%
SUTTER	136	0.2%
EL DORADO	124	0.2%
SANTA CRUZ	109	0.1%
AMADOR	102	0.1%
SAN BENITO	102	0.1%
TUOLUMNE	79	0.1%
CALAVERAS	78	0.1%
YUBA	77	0.1%
LASSEN	69	0.1%
HUMBOLDT	68	0.1%
SHASTA	59	0.1%
MENDOCINO	52	0.1%
TEHAMA	47	0.1%
MARIPOSA	45	0.1%
DEL NORTE	39	0.1%
TULARE	34	0.0%
SAN FRANCISCO	29	0.0%
PLUMAS	16	0.0%
INYO	7	0.0%
MONO	3	0.0%
COLUSA	1	0.0%
SIERRA	1	0.0%
* Average annual use (lbs ai) may reflect data entry errors in the CPUR database application. In some cases, maximum application rates in the CPUR data as provided by BEAD were higher than the labeled maximum use rate. Seen notes in Table 2-4 .		

2.5 Assessed Species

Table 2-6 provides a summary of the current distribution, habitat requirements, and life history parameters for the listed species being assessed. More detailed life-history and distribution information can be found in Attachment III. See **Figure 2-3** for a map of the current range and designated critical habitat, if applicable, of the assessed listed species. The DS was listed as threatened on March 5, 1993 (58 FR 12854) by the USFWS (USFWS, 2007a). DS are mainly found in the Suisun Bay and the Sacramento-San Joaquin estuary near San Francisco Bay. During spawning DS move into freshwater. The PCEs for DSs are shallow fresh or brackish backwater sloughs for egg hatching and larval viability, suitable water with adequate river flow for larval and juvenile transport, suitable rearing habitat, and unrestricted access to suitable spawning habitat.

Table 2-6. Summary of Current Distribution, Habitat Requirements, and Life History Information for the Assessed Listed Species¹

Assessed Species	Size	Current Range	Habitat Type	Designated Critical Habitat?	Reproductive Cycle	Diet
Delta Smelt (DS) (<i>Hypomesus transpacificus</i>)	Up to 120 mm in length	Suisun Bay and the Sacramento-San Joaquin estuary (known as the Delta) near San Francisco Bay, CA	The species is adapted to living in fresh and brackish water. They typically occupy estuarine areas with salinities below 2 parts per thousand (although they have been found in areas up to 18ppt). They live along the freshwater edge of the mixing zone (saltwater-freshwater interface).	Yes	They spawn in fresh or slightly brackish water upstream of the mixing zone. Spawning season usually takes place from late March through mid-May, although it may occur from late winter (Dec.) to early summer (July-August). Eggs hatch in 9 – 14 days.	They primarily eat planktonic copepods, cladocerans, amphipods, and insect larvae. Larvae feed on phytoplankton; juveniles feed on zooplankton.

¹ For more detailed information on the distribution, habitat requirements, and life history information of the assessed listed species, see Attachment II.

Delta Smelt Habitat

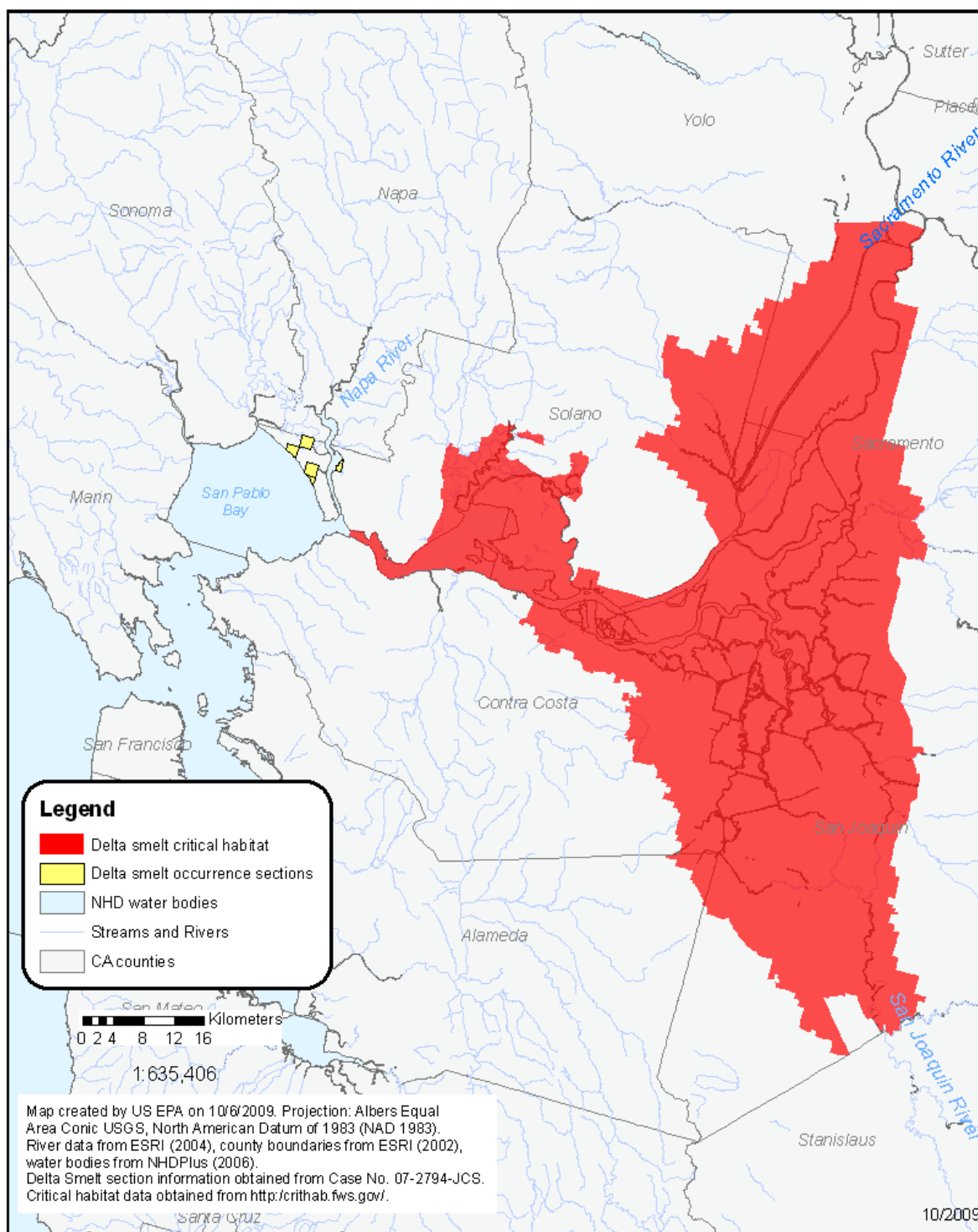


Figure 2-3. DS Critical Habitat and Occurrence Sections identified in Case No. 07-2794-JCS

2.6 Designated Critical Habitat

Critical habitat has been designated for the DS. Risk to critical habitat is evaluated separately from risk to effects on the species. ‘Critical habitat’ is defined in the ESA as the geographic area occupied by the species at the time of the listing where the physical and biological features necessary for the conservation of the species exist, and there is a need for special management to protect the listed species. It may also include areas outside the occupied area at the time of listing if such areas are ‘essential to the conservation of the species. Critical habitat designations identify, to the extent known using the best scientific and commercial data available, habitat areas that provide essential life cycle needs of the species or areas that contain certain primary constituent elements (PCEs) (as defined in 50 CFR 414.12(b)). **Table 2-7** describes the PCEs for the critical habitats designated for the DS.

Table 2-7. Designated Critical Habitat PCEs for the DS¹.

Species	PCEs	Reference
Delta Smelt	Spawning Habitat—shallow, fresh or slightly brackish backwater sloughs and edgewaters to ensure egg hatching and larval viability. Spawning areas also must provide suitable water quality (<i>i.e.</i> , low “concentrations of pollutants) and substrates for egg attachment (<i>e.g.</i> , submerged tree roots and branches and emergent vegetation).	59 FR 65256 65279, 1994
	Larval and Juvenile Transport—Sacramento and San Joaquin Rivers and their tributary channels must be protected from physical disturbance and flow disruption. Adequate river flow is necessary to transport larvae from upstream spawning areas to rearing habitat in Suisun Bay. Suitable water quality must be provided so that maturation is not impaired by pollutant concentrations.	
	Rearing Habitat—Maintenance of the 2 ppt isohaline and suitable water quality (low concentrations of pollutants) within the Estuary is necessary to provide delta smelt larvae and juveniles a shallow protective, food-rich environment in which to mature to adulthood.	
	Adult Migration— Unrestricted access to suitable spawning habitat in a period that may extend from December to July. Adequate flow and suitable water quality may need to be maintained to attract migrating adults in the Sacramento and San Joaquin River channels and their associated tributaries. These areas also should be protected from physical disturbance and flow disruption during migratory periods.	
¹ These PCEs are in addition to more general requirements for habitat areas that provide essential life cycle needs of the species such as, space for individual and population growth and for normal behavior; food, water, air, light, minerals, or other nutritional or physiological requirements; cover or shelter; sites for breeding, reproduction, rearing (or development) of offspring; and habitats that are protected from disturbance or are representative of the historic geographical and ecological distributions of a species.		
² PCEs that are abiotic, including, physical-chemical water quality parameters such as salinity, pH, and hardness are not evaluated.		

More detail on the designated critical habitat applicable to this assessment can be found in Attachment II. Activities that may destroy or adversely modify critical habitat are those that alter the PCEs and jeopardize the continued existence of the species. Evaluation of actions related to use of diquat dibromide that may alter the PCEs of the designated critical habitat for the DS form the basis of the critical habitat impact analysis.

As previously noted in **Section 2.1**, the Agency believes that the analysis of direct and indirect effects to listed species provides the basis for an analysis of potential effects on the designated critical habitat. Because diquat dibromide is expected to directly impact living organisms within the action area, critical habitat analysis for diquat dibromide is limited in a practical sense to those PCEs of critical habitat that are biological or that can be reasonably linked to biologically mediated processes.

2.7 Action Area and LAA Effects Determination Area

2.7.1 Action Area

The action area is used to identify areas that could be affected by the Federal action. The Federal action is the authorization or registration of pesticide use or uses as described on the label(s) of pesticide products containing a particular active ingredient. The action area is defined by the Endangered Species Act as, “all areas to be affected directly or indirectly by the Federal action and not merely the immediate area involved in the action” (50 CFR §402.2). Based on an analysis of the Federal action, the action area is defined by the actual and potential use of the pesticide and areas where that use could result in effects. Specific measures of ecological effect for the assessed species that define the action area include any direct and indirect toxic effect to the assessed species and any potential modification of its critical habitat, including reduction in survival, growth, and fecundity as well as the full suite of sublethal effects available in the effects literature. It is recognized that the overall action area for the national registration of diquat dibromide is likely to encompass considerable portions of the United States based on the large array of agricultural and/or non-agricultural uses. However, the scope of this assessment limits consideration of the overall action area to those portions that may be applicable to the protection of the DS and their designated critical habitat within the state of California. For this assessment, the entire state of California is considered the action area. The purpose of defining the action area as the entire state of California is to ensure that the initial area of consideration encompasses all areas where the pesticide may be used now and in the future, including the potential for off-site transport via spray drift and downstream dilution that could influence the San Francisco Bay Species. Additionally, the concept of a state-wide action area takes into account the potential for direct and indirect effects and any potential modification to critical habitat based on ecological effect measures associated with reduction in survival, growth, and reproduction, as well as the full suite of sublethal effects available in the effects literature.

It is important to note that the state-wide action area does not imply that direct and/or indirect effects and/or critical habitat modification are expected to or are likely to occur over the full extent of the action area, but rather to identify all areas that may potentially be affected by the action. The Agency uses more rigorous analysis including consideration of available land cover data, toxicity data, and exposure information to determine areas where DS and its designated critical habitat may be affected or modified via endpoints associated with reduced survival, growth, or reproduction.

2.7.2 LAA Effects Determination Area

A stepwise approach is used to define the Likely to Adversely Affect (LAA) Effects Determination Area. An LAA effects determination applies to those areas where it is expected that the pesticide's use will directly or indirectly affect the species and/or modify its designated critical habitat using EFED's standard assessment procedures (see Attachment I) and effects endpoints related to survival, growth, and reproduction. This is the area where the "Potential Area of LAA Effects" (initial area of concern + drift distance or downstream dilution distance) overlaps with the range and/or designated critical habitat for the species being assessed. If there is no overlap between the potential area of LAA effects and the habitat or occurrence areas, a no effect determination is made. The first step in defining the LAA Effects Determination Area is to understand the federal action. The federal action is defined by the currently labeled uses for diquat dibromide. An analysis of labeled uses and review of available product labels was completed. Several currently labeled uses are special local needs (SLN) uses not specified for use in California or are restricted to specific states; these uses are excluded from this assessment. In addition, a distinction has been made between food use crops and those that are non-food/non-agricultural uses. For those uses relevant to the assessed species, a detailed list of all registered California uses are provided in **Table 2-3**. In general, the agricultural uses include: fruit trees, nut trees, alfalfa, clover, canola, potato, berries, grapes, artichoke, and asparagus. Non-agricultural uses include: ornamentals, turf, golf courses, nurseries, mulch, greenhouse, outdoor premise of buildings, forestry, lakes, ponds, reservoirs, drainage systems, streams, rivers, swamps, wetlands, and fencerows.

Following a determination of the assessed uses, an evaluation of the potential "footprint" of diquat dibromide use patterns (*i.e.*, the area where pesticide application may occur) is determined. This "footprint" represents the initial area of concern, based on an analysis of available land cover data for the state of California.

Once the initial area of concern is defined, the next step typically is to define the potential boundaries of the Potential Area of LAA Effects by determining the extent of offsite transport via spray drift and runoff, and defining the additional areas beyond the footprint where exposure to the pesticide is predicted to exceed the listed species LOCs. A spray drift analysis would be used to define how far from the initial area of concern an effect to a given species may be expected via spray drift (*e.g.*, the drift distance). In addition to the buffered area from the spray drift analysis, the Potential Area of LAA Effects area also typically considers the downstream extent of predicted pesticide concentrations that would exceed the LOC based on downstream dilution analysis. However, due to the widespread use of diquat dibromide across multiple land cover classes, this analysis was not performed.

2.8 Assessment Endpoints and Measures of Ecological Effect

For more information on the assessment endpoints and measures of ecological effect see Attachment I.

2.8.1 Assessment Endpoints

A complete discussion of all the toxicity data available for this risk assessment, including resulting measures of ecological effect selected for each taxonomic group of concern, is included in **Section 4** of this document. **Table 2-8** identifies the taxa used to assess the potential for direct and indirect effects from the uses of diquat dibromide for each listed species assessed here. The specific assessment endpoints used to assess the potential for direct and indirect effects to each listed species are provided in **Table 2-9**.

Table 2-8. Taxa Used in the Analyses of Direct and Indirect Effects for the Assessed Listed Species.

Listed Species	Terr. Plants	FW Fish	FW Inverts.	E/M Fish	E/M Inverts.	Aquatic Plants
Delta smelt	Indirect (habitat)	Direct ¹	Indirect (prey)	Direct ¹	Indirect (prey)	Indirect (food/habitat)
Abbreviations: Terr. = Terrestrial; Invert. = Invertebrate; FW = Freshwater; E/M = Estuarine/Marine ¹ The most sensitive fish species was selected across freshwater and estuarine/marine test species because the delta smelt may be found in freshwater or brackish environments. In this case, the toxicity of freshwater species (the walleye and fathead minnow) was used because it was the most sensitive.						

Table 2-9. Taxa and Assessment Endpoints Used to Evaluate the Potential for Use of Diquat Dibromide to Result in Direct and Indirect Effects to the Assessed Listed Species or Modification of Critical Habitat.

Taxa Used to Assess Direct and Indirect Effects to Assessed Species and/or Modification to Critical Habitat or Habitat	Assessed Listed Species	Assessment Endpoints	Measures of Ecological Effects
1. Freshwater Fish	<u>Direct Effect</u> – -Delta Smelt*	Survival, growth, and reproduction of individuals via direct effects	1a. Most sensitive fish acute LC ₅₀ 1b. Most sensitive fish early-life stage NOAEC
2. Freshwater Invertebrates	<u>Indirect Effect (prey)</u> – -Delta Smelt	Survival, growth, and reproduction of individuals or modification of critical habitat/habitat via indirect effects on aquatic prey food supply (i.e., freshwater invertebrates)	2a. Most sensitive freshwater invertebrate EC ₅₀ 2b. Most sensitive freshwater invertebrate chronic NOAEC
3. Estuarine/Marine Fish	<u>Direct Effect</u> – - Delta Smelt*	Survival, growth, and reproduction of individuals via direct effects	3a. Most sensitive estuarine/marine fish EC ₅₀ 3b. Most sensitive estuarine/marine fish chronic NOAEC

Taxa Used to Assess Direct and Indirect Effects to Assessed Species and/or Modification to Critical Habitat or Habitat	Assessed Listed Species	Assessment Endpoints	Measures of Ecological Effects
4. Estuarine/Marine Invertebrates	<u>Indirect Effect (prey)</u> -Delta Smelt	Survival, growth, and reproduction of individuals or modification of critical habitat/habitat via indirect effects on aquatic prey food supply (<i>i.e.</i> , estuarine/marine invertebrates)	4a. Most sensitive estuarine/marine invertebrate EC ₅₀ 4b. Most sensitive estuarine/marine invertebrate chronic NOAEC
5. Aquatic Plants (freshwater/marine)	<u>Indirect Effect (food/habitat)</u> -Delta Smelt	Survival, growth, and reproduction of individuals or modification of critical habitat/habitat via indirect effects on habitat, cover, food supply, and/or primary productivity (<i>i.e.</i> , aquatic plant community)	5a. Vascular plant IC ₅₀ 5b. Non-vascular plant IC ₅₀
6. Terrestrial Plants	<u>Indirect Effect (food/habitat) (non-obligate relationship)</u> -Delta Smelt	Survival, growth, and reproduction of individuals or modification of critical habitat/habitat via indirect effects on food and habitat (<i>i.e.</i> , riparian and upland vegetation)	6a. IC ₂₅ for monocots 6b. IC ₂₅ for dicots
*The most sensitive fish species across freshwater and estuarine/marine environments is used to assess effects for these species because they may be found in freshwater or estuarine/marine environments.			

2.8.2 Assessment Endpoints for Designated Critical Habitat

As previously discussed, designated critical habitat is assessed to evaluate actions related to the use of diquat dibromide that may alter the PCEs of the assessed species' designated critical habitat. PCEs for the assessed species were previously described in **Section 2.6**. Actions that may modify critical habitat are those that alter the PCEs and jeopardize the continued existence of the assessed species. Therefore, these actions are identified as assessment endpoints. It should be noted that evaluation of PCEs as assessment endpoints is limited to those of a biological nature (*i.e.*, the biological resource requirements for the listed species associated with the critical habitat) and those for which diquat dibromide effects data are available.

Assessment endpoints used to evaluate potential for direct and indirect effects are equivalent to the assessment endpoints used to evaluate potential effects to designated critical habitat. If a potential for direct or indirect effects is found, then there is also a potential for effects to critical

habitat. Some components of these PCEs are associated with physical abiotic features (*e.g.*, presence and/or depth of a water body, or distance between two sites), which are not expected to be measurably altered by use of pesticides.

2.9 Conceptual Model

2.9.1 Risk Hypotheses

Risk hypotheses are specific assumptions about potential adverse effects (*i.e.*, changes in assessment endpoints) and may be based on theory and logic, empirical data, mathematical models, or probability models (USEPA, 1998). For this assessment, the risk is stressor-linked, where the stressor is the release of diquat dibromide to the environment. The following risk hypotheses are presumed in this assessment:

The labeled use of diquat dibromide within the action area may:

- directly affect DS by causing mortality or by adversely affecting growth or fecundity;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing the composition of food supply;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing the composition of the aquatic plant community in the species' current range, thus affecting primary productivity and/or cover;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing the composition of the terrestrial plant community in the species' current range;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing aquatic habitat in their current range (via modification of water quality parameters, habitat morphology, and/or sedimentation);
- indirectly affect CTS and/or modify their designated critical habitat by reducing or changing terrestrial habitat in their current range (via reduction in small burrowing mammals leading to reduction in underground refugia/cover).

2.9.2 Diagram

The conceptual model is a graphic representation of the structure of the risk assessment. It specifies the diquat dibromide release mechanisms, biological receptor types, and effects endpoints of potential concern. The conceptual models for the DS and the conceptual models for the aquatic and terrestrial PCE components of critical habitat are shown in **Figure 2-4** and **Figure 2-5**. Although the conceptual models for direct/indirect effects and modification of designated critical habitat PCEs are shown on the same diagrams, the potential for direct/indirect effects and modification of PCEs will be evaluated separately in this assessment. Exposure routes shown in dashed lines are not quantitatively considered because the contribution of those potential exposure routes to potential risks to DS and modification to designated critical habitat is expected to be negligible.

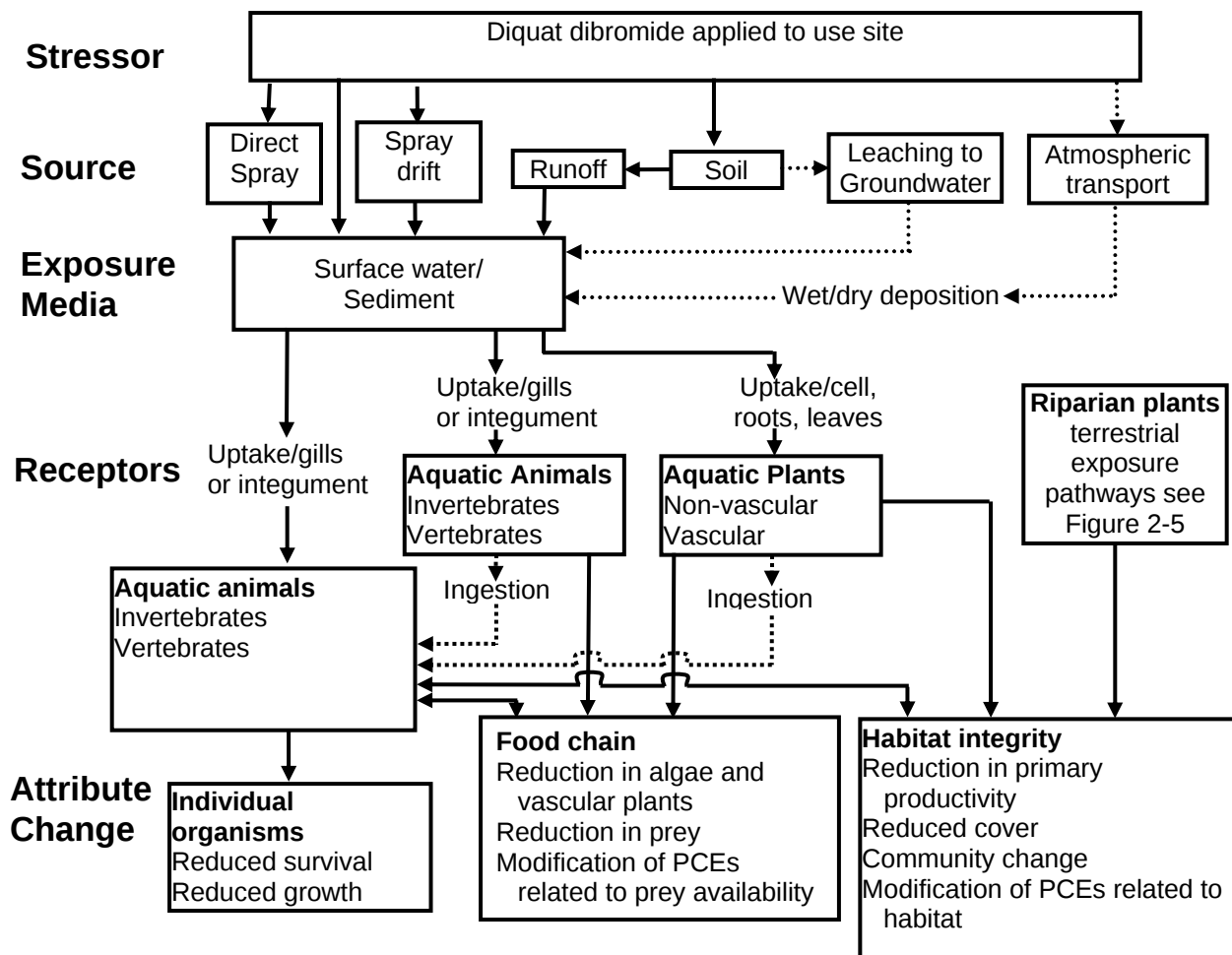


Figure 2-4. Conceptual Model Depicting Stressors, Exposure Pathways, and Potential Effects to Aquatic Organisms from the Use of Diquat Dibromide Use.

Dotted lines indicate exposure pathways that have a low likelihood of contributing to ecological risk.

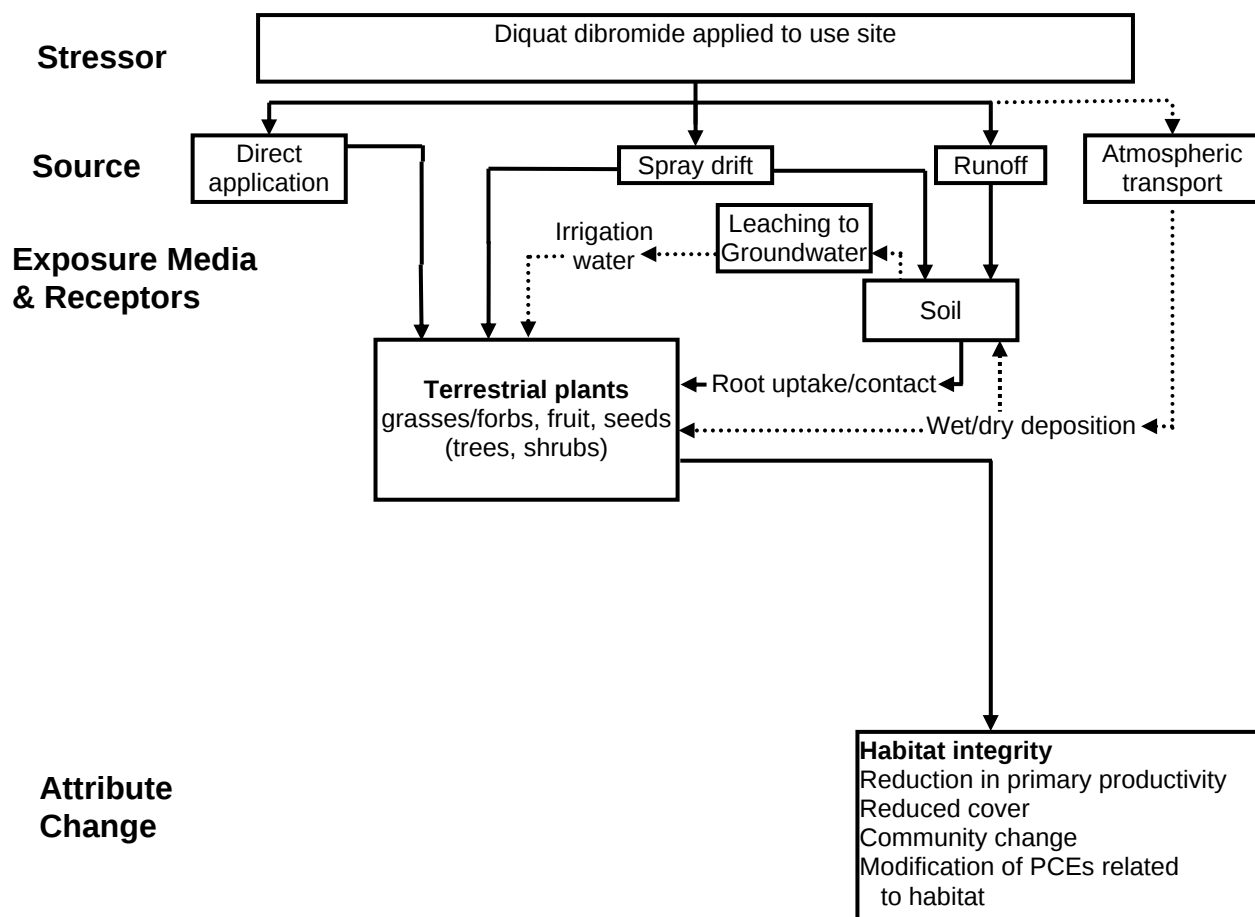


Figure 2-5. Conceptual model depicting stressors, exposure pathways, and potential effects to terrestrial plants from the use of diquat dibromide.

Dotted lines indicate exposure pathways that have a low likelihood of contributing to ecological risk.

2.10 Analysis Plan

In order to address the risk hypothesis, the potential for direct and indirect effects to the assessed species, prey items, and habitat is estimated based on a taxon-level approach. In the following sections, the use, environmental fate, and ecological effects of diquat dibromide are characterized and integrated to assess the risks. This is accomplished using a risk quotient (ratio of exposure concentration to effects concentration) approach. Although risk is often defined as the likelihood and magnitude of adverse ecological effects, the risk quotient-based approach does not provide a quantitative estimate of likelihood and/or magnitude of an adverse effect. However, as outlined in the Overview Document (USEPA, 2004), the likelihood of effects to individual organisms from particular uses of diquat dibromide is estimated using the probit dose-response slope and either the level of concern (discussed below) or actual calculated risk quotient value.

Descriptions of routine procedures for evaluating risk to the San Francisco Bay Species are provided in Attachment I.

2.10.1 Measures of Exposure

The environmental fate properties of diquat dibromide along with available monitoring data indicate that water and sediment runoff and spray drift are the principle potential transport mechanisms of diquat dibromide to the aquatic and terrestrial habitats. In this assessment, transport of diquat dibromide through runoff and spray drift is considered in deriving quantitative estimates of diquat dibromide exposure to the DS, their prey and habitats. With a vapor pressure of less than 1×10^{-7} torr and a Henry's Law constant of less than 1.4×10^{-13} atm-m³/mole @ 20°C, volatilization and atmospheric transport are very unlikely. Due to the nature of the adsorbed diquat dibromide (persistent and immobile), it is not expected to be a ground-water contaminant. With a bioconcentration factor (BCF) of less than 2.5, bioaccumulation is unlikely.

Measures of exposure are based on aquatic and terrestrial models that predict estimated environmental concentrations (EECs) of diquat dibromide using maximum labeled application rates and methods of application. The models used to predict aquatic EECs are Tier 1 Rice model and the Pesticide Root Zone Model coupled with the Exposure Analysis Model System (PRZM/EXAMS). The model used to derive EECs relevant to terrestrial and wetland plants is TerrPlant. These models are parameterized using relevant reviewed registrant-submitted environmental fate data. More information on these models is available in Attachment I.

2.10.2 Measures of Effect

Data identified in **Section 2.8** are used as measures of effect for direct and indirect effects. Data were obtained from registrant submitted studies or from literature studies identified by ECOTOX. More information on the ECOTOXicology (ECOTOX) database and how toxicological data are used in assessments is available in Attachment I.

2.10.2.1 Integration of Exposure and Effects

Risk characterization is the integration of exposure and ecological effects characterization to determine the potential ecological risk from agricultural and non-agricultural uses of diquat dibromide, and the likelihood of direct and indirect effects to the assessed species in aquatic and terrestrial habitats. The exposure and toxicity effects data are integrated in order to evaluate the risks of adverse ecological effects on non-target species. The risk quotient (RQ) method is used to compare exposure and measured toxicity values. EECs are divided by acute and chronic toxicity values. The resulting RQs are then compared to the Agency's levels of concern (LOCs) (USEPA, 2004)(see Appendix C). More information on standard assessment procedures is available in Attachment I.

2.10.3 Data Gaps

- There are no data gaps for diquat dibromide in guideline environmental fate study requirements.

- There are no estuarine/marine fish data for evaluation of chronic toxicity of diquat dibromide. For chronic toxicity, the acute-to-chronic ratio (ACR) calculations are conducted using freshwater fish toxicity data and applying to the acute sheepshead minnow (*Cyprinodon variegatus*) data.
- There are no estuarine/marine invertebrate data for evaluation of chronic toxicity of diquat dibromide. For chronic toxicity, the acute-to-chronic ratio (ACR) calculations are conducted using daphnid toxicity data and applying to the acute Crustacean amphipod (*Hyalella* spp.) data.
- There are no acute or chronic data for benthic invertebrates. This is of note for diquat dibromide as it sorbs strongly to sediment and pore water concentrations are expected to be higher than in the water column. This lack of information will be noted as an uncertainty in this risk assessment.

3 Exposure Assessment

Diquat dibromide is formulated as a liquid, emulsifiable concentrate, and ready-to-use (RTU). Application methods and equipment include: ground application, aerial application (aircraft and helicopter), boat, various sprayers (backpack, handgun, ground boom) and trailing hose. Aerial modes of application tend to use lower volumes of pesticide applied in finer sprays than applications coincident with sprayers and thus have a higher potential for off-target movement via spray drift.

The active ingredient, diquat dibromide, is a salt and completely dissociates in water. Toxicity is assumed to be associated with the diquat cation. The ratio of molecular weights of 0.536 (184.2 g/mole for the diquat cation and 344g/mole for diquat dibromide) is used to convert a.i. to cation of diquat dibromide. For this assessment, application rates and toxicity will be listed in terms of the diquat cation.

3.1 Label Application Rates and Intervals

Diquat dibromide labels may be categorized into two types: labels for manufacturing uses (including technical grade diquat dibromide and formulating products) and end-use or formulated products. Technical and formulating products contain diquat dibromide of high purity but are not used directly in the environment. Rather, they are used to make formulated products, which can be used as a nonselective contact herbicide for non-crop weed control, aquatic weed control, and as a plant regulator and desiccant for agricultural seed crops. The formulated product labels legally limit diquat dibromide's potential use to only those sites that are specified on the labels.

Currently registered agricultural and non-agricultural uses of diquat dibromide within California include drainage system, lakes/ponds/reservoirs, streams/rivers/channeled water, swamps/marshes/wetland/stagnant water, forest trees, greenhouse, ornamental (non-flowering plants, woody shrubs and vine, ground cover, herbaceous plants, lawns and turf, non-flowering

plants), shade tree, agricultural/farm structures/buildings and equipment, industrial/construction areas, commercial/industrial lawns, fencerows/hedgerows, paths/patios, paved areas (private roads/sidewalks), household/domestic dwellings outdoor premises, mulch, nursery stock, alfalfa, clover, canola, potato, acerola, date, dewberry, elderberry, fig, filbert (hazelnut), golf course turf, gooseberry, grapefruit, grapes, guava, huckleberry, almond, apple, apricot, artichoke, asparagus, avocado, blackberry, blueberry, boysenberry, cherry, jojoba, kiwi fruits, lemon, lime, loganberry, macadamia nut, mango, nectarine, olive, orange, papaya, passion fruit, peach, pear, pecan, persimmon, pistachio, plum, pomegranate, prune, tangerines, and walnut. Non-aquatic uses being assessed and the scenarios used to model potential exposure from those uses are summarized in **Table 3-1**. These use scenarios are based on the standard modeling scenarios developed by EFED, including those developed for organophosphate assessments and listed species litigation assessments. The maximum label rates and the maximum number of applications are assumed for all modeling scenarios. The re-treatment interval is assumed to be 30 days. Exposure concentrations from assessed aquatic uses were based on target concentrations listed on product labels (acute) and the Tier I rice model (chronic). Details for aquatic use modeling are provided in **Section 3.2.4**.

Table 3-1. Diquat Dibromide Uses, Scenarios, and Application Information

PRZM/ EXAMS Scenario	Uses Represented by Scenario	Application Method/ Formulation	Application Rate (lbs ai/acre)	Application Rate (lbs cation/acre)	Maximum Number of Applications	First Date of Application / Interval
CA Alfalfa OP	Alfalfa, Clover, Jojoba	Aircraft, Ground / L	0.9325	0.5	1	July 1
CA Almond STD	Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
CA Avocado RLF	Avocado	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
CA Citrus STD	Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon Tangerine	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
CA Forestry RLF	Forestry	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
CA Fruit STD	Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
CA Grape STD	Grapes, Kiwi Fruits	Ground / L	0.9325	0.5	2	Jan. 15 / 30 days

PRZM/ EXAMS Scenario	Uses Represented by Scenario	Application Method/ Formulation	Application Rate (lbs ai/acre)	Application Rate (lbs cation/acre)	Maximum Number of Applications	First Date of Application / Interval
CA Nursery	Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	Ground / L	1.865	1.0	2	Jan. 15 / 30 days
CA Olive RLF	Olive	Ground / L	0.9325	0.5	2	Jan. 15 / 30 days
CA Potato RLF	Potatoes	Aircraft, Ground / L	0.9325	0.5	1	May 15
CA Residenti al RLF	Household/ Domestic Dwellings Outdoor Premises , Paved Areas	Ground / EC	2.09	1.12	2	Jan. 15 / 30 days
CA Right Of Way RLF	Right of Way Areas (including Roadsides, CRP acreage)	Ground / L	1.865	1.0	2	July 15 / 30 days
CA Row Crop RLF	Artichokes, Asparagus	Ground / L	0.9325	0.5	2	Jan. 15 / 30 days
CA Turf RLF	Recreation Area Turf, Golf Course	Ground / L	0.9325	0.5	2	Jan. 15 / 30 days
CA Wheat RLF	Canola	Aircraft, Ground / L	0.9325	0.5	1	May 15
CA Wine Grapes RLF	Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	Ground / L	0.9325	0.5	2	Feb. 15 / 30 days
1 Uses assessed based on memorandum from Pesticide Re-evaluation Division (PRD) dated 11/17/2010 and EFED Label Data report and associated Label Use Information Reports prepared on 9/23/2010.						

3.2 Aquatic Exposure Assessment

For all terrestrial applications of diquat dibromide, the EECs (Estimated Environmental Concentrations) are calculated using the EPA Tier II PRZM (Pesticide Root Zone Model) and EXAMS (Exposure Analysis Modeling System) with the EFED Standard Pond environment. PRZM is used to simulate pesticide transport as a result of runoff and erosion from an agricultural field, and EXAMS estimates environmental fate and transport of pesticides in surface water. Aquatic exposure is modeled for the parent alone. The most recent PRZM/EXAMS linkage program (PE5, PE Version 5, dated Nov. 15, 2006) was used for all surface water simulations. Linked crop-specific scenarios and meteorological data were used to

estimate exposure resulting from use on crops and turf. Details and modeling outputs are provided in **Sections 3.2.1 to 3.2.3**.

For all aquatic applications of diquat dibromide, the EECs were estimated using target application concentrations based on label information and the Tier 1 rice model. Details and modeling outputs are provided in **Section 3.2.4**.

Use-specific management practices for all of the assessed uses of diquat dibromide were used for modeling, including application rates, number of applications per year, application intervals, and the first application date for each use. The date of first application was developed based on several sources of information including data provided by BEAD, a summary of individual applications from the CDPR PUR data, and Crop Profiles maintained by the USDA.

As an example, the distribution of diquat dibromide applications to alfalfa from the CDPR PUR data for 2008 used to pick application dates is shown in **Figure 3-1**. The data indicate that diquat dibromide could be applied to alfalfa at almost any time of the year. Therefore, application dates were chosen to coincide with the time of year with the highest rainfall. More detail on the crop profiles may be found at: <http://www.ipmcenters.org/CropProfiles/>.

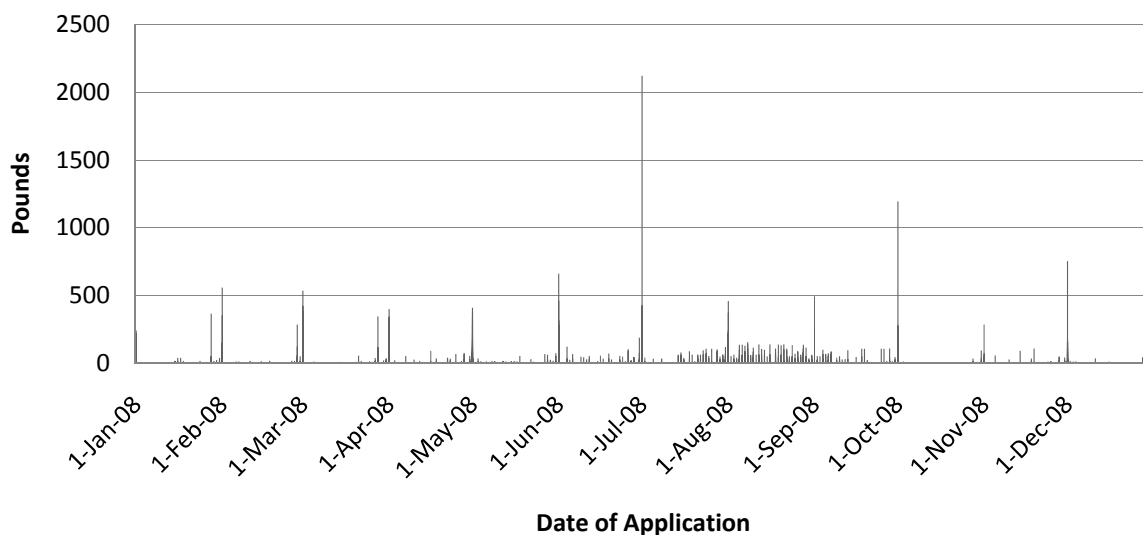


Figure 3-1. Summary of Applications (total lbs a.i. applied/day) of Diquat Dibromide to Alfalfa in 2008 from CDPR PUR data.

3.2.1 PRZM/EXAMS Model Inputs

The appropriate PRZM and EXAMS input parameters for diquat dibromide and related compounds were selected from the environmental fate data submitted by the registrant in accordance with US EPA-OPP EFED water model parameter selection guidelines, *Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides*.

Version 2.1, October 22, 2009 and *PE5 User's Manual ((P)RZM (E)XAMS Model Shell, Version (5), November 15, 2006)*. Input parameters can be grouped by physical-chemical properties and other environmental fate data, application information, and use scenarios. Physical and chemical properties and environmental fate data relevant to assess the behavior of diquat dibromide in the environment are presented in **Table 3-2**.

Table 3-2. Summary of PRZM/EZAMS Environmental Fate Data Used for Aquatic Exposure Inputs for Diquat Dibromide Endangered Species Assessment¹

Fate Property	Value	MRID ^a (or source)
Molecular Weight	344.05	Footprint @ http://sitem.herts.ac.uk/aeru/footprint/en/ , accessed on April 21, 2010
Vapor Pressure (Torr)	$<1 \times 10^{-7}$	MRID 40245101
Solubility in Water (mg/L)	700,000	MRID 00136329,40302701
Photolysis in Water half-life (d)	74	MRID 40418801; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Aerobic Soil Metabolism Half-life (d)	0 (stable)	MRID# 40972301
Hydrolysis half-life (d)	0 (stable)	MRID# 154100 and 154101; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Aerobic Aquatic Metabolism (water column) half-life (d)	0 (stable)	MRID# 40927601; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Anaerobic Aquatic Metabolism (benthic) half-life (d)	0 (stable)	MRID# 40972302; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Kd (mg/L)	4895	Lowest non-sand value; MRID# 40348601; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Application Efficiency	95 % for aerial 99 % for ground	Default value; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
Spray Drift Fraction	5 % for aerial 1% for ground	Default value; Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, 2009
1 – Inputs determined in accordance with EFED “Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides. Version 2.1” dated October 22, 2009.		

3.2.2 Post-processing of PRZM/EXAMS Outputs to Develop EECs for Residential and Rights-of-ways

The LUIS Report lists diquat dibromide uses that are modeled using the rights-of-way and residential RLF scenarios. Rights-of-way uses include fencerows, hedgerows, paved areas, and private roads/sidewalks applications. Residential uses include ornamental and/or shade trees, ornamental ground cover, ornamental herbaceous plants, ornamental lawns and turf, ornamental non-flowering plants, ornamental woody shrubs and vines applications. Both these scenarios contain areas with impervious (*i.e.*, cement, asphalt, metal surfaces) and pervious surfaces. It is

assumed that diquat dibromide will be applied to the pervious surfaces where weeds are expected to grow. It is also assumed that diquat dibromide is not applied to impervious surfaces in rights-of-way, but that there is a 1% incidental spray onto impervious surfaces surrounding rights-of-way.

In a standard PRZM scenario, it is assumed that an entire 10-hectare field is composed only of the identified crop and that the field has uniform surface properties throughout the field. In the rights-of-way and residential scenarios, this is not a reasonable assumption because rights-of-way and residential areas generally contain both impervious and pervious surfaces. Since the two surfaces have different properties (especially different curve numbers influencing the runoff from the surfaces) and different amounts of diquat dibromide applied, the standard approach for deriving aquatic EECs is revised using the following approach:

- 1) Aquatic EECs are derived for the pervious portion of the rights-of-way, using the maximum use rate of diquat dibromide on the CA rights-of-way and CA residential scenarios. At this point, it is assumed that 100% of both the rights-of-way and residential scenarios are composed of pervious surface. Specific inputs for this modeling are defined below.
- 2) Aquatic EECs are derived for the impervious portion of the rights-of-way using 1% for liquid formulation of the maximum use rate of diquat dibromide on the CA impervious and CA Residential scenarios. At this point, it is assumed that 100% of the rights-of-way and residential scenarios are composed of impervious surface.
- 3) The daily aquatic EECs (contained in the PRZM/EXAMS output file with the suffix "TS") are input into a Microsoft[®] Excel[®] worksheet.
- 4) Daily aquatic EECs for the impervious surface are multiplied by 50%. Daily aquatic EECs for the pervious surface are multiplied by 50%. The resulting EECs for impervious and pervious surfaces are added together to get an adjusted EEC for each day of the 30-year simulation period (**Equation 3.1**).

Equation 3.1

$$\text{Revised EEC} = (\text{impervious EEC} * 50\%) + (\text{pervious EEC} * 50\%)$$

- 5) Rolling averages for the relevant durations of exposure (21-day and 60-day averages) are calculated. The 1-in-10 year peak, 21-day, and 60-day values are used to define the acute and chronic EECs for the aquatic habitat.

In this modeling approach, it is assumed that both the rights-of-way and residential scenarios are composed of equal parts pervious and impervious surfaces (*i.e.*, in step 4, the EECs of both surfaces are multiplied by 50%). However, in reality, it is likely that rights-of-way and residential areas contain different ratios of the two surfaces. In general, incorporation of impervious surfaces into the exposure assessment results in increasing runoff volume in the watershed, which tends to reduce overall pesticide exposure (when assuming 1% overspray to the impervious surface).

3.2.3 PRZM/EXAMS Results

The aquatic EECs for the various scenarios are listed in **Table 3-3**. Example PRZM/EXAMS output is attached as Appendix D. For food uses, the aerial applications typically resulted in higher aquatic EECs (due to greater spray drift). The peak concentrations ranged from 0.018 µg cation/L (Right of Way) to 20.546 µg cation/L (Nursery). The 21-day average concentrations ranged from 0.011 µg cation/L (Right of Way) to 8.220 µg cation/L (Nursery). The 60-day average concentrations ranged from 0.011 µg cation/L (Right of Way) to 8.160 µg/L (Nursery). For the Nursery uses, the EECs were estimated based on two applications of 1.865 lb ai/ac with a 30-day interval. This rate is the second highest among all terrestrial uses.

Aqueous photolysis is the only degradation mechanism among all the possible modeling inputs. Since the rate of degradation by photolysis is relatively slow (half-life = 74 days), the modeling results would expect to show accumulation over time. Accumulation was observed in the modeling results however, total accumulation in the water column was small.

Table 3-3. Aquatic EECs (µg/L*) for Diquat Dibromide Uses in California

Scenario	Crops/Uses Represented	Peak EEC (µg/L)		21-day average EEC (µg/L)		60-day average EEC (µg/L)	
		Salt	Cation	Salt	Cation	Salt	Cation
CA Alfalfa OP (aerial and ground)	Alfalfa, Clover, Jojoba	3.780	2.026	1.580	0.847	1.540	0.826
		1.816	0.973	1.226	0.657	1.224	0.656
CA Almond STD	Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	5.233	2.805	2.619	1.404	2.607	1.398
CA Avocado RLF	Avocado	17.002	9.113	4.475	2.399	4.428	2.374
CA Citrus STD	Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon, Tangerine	1.217	0.652	0.767	0.411	0.735	0.394
CA Forestry RLF	Forestry	17.365	9.308	7.398	3.967	7.312	3.921
CA Fruit STD	Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate	2.373	1.272	0.748	0.401	0.732	0.392
CA Grape STD	Grapes, Kiwi Fruits	4.950	2.653	1.576	0.845	1.546	0.829

Scenario	Crops/Uses Represented	Peak EEC (µg/L)		21-day average EEC (µg/L)		60-day average EEC (µg/L)	
		Salt	Cation	Salt	Cation	Salt	Cation
CA Nursery	Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	38.333	20.546	15.330	8.220	15.219	8.160
CA Olive RLF	Olive	2.743	1.470	0.924	0.495	0.897	0.481
CA Potato RLF (aerial and ground)	Potatoes	3.487	1.869	1.297	0.695	1.209	0.648
		2.008	1.076	0.913	0.490	0.877	0.470
CA Residential RLF	Household/ Domestic Dwellings Outdoor Premises, Paved Areas	0.922	0.494	0.550	0.295	0.547	0.293
CA Right Of Way RLF	Right of Way Areas (including Roadsides, CRP acreage)	0.033	0.018	0.020	0.011	0.020	0.011
CA Row Crop RLF	Artichokes, Asparagus	11.334	6.075	4.978	2.669	4.900	2.627
CA Turf RLF	Recreation Area Turf, Golf Course	1.822	0.977	0.810	0.434	0.790	0.424
CA Wheat RLF (aerial and ground)	Canola	6.874	3.684	4.386	2.352	4.306	2.309
		5.539	2.969	4.149	2.225	4.100	2.198
CA Wine Grapes RLF	Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	13.964	7.485	6.410	3.437	6.298	3.377
The formulations (e.g., Reward and Reglone) contain 2 lbs. diquat cation per gal. as 3.73 lbs. salt per gal. The PE5 calculations are based on the diquat dibromide salt. In order to derive the cation concentrations, the EEC values of the salt were multiplied by 0.536 (2/3.73).							

3.2.4 Surface Water Modeling Approach and Inputs for Direct Application to Water Scenarios

For acute exposure, the label Diquat Weed Killer (EPA Reg. No. 3862-129) instructions were utilized. The maximum target water concentration was 2.5 mg cation/L. Although the label specifies to treat only 1/3 to 1/2 of the water body at one time and to wait 14 days to treat the next portion of the water body, peak concentrations in the treated areas would be expected to be

approximately 2.5 mg cation/L. This value will be used for the direct application to water acute EEC.

For chronic exposure, the Tier 1 rice model developed by EFED was used to provide the EECs for direct aquatic applications. The rice model only models for one single application, therefore, the EECs are for one application only. The model is described below:

$$C_w = \frac{m_{ai}'}{0.00105 + 0.00013K_d}$$

where:

C_w = water concentration [$\mu\text{g/L}$]

m_{ai}' = mass applied per unit area [kg/ha]

K_d = water-sediment partitioning coefficient [L/kg]

The aquatic uses of diquat dibromide include aquatic food and aquatic non-food uses. For food use, the maximum rate is 1.87 lb ai/ac-ft, and for non-food use the maximum rate is 7.46 lb ai/ac-ft. Although the labels specify to treat only $\frac{1}{3}$ to $\frac{1}{2}$ of the water body at a time, modeling assumed the entire water body was treated. Because laboratory data indicated diquat dibromide is stable, it is unlikely that significant degradation would occur during the 14-day interval prior to treating the second half of the water body.

Table 3-4. Tier I Rice Model v1.0 Input Parameters for Diquat Dibromide.			
Input Parameter	Value	Justification	Source
Application Rate (kg a.i./ha)	0.6859	1.87 lbs a.i./A-ft x 1.121 kg·A/ha·lbs * 30.48 cm/ft x 10/10 = 0.6859 kg a.i./ha-10 cm	Aquatic Food Use Rate* (1.87 lb/ac-ft)
Application Rate (kg a.i./ha)	2.549	7.46 lbs a.i./A-ft x 1.121 kg·A/ha·lbs * 30.48 cm/ft x 10/10 = 1.765 kg a.i./ha-10 cm	Aquatic Non-Food Use Rate* (7.46 lb ai/ac-ft)
Soil-to-Water Partition Coefficient (K_d) (L/kg)	4895	Lowest non-sand K_d Value	MRID # 40348601
*different % of a.i. for different formulation.			

Table 3-5. Estimated Environmental Concentrations (EEC) of Diquat Dibromide for Aquatic Uses Based on Tier I Rice Model.		
Use	Chronic EEC ($\mu\text{g salt/L}$)	Chronic EEC ($\mu\text{g cation/L}$)
Aquatic Food Use	1.076	0.577
Aquatic Non-Food Use	3.999	2.143

These concentrations (0.577 $\mu\text{g cation/L}$ for aquatic food use and 2.14 $\mu\text{g cation/L}$ for aquatic non-food use) in the water body represent about 15.7% of the applied diquat dibromide, the remaining 84.3% of the applied amounts are associated with suspended solids and the benthic

sediment layer. These results are not unexpected given the high partition coefficient value of 4895 L/Kg.

3.2.5 Existing Monitoring Data

A critical step in the process of characterizing EECs is comparing the modeled estimates with available surface water monitoring data. Three monitoring sources have been reviewed to see whether diquat dibromide exists at significant levels. The first source is U. S. Geological Survey's National Water-Quality Assessment (NAWQA) program. Diquat dibromide is not included among the 88 pesticide constituents monitored in the program. The second monitoring source is the California Department of Pesticide Regulation database (<http://www.cdpr.ca.gov/docs/emon/surfwttr/surfcont.htm>). For the CA surface water database, only three entries were reported in Tulare County for diquat dibromide on 01/03/2006 (**Table 3-6**). All three values are reported as no detections; the LOD and LOQ were not reported. Diquat dibromide was not included in the California ground water monitoring studies. The EPA STORET data warehouse (www.epa.gov/storet) contained seven records for diquat dibromide from January 1, 1999, to present, for sampling done in California. All seven are reported as below quantification limit of 0.4 µg cation/L (**Table 3-6**).

Table 3-6. Surface water concentrations of Diquat Dibromide.

Database	Site Description	Conc [µg/L]	latitude	longitude
CDPR	Crocs Creek at Highway 99 (Revised); Regional Board Irr. Lands Mon. Site Code: 558CCRSP4	below detection limit	36.4073	-119.4542
CDPR	St. Johns River; Regional Board Irr. Lands Mon. Site code: 558SJRSP2	below detection limit	36.3559	-119.2787
CDPR	Stone Corral I.D. Discharge; Regional Board Irr. Lands Mon. Site code: 558SCDSP3	below detection limit	36.4568	-119.2233
STORET	Zanja de Cota Creek Downstream, 8/12/2009	Present Below Quantification Limit	34.59342	-120.094
STORET	Zanja de Cota Creek Downstream, 2/10/2009	Present Below Quantification Limit	34.59342	-120.094
STORET	Zanja de Cota Creek West Fork Upstream, 2/17/2009	Present Below Quantification Limit	34.60963	-120.087
STORET	Zanja de Cota Creek Mid-point, 2/10/2009	Present Below Quantification Limit	34.60662	-120.09
STORET	Zanja de Cota Creek West Fork Upstream, 8/12/2009	Present Below Quantification Limit	34.60963	-120.087
STORET	Zanja de Cota Creek Mid-point, 8/12/2009	Present Below Quantification Limit	34.60662	-120.09
STORET	Zanja de Cota Creek East Fork Upstream, 8/12/2009	Present Below Quantification Limit	34.60745	-120.089

3.3 Terrestrial Plant Exposure Assessment

TerrPlant (Version 1.1.2) is used to calculate EECs for non-target plant species inhabiting dry and semi-aquatic areas. Parameter values for application rate, drift assumption and incorporation depth are based upon the use and related application method (**Table 3-7**). A runoff value of 0.05 is utilized based on diquat dibromide's solubility (700 g/L). For aerial and ground application methods, drift is assumed to be 5% and 1%, respectively. EECs relevant to terrestrial plants consider pesticide concentrations in drift and in runoff. These EECs are listed by use in **Table 3-7**.

Table 3-7. TerrPlant Inputs and Resulting EECs for Plants Inhabiting Dry and Semi-aquatic Areas Exposed to Diquat Dibromide via Runoff and Drift

Modeled Scenario	Application rate (lbs cation/A)	Drift Value (%)	Spray drift EEC (lbs cation/A)	Dry area EEC (lbs cation/A)	Semi-aquatic area EEC (lbs cation/A)
Aerial Applications					
Alfalfa, Clover, Jojoba	0.50	5	0.025	0.05	0.275
Potatoes					
Canola					
Ground Applications					
Alfalfa, Clover, Jojoba	0.50	1	0.005	0.03	0.255
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut					
Avocado					
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon Tangerine					
Forestry					
Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears. Peaches, Plums, Prune, Pomegranate					
Grapes, Kiwi Fruits					
Olive					
Potatoes					
Artichokes, Asparagus					
Recreation Area Turf, Golf Course					
Canola					
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit					

Right of Way Areas (including Roadsides, CRP acreage)	1.0	1	0.01	0.05	0.51
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations					
Household/ Domestic Dwellings Outdoor Premises, Paved Areas	1.12	1	0.011	0.067	0.571
Direct Water (food use)	6.0	1	0.6	NA	NA
Direct Water (non-food)	24.0	1	2.4	NA	NA
*maximum labeled application rate is 1.0 and 4.0 lbs cation/acre-ft; this analysis assumes water depth of 6 ft. NA – EECs that are composed of both drift and runoff are not relevant for Direct Water applications as runoff is not expected.					

4 Effects Assessment

This assessment evaluates the potential for diquat dibromide to directly or indirectly affect DS or modify their designated critical habitat. Assessment endpoints for the effects determination for each assessed species include direct toxic effects on the survival, reproduction, and growth, as well as indirect effects, such as reduction of the prey base or modification of its habitat. In addition, potential modification of critical habitat is assessed by evaluating effects to the PCEs, which are components of the critical habitat areas that provide essential life cycle needs of each assessed species.

As described in the Agency's Overview Document (USEPA, 2004), the most sensitive endpoint for each taxon is used for risk estimation. For this assessment, evaluated taxa include freshwater fish, freshwater invertebrates, estuarine/marine fish, estuarine/marine invertebrates, aquatic plants, and terrestrial plants. Acute (short-term) and chronic (long-term) toxicity information is characterized based on registrant-submitted studies and a comprehensive review of the open literature available through ECOTOX on diquat dibromide.

4.1 Ecotoxicity Study Data Sources

Toxicity endpoints are established based on data generated from guideline studies submitted by the registrant, and from open literature studies that meet the criteria for inclusion into the ECOTOX database maintained by EPA/Office of Research and Development (ORD) (USEPA, 2004). Open literature data presented in this assessment were obtained from the diquat dibromide RED (July 1995) as well as ECOTOX information obtained on October 8, 2010. In order to be included in the ECOTOX database, papers must meet the following minimum criteria:

- (1) the toxic effects are related to single chemical exposure;
- (2) the toxic effects are on an aquatic or terrestrial plant or animal species;
- (3) there is a biological effect on live, whole organisms;
- (4) a concurrent environmental chemical concentration/dose or application rate is reported; and

- (5) there is an explicit duration of exposure.

Open literature toxicity data for ‘target’ terrestrial plant species, which include efficacy studies, are not currently considered in deriving the most sensitive endpoint for terrestrial plants. Efficacy studies do not typically provide endpoint values that are useful for risk assessment (*e.g.*, NOAEC, EC₅₀, etc.), but rather are intended to identify a dose that maximizes a particular effect (*e.g.*, EC₁₀₀). Therefore, efficacy data and non-efficacy toxicological target data are not included in the ECOTOX open literature summary table provided in Appendix G. The list of citations including toxicological and/or efficacy data on target plant species not considered in this assessment is provided in Appendix F. Agency reviews of open literature are included in Appendix H.

Data that pass the ECOTOX screen are evaluated along with the registrant-submitted data, and may be incorporated qualitatively or quantitatively into this endangered species assessment. In general, effects data in the open literature that are more conservative than the registrant-submitted data are considered. The degree to which open literature data are quantitatively or qualitatively characterized for the effects determination is dependent on whether the information is relevant to the assessment endpoints (*i.e.*, survival, reproduction, and growth) identified in **Section 2.8**. For example, endpoints such as behavior modifications are likely to be qualitatively evaluated, because quantitative relationships between modifications and reduction in species survival, reproduction, and/or growth are not available. Although the effects determination relies on endpoints that are relevant to the assessment endpoints of survival, growth, or reproduction, it is important to note that the full suite of sublethal endpoints potentially available in the effects literature (regardless of their significance to the assessment endpoints) are considered, as they are relevant to the understanding of the area with potential effects, as defined for the action area.

Citations of all open literature not considered as part of this assessment because they were either rejected by the ECOTOX screen or accepted by ECOTOX but not used (*e.g.*, the endpoint is less sensitive) are included in Appendix F. Appendix F also includes a rationale for rejection of those studies that did not pass the ECOTOX screen and those that were not evaluated as part of this endangered species risk assessment.

A detailed spreadsheet of the available ECOTOX open literature data, including the full suite of lethal and sublethal endpoints is presented in Appendix G.

In addition to registrant-submitted and open literature toxicity information, other sources of information, including use of the acute probit dose response relationship to establish the probability of an individual effect and reviews of ecological incident data, are considered to further refine the characterization of potential ecological effects associated with exposure to diquat dibromide. A summary of the available aquatic and terrestrial ecotoxicity information and the incident information for diquat dibromide are provided in **Sections 4.1** through **4.4**.

The active ingredient, diquat dibromide, is a salt and completely dissociates in water. Toxicity is assumed to be associated with the diquat cation. The ratio of molecular weights of 0.536 (184.2 g/mole for diquat cation and 344g/mole for diquat dibromide) is used to convert a.i. to cation of

diquat dibromide. For this assessment, application rates and toxicity will be listed in terms of the diquat cation.

Degradates of diquat dibromide were not included in the toxicity analysis. No major degradates were isolated from any of the environmental fate studies except for the aqueous photolysis study. 1,2,3,4-tetrahydro-1-oxopyrido (1,2-a) pyrazin-5-ium ion appears to be the major photodegradate, with a half-life of 74 days (aquatic environment without sediment). However, in the natural aquatic environment with sediment, photolysis would not be considered as a means of diquat dibromide dissipation due to the high adsorption with the sediments; therefore, no further evaluation of degradates was conducted.

4.2 Toxicity of Diquat Dibromide to Aquatic Organisms

Table 4-1 summarizes the most sensitive aquatic toxicity endpoints, based on an evaluation of both the submitted studies and the open literature, as previously discussed. A brief summary of submitted and open literature data considered relevant to this ecological risk assessment for the DS is presented below. Additional information is provided in Appendix E. All endpoints are expressed in terms of the diquat cation unless otherwise specified.

Toxicity to fish and aquatic invertebrates is categorized using the system shown in **Table 4-2** (USEPA, 2004). Toxicity categories for aquatic plants have not been defined.

Table 4-1. Aquatic Toxicity Profile for Diquat Dibromide

Assessment Endpoint	Acute/ Chronic	Species TGAI/TEP % diquat cation	Toxicity Value Used in Risk Assessment	Citation or MRID # (Author, Date) ¹	Comment
Freshwater fish	Acute	(Walleye <i>Stizostedion vitreum</i>) EUP 240 g cation/L	96-hr LC ₅₀ = 0.750 mg cation/L	E14903 Paul <i>et al.</i> (1994)	Quantitative
	Chronic	fathead minnow (<i>Pimephales promelas</i>) EUP 21.1% cation	NOAEC/LOAEC= 0.122/0.316 mg cation/L (larval wet weight)	MRID 403807-03 (Surprenant, 1987) and D155699	Acceptable (12% reduction in larval wet weight at the LOAEC)
Freshwater invertebrates	Acute	Crustacean amphipod (<i>Hyalella</i> spp.) EUP %cation unknown	EC ₅₀ = 0.14 mg cation/L	MRID 00115862 Nicholson <i>et al.</i> , 1974	Supplemental (no raw data)
	Chronic	NA	NOAEC = 0.002 mg cation/L	NA	Estimated using ACR (see Section 4.2.2.b)

Assessment Endpoint	Acute/ Chronic	Species TGAI/TEP % diquat cation	Toxicity Value Used in Risk Assessment	Citation or MRID # (Author, Date) ¹	Comment
Estuarine/ marine fish	Acute	sheepshead minnow (<i>Cyprinodon variegatus</i>) EUP 21.1% cation	LC ₅₀ = 51.1 mg cation/L	MRID 403161-01 (Nicholson, 1987)	Acceptable (A precipitate was observed on the bottom of the aquaria in the two highest treatment levels at 72 and 96 hours of the exposure period. The study author did not state whether the test solutions were centrifuged prior to analytical measurement of diquat dibromide.)
	Chronic	NA	NOAEC = 3.57 mg cation/L	NA	Estimated using ACR (see Section 4.2.3.b)
Estuarine/ marine invertebrates	Acute	Mysid shrimp (<i>Americamysis bahia</i>) EUP 21.1% cation	96-hr LC ₅₀ = 0.42 mg cation/L	MRID 40315701 (Hoberg, 1987)	Acceptable
	Chronic	NA	NOAEC = 0.019 mg cation/L	NA	Estimated using ACR (see Section 4.2.4.b)
Aquatic plants	Vascular	Giant duckweed (<i>Spirodela punctata</i>)	Foliar application (IC ₅₀ = 0.004 lb cation/acre) Rootzone application (IC ₅₀ = 0.00075 mg cation/L)	MRID 41883002 (Bellet, 1990)	Supplemental (no raw data, Florida microcosm studies, NOAEC and/or IC ₀₅ were not reported)
	Non-vascular	Green algae (<i>Kirchneria subcapitata</i>) EUP 26.8% cation	IC ₅₀ = 0.0094 mg cation/L NOAEC = 0.0068 mg cation/L	MRID 43532703 Smyth and Tapp, 1988	Acceptable (endpoints based on cell density)
1-ECOTOX references are designated with an E followed by the ECOTOX reference number.					

Table 4-2. Categories of Acute Toxicity for Fish and Aquatic Invertebrates

LC ₅₀ (mg/L)	Toxicity Category
< 0.1	Very highly toxic
> 0.1 - 1	Highly toxic
> 1 - 10	Moderately toxic
> 10 - 100	Slightly toxic
> 100	Practically nontoxic

4.2.1 Toxicity to Freshwater Fish

A summary of acute and chronic freshwater fish data submitted to the Agency is in **Sections 4.2.1.a** and **4.2.1.b**. A summary of evaluated data from the open literature is in **Section 4.2.1.c**.

4.2.1.a Freshwater Fish: Acute Exposure (Mortality) Studies

Acute toxicity to freshwater fish can be summarized as slightly toxic to practically non-toxic for diquat dibromide. Definitive LC₅₀ values range from 14 to 231 mg cation/L; non-definitive LC₅₀ values range from >51 to >366 mg cation/L. No studies are available for technical diquat dibromide; all submitted studies were conducted using various end use products for which specific chemical compositions were not available. Ten studies were conducted on bluegill sunfish (*Lepomis macrochirus*), with definitive LC₅₀ values ranging from 14 to 231 mg cation/L and non-definitive LC₅₀ values ranging from >102 to >366 mg cation/L. Other tested species include rainbow trout (*Onchorhynchus mykiss*), brown trout (*Salmo trutta*), yellow perch (*Perca flavescens*), black bullhead (*Ameiurus melas*), and goldfish *Carassius auratus*).

4.2.1.b Freshwater Fish: Chronic Exposure (Growth/Reproduction) Studies

One early life-stage toxicity test conducted on the fathead minnow (*Pimephales promelas*) was submitted to the Agency for review (MRID 403807-03 and D155699). The test was conducted using Diquat Concentrate (an EUP with 41.4% ai, 21.1% cation). The NOAEC and LOAEC were established at 0.122 and 0.316 mg cation/L, respectively based on larval wet weight. This study was initially classified as Supplemental (missing raw data) and later upgraded to Acceptable (D155699, June 24, 1994).

The NOAEC of 0.122 mg cation/L is used to quantitatively estimate chronic risk for freshwater fish.

4.2.1.c Freshwater Fish: Open Literature Data

Paul et al. (1994, E14903) conducted studies evaluating the toxicity of diquat dibromide to several age classes of walleye (*Stizostedion vitreum*), largemouth bass (*Micropterus salmoides*), and smallmouth bass (*Micropterus dolomieu*). Diquat dibromide (tested as the end-use product Diquat HA) LC₅₀'s were 0.75, 1.5, and 4.9 mg cation/L in 8-10 day, 41-43 day, and 84-86 day

walleye, respectively. The LC₅₀ for 6-8 day smallmouth bass was 3.9 mg cation/L, and the LC₅₀ for 9-13 day largemouth bass was 4.9 mg cation/L.

As this was the most sensitive endpoint and there were no data available for the technical, the LC₅₀ of 0.75 mg cation/L is used to quantitatively estimate acute risk for freshwater fish.

4.2.2 Toxicity to Freshwater Invertebrates

A summary of acute and chronic freshwater invertebrate data, including data published in the open literature, is provided below. No studies evaluating toxicity of diquat dibromide to freshwater invertebrates with more sensitive toxicity values than data submitted to the Agency were identified.

4.2.2.a Freshwater Invertebrates: Acute Exposure Studies

Acute toxicity to freshwater invertebrates can be summarized as highly toxic to practically non-toxic for diquat dibromide. Definitive EC₅₀ values range from 0.14 to 7.1 mg cation/L for an amphipod (*Hyalella* spp.), daphnid (*Daphnia magna*), and the apple snail (*Pomacea paludosa*). A non-definitive EC₅₀ value was obtained for the *Gammarus fasciatus* (EC₅₀ >50.9 mg cation/L) during a 24-hour test. Two studies were conducted using the technical (daphnid, EC₅₀ = 1.17 mg cation/L, MRID 000115576; and daphnid, EC₅₀ = 7.1 mg/L, MRID 05001465). Other freshwater invertebrate studies were conducted using various end-use products.

The uncertainties regarding toxicity testing with technical as compared to testing with end-use products were evaluated. Three studies were conducted for the daphnid:

- an end-use product resulting in an EC₅₀ of 0.77 mg cation/L (MRID 00115577),
- the technical resulting in an EC₅₀ of 1.17 mg cation/L (MRID 000115576), and
- the technical resulting in an EC₅₀ of 7.1 mg cation/L (MRID 05001465).

Both MRID 00115577 and 00115576 were conducted by the same author in the same laboratory and resulted in very similar EC₅₀ values. Results from MRID 0500465 indicate a reduced toxicity for the technical as compared to the end-use product in MRID 00115577; however, this was only a 26-hr study and the percent a.i. and/or percent cation of the test material were not provided. Since the two studies with greater confidence have similar results, it was concluded that there was insufficient evidence to suggest that the diquat dibromide end-use product enhanced toxicity. It is suggested that the range in toxicity endpoints for freshwater invertebrates may be due primarily to differences in species sensitivity and random variability.

4.2.2.b Freshwater Invertebrates: Chronic Exposure Studies

One life-cycle toxicity test conducted on the daphnid (*Daphnia magna*) was submitted to the Agency for review (MRID 403807-02 and D155699). The test was conducted using Diquat Concentrate (an EUP with 41.4% ai, 21.1% cation). The NOAEC and LOAEC were established at 0.036 and 0.087 mg cation/L, respectively, based on survival. This study was initially classified as Supplemental (missing raw data) and later upgraded to Acceptable with adequate data (D155699, June 24, 1994).

This study was conducted with an end-use product, and no chronic freshwater invertebrate studies conducted with the technical were available. Based on the review of the freshwater invertebrate acute data, it was assumed that toxicities of the technical and the end use products were similar when compared on a cation basis.

Using the available data, the most sensitive acute and chronic values are from different species of freshwater invertebrates (*Hyaella* and daphnid). Since both acute and chronic data are available for the daphnid, an Acute to Chronic Ratio (ACR) can be calculated. Using the acute LC₅₀ of 0.77 mg cation/L (MRID 00115577) and the chronic NOAEC of 0.036 mg cation/L (MRID 403807-02 and D155699), the resulting ACR based on the most sensitive daphnid data is 21.4. This ratio was applied to the acute *Hyaella* LC₅₀, resulting in an estimated NOAEC = 0.002 mg cation/L. This estimated NOAEC for *Hyaella* will be used to quantitatively estimate chronic risk to freshwater invertebrates.

4.2.3 Toxicity to Estuarine/Marine Fish

A summary of acute and chronic estuarine/marine fish data, including data published in the open literature is provided below. No open literature studies evaluating toxicity of diquat dibromide to estuarine/marine fish with more sensitive toxicity values than data submitted to the Agency were identified.

4.2.3.a Estuarine/Marine Fish: Acute Exposure Studies

One acute toxicity test conducted on the sheepshead minnow (*Cyprinodon variegatus*) was submitted to the Agency for review (MRID 403161-01). The test was conducted using Diquat Concentrate (an EUP with 41.4% ai, 21.1% cation). The LC₅₀ was established at 51.1 mg cation/L and the slope was 2.14. This study was classified as Acceptable; however, the study author noted that all test solutions containing Diquat Concentrate were brown-colored, and the color intensity increased with the concentration of test material. A precipitate was observed on the bottom of the aquaria in the two highest treatment levels at 72 and 96 hours of the exposure period. The study author did not state whether the test solutions were centrifuged prior to analytical measurement of diquat dibromide. If solutions were not centrifuged, the measured concentrations are likely higher than the bioavailable diquat dibromide dissolved in the water column. It is also unknown if the precipitate was another component of the tested end-use product (Diquat Concentrate). There is considerable uncertainty in the endpoint (LC₅₀ = 51 mg/cation/L) as this value may reflect both the bioavailable material and material present in the aquaria as precipitate.

A second acute toxicity test was conducted on the longnose killifish (*Fundulus similis*) (MRID 40228401). The LC₅₀ was reported as > 20 mg cation/L. This study is classified as Supplemental as no raw data were available and it was only a 48-hr study.

The LC₅₀ of 51.1 mg cation/L is used to quantitatively estimate acute risk for estuarine/marine fish.

4.2.3.b Estuarine/Marine Fish: Chronic Exposure Studies

No chronic toxicity studies for estuarine/marine fish were submitted to the Agency. A chronic toxicity value was estimated for the estuarine/marine fish using the most sensitive acute and chronic freshwater fish data as well as the acute toxicity value for estuarine/marine fish. Typically an Acute to Chronic Ratio (ACR) would be constructed using freshwater fish acute and chronic data from the same species; however, no acute fathead minnow data were available and the only chronic data were from the fathead minnow. Definitive LC₅₀s for freshwater fish ranged from 0.75 to 231 mg cation/L. For those species with multiple acute tests, the definitive LC₅₀s ranged from 14 to 213 mg cation/L (bluegill sunfish, seven studies conducted) and from 0.75 to 4.6 mg cation/L (walleye, three age classes tested). Because of the wide range of LC₅₀s obtained for the bluegill sunfish alone, the total variability in LC₅₀s cannot be attributed solely to species differences.

An ACR of 14.3 was calculated from the acute LC₅₀ of 0.750 mg cation/L (walleye; E14903) and the chronic NOAEC of 0.122 mg cation/L (fathead minnow; (MRID 403807-03 and D155699). There is considerable uncertainty in this ACR estimate since it is derived from two different species. This ratio was applied to the acute sheepshead minnow LC₅₀, resulting in an estimated NOAEC = 3.57 mg cation/L. This estimated NOAEC for sheepshead minnow will be used to quantitatively estimate chronic risk for estuarine/marine fish.

4.2.4 Toxicity to Estuarine/Marine Invertebrates

A summary of acute and chronic estuarine/marine invertebrate data is provided below. No studies evaluating toxicity of diquat dibromide to estuarine/marine invertebrates with more sensitive toxicity values than data submitted to the Agency were identified.

4.2.4.a Estuarine/Marine Invertebrates: Acute Exposure Studies

One acute toxicity test conducted on the Mysid shrimp (*Americamysis bahia* formerly *Mysidopsis bahia*) was submitted to the Agency for review (MRID 403157-01). The test was conducted using Diquat Concentrate (an EUP with 41.4% a.i., 21.1% cation). The 96-hr LC₅₀ was established at 0.42 mg cation/L and the slope was 5.4.

One oyster shell growth test conducted on the Eastern oyster (*Crassostrea virginica*) was submitted to the Agency for review (MRID 403160-01). The test was conducted using Diquat Concentrate (an EUP with 41.4% ai, 21.1% cation). The 96-hr IC₅₀ based on shell growth was established at > 54.9 mg cation/L, with a 28% reduction in shell growth at the highest test concentration relative to the control. This study had a flow-through rate much higher than recommended (reported 200 mL/oyster/hr and recommended 5 mL/oyster/hr).

Two non-definitive tests were available from MRID 40228401 (supplemental, no raw data submitted). A 48-hr test on the pink shrimp (*Penaeus duorarum*) resulted in an EC₅₀ >20 mg cation/L, and a 96-hr growth test on the Eastern oyster resulted in an EC₅₀ of >0.50 mg cation/L.

The LC₅₀ of 0.42 mg cation/L is used to quantitatively estimate acute risk for estuarine/marine invertebrates.

4.2.4.b Estuarine/Marine Invertebrates: Chronic Exposure Studies

No chronic toxicity studies for estuarine/marine invertebrates were submitted to the Agency.

A chronic toxicity value was estimated for the mysid, the most acutely sensitive estuarine/marine invertebrate, using acute and chronic values for the daphnids. Daphnids had an acute LC₅₀ of 0.77 mg cation/L (MRID 00115577) and a chronic NOAEC of 0.036 mg cation/L (MRID 403807-02 and D155699) resulting in an Acute to Chronic Ratio (ACR) of 21.4. This ratio was applied to the acute mysid LC₅₀, resulting in an estimated NOAEC = 0.019 mg cation/L. This estimated NOAEC for mysids will be used to quantitatively estimate chronic risk for estuarine/marine invertebrates.

4.2.5 Toxicity to Aquatic Plants

Aquatic plant toxicity studies are used as one of the measures of effect to evaluate whether diquat dibromide may affect primary production. Aquatic plants may also serve as dietary items of the DS. In addition, freshwater vascular and non-vascular plant data are used to evaluate a number of the PCEs associated with the critical habitat impact analysis.

A summary of aquatic plant data, including data published in the open literature, is provided below. No studies evaluating toxicity of diquat dibromide to aquatic plants with more sensitive toxicity values than data submitted to the Agency were identified.

One acceptable non-vascular aquatic plant study with a diquat dibromide formulation was conducted on *Kirchneria subcapitata* (MRID 43532703) with resulting IC₅₀ and NOAEC values of 0.0094 mg cation/L and 0.0068 mg cation/L, respectively. Four supplemental non-vascular aquatic plant studies were conducted on two marine diatoms, one marine algae, and one green algae using a diquat dibromide formulation (MRID 40228401). Resulting 240-hr IC₅₀s ranged from 7.6 to 102 mg cation/L. NOAECs and IC₀₅s were not provided and could not be calculated (no raw data submitted).

Supplemental studies were available for eight vascular aquatic plant species treated with a diquat dibromide formulation (MRID 41883002). IC₅₀s based on a root zone application ranged from 0.00075 to 3.515 mg cation/L. IC₅₀s based on a foliar application ranged from 0.004 to 14.4 lbs cation/acre. For both application methods, giant duckweed (*Spirodela punctata*) was the most sensitive species. NOAECs and IC₀₅s were not provided and could not be calculated (no raw data submitted) in this Florida microcosm study.

This risk assessment will utilize data from the most sensitive non-vascular plant (*Kirchneria subcapitata*) and vascular plant (*Lemna gibba*) studies. For *Kirchneria subcapitata*, the IC₅₀ and NOAEC are 0.0094 mg cation/L and 0.0068 mg cation/L, respectively (MRID 43532703). For *Lemna gibba*, the IC₅₀ and IC₀₅ are 49.7 and 14.7 µg cation/L (NOAEC not definitive).

4.3 Toxicity of Diquat Dibromide to Terrestrial Organisms

Table 4-3 summarizes the most sensitive terrestrial plant toxicity endpoints, based on an evaluation of both the submitted studies and the open literature. A brief summary of submitted and open literature data considered relevant to this ecological risk assessment is presented below. Additional information is provided in Appendix E.

Table 4-3. Terrestrial Toxicity Profile for Diquat Dibromide

Endpoint	Species	Toxicity Value Used in Risk Assessment	Citation MRID/ ECOTOX reference No.	Comment
Terrestrial plants	<i>Seedling Emergence</i> Monocots	IC ₂₅ > 4.65 lbs cation/acre NOAEC = 4.65 lbs cation/acre	MRID 40165101 (Shilling and Mossler, 1987)	Acceptable (no effects were observed for any of the species tested)
	<i>Seedling Emergence</i> Dicots	IC ₂₅ > 4.65 lbs cation/acre NOAEC = 4.65 lbs cation/acre	MRID 40165101 (Shilling and Mossler, 1987)	Acceptable (no effects were observed for any of the species tested)
	<i>Vegetative Vigor</i> Monocots	IC ₂₅ = 0.011 lbs cation/acre	MRID 41883001 (Bellet, 1990)	Supplemental (no raw data, Florida field study, NOAEC/IC ₀₅ not available), most sensitive with a definitive IC ₂₅ was corn (shoot height).
	<i>Vegetative Vigor</i> Dicots	IC ₂₅ = 0.005 lbs cation/acre	MRID 41883001 (Bellet, 1990)	Supplemental (no raw data, Florida field study, NOAEC/IC ₀₅ not available), most sensitive with a definitive IC ₂₅ was cotton (dry weight). For sunflower, a non-definitive IC ₂₅ < 0.020 lbs cation/acre was determined for dry weight

4.3.1 Toxicity to Terrestrial Plants

Plant toxicity data from both registrant-submitted studies and studies in the scientific literature were reviewed for this assessment. Registrant-submitted studies are conducted under conditions and with species defined in EPA toxicity test guidelines. Sublethal endpoints such as plant growth, dry weight, and biomass are evaluated for both monocots and dicots, and effects are evaluated at both seedling emergence and vegetative life stages. Guideline studies generally evaluate toxicity to ten crop species. These tests are conducted on herbaceous crop species only, and extrapolation of effects to other species, such as the woody shrubs and trees and wild herbaceous species, contributes uncertainty to risk conclusions.

Commercial crop species have been selectively bred, and may be more or less resistant to particular stressors than wild herbs and forbs. The direction of this uncertainty for specific plants and stressors, including diquat dibromide, is largely unknown. Homogenous test plant seed lots also lack the genetic variation that occurs in natural populations, so the range of effects seen from tests is likely to be smaller than would be expected from wild populations.

The results of the Tier I seedling emergence and Tier II vegetative vigor toxicity tests on non-target plants are summarized below in **Table 4-4**.

Table 4-4. Non-target Terrestrial Plant Seedling Emergence and Vegetative Vigor Toxicity for Diquat Dibromide

Crop	Species	NOAEC (lb cation/A)	IC ₂₅ (lb cation/A)	Most sensitive parameter	Slope
Seedling Emergence (Tier I)					
Monocots	Barnyard grass (<i>Echinochloa sp.</i>)	4.65	>4.65	na	na
	Corn (<i>Zea mays</i>)	4.65	>4.65	na	na
	Onion (<i>Allium cepa</i>)	4.65	>4.65	na	na
	Rye (<i>Lolium perenne</i>)	4.65	>4.65	na	na
Dicots	Potato (<i>Solanum tuberosum</i>)	4.65	>4.65	na	na
	Sicklepod (<i>Senna obtusifolia</i>)	4.65	>4.65	na	na
	Jimson weed (<i>Datura stramonium</i>)	4.65	>4.65	na	na
	Morning glory (<i>Ipomea sp</i>)	4.65	>4.65	na	na
	Soybean (<i>Glycine max</i>)	4.65	>4.65	na	na
	Sunflower (<i>Helianthus annuus</i>)	4.65	>4.65	na	na
Vegetative Vigor (Tier II)					
Monocots	Sweet corn	0.017	0.023	Dry weight	na
	Wheat	0.070	0.091	Dry weight	na
	Corn (<i>Zea mays</i>)	NA	0.011	Shoot height	na
	Onion (<i>Allium cepa</i>)	NA	0.177	Shoot height	na
Dicots	Soybean (<i>Glycine max</i>)	NA	0.007	Dry weight	na
	Sunflower (<i>Helianthus annuus</i>)	NA	<0.020	Dry weight	na
	Cotton	NA	0.005	Shoot height	na
	Yellow nutsedge	NA	0.141	Shoot height	na

4.4 Toxicity of Chemical Mixtures

As previously discussed, the results of available toxicity data for mixtures of diquat dibromide with other pesticides are presented in Appendix A. Diquat dibromide currently has 35 registered products that contain multiple active ingredients. Analysis of the available open literature and acute oral mammalian LD₅₀ data for multiple active ingredient products shows that an assessment based on the toxicity of the single active ingredient of diquat dibromide is appropriate. A qualitative examination of acute toxicity data (e.g., LD₅₀) trends, with associated confidence intervals, across the range of percent active ingredient, show no discernable trends in

potency that would suggest synergistic (*i.e.*, more than additive) or antagonistic (*i.e.*, less than additive) interactions.

4.5 Incident Database Review

A review of the Ecological Incident Information System (EIIS, version 2.1), the 'Aggregate Incident Reports' (v. 1.0) database, and the Avian Monitoring Information System (AIMS) for ecological incidents involving diquat dibromide was completed on November 2, 2010 using both PCcode 032201 (diquat dibromide) and 032202 (diquat).. The results of this review for terrestrial, plant, and aquatic incidents are summarized below, and a complete list of incidents including associated uncertainties is included as Appendix I.

Seven aquatic incidents classified as 'possible,' 'probable,' or 'highly probable' were reported in EIIS. All seven incidents were as a result of direct application of diquat dibromide to a water body. Reported effects for all incidents were mortality, with species ranging from clams to fish to frogs. Of these seven reported incidents, two were misuses, three were registered uses, and two were of unknown legality of use. For two of the incidents that were registered uses, the cause of death was reported as likely to be due to low dissolved oxygen following the large algae kill. No further information regarding cause of mortality was provided for the third registered use incident or the two unknown use incidents.

Fourteen terrestrial incidents classified as 'possible,' 'probable,' or 'highly probable' were reported in EIIS. Five of the 14 incidents were recorded in EIIS as misuses, four were recorded as registered uses, and the remaining five were recorded as unknown legality. Exposures were recorded as direct spray or spray drift. Reported effects were plant damage and plant mortality.

In the Aggregate Incident Reports database, 23 fish and wildlife incidents, 45 plant incidents, and two other nontarget incidents were reported. No incident reports for diquat dibromide were identified in the AIMS database.

4.6 Use of Probit Slope Response Relationship to Provide Information on the Endangered Species Levels of Concern

The Agency uses the probit dose response relationship as a tool for providing additional information on the potential for acute direct effects to individual listed species and aquatic animals that may indirectly affect the listed species of concern (USEPA, 2004). As part of the risk characterization, an interpretation of acute RQs for listed species is discussed. This interpretation is presented in terms of the chance of an individual event (*i.e.*, mortality or immobilization) should exposure at the EEC actually occur for a species with sensitivity to diquat dibromide on par with the acute toxicity endpoint selected for RQ calculation. To accomplish this interpretation, the Agency uses the slope of the dose response relationship available from the toxicity study used to establish the acute toxicity measures of effect for each taxonomic group that is relevant to this assessment. The individual effects probability associated with the acute RQ is based on the mean estimate of the slope and an assumption of a probit dose response relationship. In addition to a single effects probability estimate based on the mean,

upper and lower estimates of the effects probability are also provided to account for variance in the slope, if available.

Individual effect probabilities are calculated using an Excel spreadsheet tool IECV1.1 (Individual Effect Chance Model Version 1.1) developed by the U.S. EPA, OPP, Environmental Fate and Effects Division (June 22, 2004). The model allows for such calculations by entering the mean slope estimate (and the 95% confidence bounds of that estimate) as the slope parameter for the spreadsheet. In addition, the acute RQ is entered as the desired threshold.

5 Risk Characterization

Risk characterization is the integration of the exposure and effects characterizations. Risk characterization is used to determine the potential for direct and/or indirect effects to the DS or for modification to their designated critical habitat from the use of diquat dibromide in CA. The risk characterization provides an estimation (**Section 5.1**) and a description (**Section 5.2**) of the likelihood of adverse effects; articulates risk assessment assumptions, limitations, and uncertainties; and synthesizes an overall conclusion regarding the likelihood of adverse effects to the assessed species or their designated critical habitat (*i.e.*, “no effect,” “likely to adversely affect,” or “may affect, but not likely to adversely affect”). In the risk estimation section, risk quotients are calculated using standard EFED procedures and models. In the risk description section, additional analyses may be conducted to help characterize the potential for risk.

5.1 Risk Estimation

Risk is estimated by calculating the ratio of exposure to toxicity. This ratio is the risk quotient (RQ), which is then compared to pre-established acute and chronic levels of concern (LOCs) for each category evaluated (Appendix C). For acute exposures to the aquatic animals, as well as terrestrial invertebrates, the LOC is 0.05. The LOC for exposures to plants is 1.0.

Acute and chronic risks to aquatic organisms are estimated by calculating the ratio of exposure to toxicity using 1-in-10 year EECs in **Table 3-3** based on the label-recommended diquat dibromide usage scenarios summarized in **Table 3-1** and the appropriate aquatic toxicity endpoint from **Table 4-1**. Exposures are also derived for terrestrial plants, as discussed in **Section 3.3** and summarized in **Table 3-7**, based on the highest application rates of diquat dibromide use within the action area.

5.1.1 Exposures in the Aquatic Habitat

5.1.1.1 Freshwater Fish

For all scenarios except direct application to water, acute risk to fish is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value for freshwater fish, and chronic risk is based on the 1 in 10 year 60-day EECs and the lowest chronic toxicity value for freshwater fish. For direct application to water, acute risk is based on label target concentrations and the lowest acute toxicity value for freshwater fish, and chronic risk is based on the rice model concentrations and the lowest chronic toxicity value for freshwater fish. Risk quotients for

freshwater fish are shown in **Table 5-1**. The Listed Species and Acute LOCs were exceeded for direct applications to water and Chronic LOCs were not exceeded for any modeled scenarios.

As the Listed Species LOCs for freshwater fish were exceeded by the calculated RQs, diquat dibromide does have the potential to directly affect the DS in the direct application to water scenarios.

Table 5-1. Acute and Chronic RQs for Freshwater Fish

Modeled Scenario	Peak EEC (µg cation/L)+	60-day EEC (µg cation/L)+	Acute RQ*	Chronic RQ*
CA Alfalfa OP (aerial and ground)	2.026	0.825	<0.01	0.01
	0.973	0.656	<0.01	0.01
CA Almond STD	2.805	1.397	<0.01	0.01
CA Avocado RLF	9.113	2.373	0.01	0.02
CA Citrus STD	0.652	0.394	<0.01	<0.01
CA Forestry RLF	9.308	3.919	0.01	0.03
CA Fruit STD	1.272	0.392	<0.01	<0.01
CA Grape STD	2.653	0.829	<0.01	0.01
CA Nursery	20.546	8.157	0.03	0.07
CA Olive RLF	1.470	0.481	<0.01	<0.01
CA Potato RLF (aerial and ground)	1.869	0.648	<0.01	0.01
	1.076	0.470	<0.01	<0.01
CA Residential RLF	0.494	0.293	<0.01	<0.01
CA Right Of Way RLF	0.018	0.011	<0.01	<0.01
CA Row Crop RLF	6.075	2.626	0.01	0.02
CA Turf RLF	0.977	0.423	<0.01	<0.01
CA Wheat RLF (aerial and ground)	3.684	2.308	<0.01	0.02
	2.969	2.198	<0.01	0.02
CA Wine Grapes RLF	7.485	3.376	0.01	0.03
Aquatic Food Use	2,500	0.577	3.33	<0.01
Aquatic Non-Food Use	2,500	2.143	3.33	0.02
+ Units of EECs reported in this table are µg cation/L. They were obtained from Tables 3-3 and 3-5 from the percent cation in technical a.i. (53.9%). * = LOC exceedances (Listed Species acute RQ ≥ 0.05; chronic RQ ≥ 1.0) are bolded. Acute RQ = use-specific peak EEC / 750 µg cation/L [walleye]. Chronic RQ = use-specific 60-day EEC / 122 µg cation/L [fathead minnow].				

5.1.1.2 Freshwater Invertebrates

For all scenarios except direct application to water, acute risk to freshwater invertebrates is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value for freshwater invertebrates, and chronic risk is based on the 1 in 10 year 21-day EECs and the

lowest chronic toxicity value for freshwater invertebrates. For direct application to water, acute risk is based on label target concentrations and the lowest acute toxicity value for freshwater invertebrates, and chronic risk is based on the rice model concentrations and the lowest chronic toxicity value for freshwater invertebrates. Risk quotients for freshwater invertebrates are shown in **Since acute** and chronic LOCs are exceeded, there is a potential for indirect effects to those listed species that rely on freshwater invertebrates during at least some portion of their life-cycle (*i.e.*, DS).

Table 5-2. The acute LOC was exceeded for nine of the 21 modeled scenarios. The chronic LOC was exceeded for avocado, forestry, nursery, row crop, wheat (aerial and ground), wine grapes, and aquatic non-food scenarios.

Since acute and chronic LOCs are exceeded, there is a potential for indirect effects to those listed species that rely on freshwater invertebrates during at least some portion of their life-cycle (*i.e.*, DS).

Table 5-2. Summary of Acute and Chronic RQs for Freshwater Invertebrates.

Modeled Scenario	Peak EEC (µg cation/L)+	21-day EEC (µg cation/L)+	Acute RQ*	Chronic RQ*
CA Alfalfa OP (aerial and ground)	2.026	0.847	0.04	0.42
	0.973	0.657	0.02	0.33
CA Almond STD	2.805	1.404	0.06	0.70
CA Avocado RLF	9.113	2.399	0.19	1.20
CA Citrus STD	0.652	0.411	0.01	0.21
CA Forestry RLF	9.308	3.965	0.19	1.98
CA Fruit STD	1.272	0.401	0.03	0.20
CA Grape STD	2.653	0.845	0.06	0.42
CA Nursery	20.546	8.217	0.43	4.11
CA Olive RLF	1.470	0.495	0.03	0.25
CA Potato RLF (aerial and ground)	1.869	0.695	0.04	0.35
	1.076	0.489	0.02	0.24
CA Residential RLF	0.494	0.295	0.01	0.15
CA Right Of Way RLF	0.018	0.011	<0.01	0.01
CA Row Crop RLF	6.075	2.668	0.13	1.33
CA Turf RLF	0.977	0.434	0.02	0.22
CA Wheat RLF (aerial and ground)	3.684	2.351	0.08	1.18
	2.969	2.224	0.06	1.11
CA Wine Grapes RLF	7.485	3.436	0.16	1.72

Aquatic Food Use	2,500	0.577	52.1	0.29
Aquatic Non-Food Use	2,500	2.143	52.1	1.07
+ Units of EECs reported in this table are µg cation/L. They were obtained from Tables 3-3 and 3-5 from the percent cation in technical a.i. (53.9%). * = LOC exceedances (acute RQ ≥ 0.05; chronic RQ ≥ 1.0) are bolded. Acute RQ = use-specific peak EEC / 48 µg cation/L [<i>Hyaella</i>]. Chronic RQ = use-specific 21-day EEC / 2 µg cation/L [ACR using daphnid and <i>Hyaella</i> data].				

5.1.1.3 Estuarine/Marine Invertebrates

For all scenarios except direct application to water, acute risk to estuarine/marine invertebrates is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value for estuarine/marine invertebrates, and chronic risk is based on the 1 in 10 year 21-day EECs and the lowest chronic toxicity value for estuarine/marine invertebrates. For direct application to water, acute risk is based on label target concentrations and the lowest acute toxicity value for estuarine/marine invertebrates, and chronic risk is based on the rice model concentrations and the lowest chronic toxicity value for estuarine/marine invertebrates. Risk quotients are shown in **Table 5-3**. The Acute LOC was exceeded for direct application to water (food uses and non-food uses). The Chronic LOC was not exceeded for any modeled scenarios.

Since the acute LOC is exceeded, there is a potential for indirect effects to those listed species that rely on estuarine/marine invertebrates during at least some portion of their life-cycle (*i.e.*, DS).

Table 5-3. Summary of Acute and Chronic RQs for Estuarine/Marine Invertebrates.

Modeled Scenario	Peak EEC (µg cation/L) +	21-day EEC (µg cation/L)+	Acute RQ*	Chronic RQ*
CA Alfalfa OP (aerial and ground)	2.026	0.847	<0.01	0.04
	0.973	0.657	<0.01	0.03
CA Almond STD	2.805	1.404	0.01	0.07
CA Avocado RLF	9.113	2.399	0.02	0.13
CA Citrus STD	0.652	0.411	<0.01	0.02
CA Forestry RLF	9.308	3.965	0.02	0.21
CA Fruit STD	1.272	0.401	<0.01	0.02
CA Grape STD	2.653	0.845	0.01	0.04
CA Nursery	20.546	8.217	0.05	0.43
CA Olive RLF	1.470	0.495	<0.01	0.03
CA Potato RLF (aerial and ground)	1.869	0.695	<0.01	0.04
	1.076	0.489	<0.01	0.03
CA Residential RLF	0.494	0.295	<0.01	0.02
CA Right Of Way RLF	0.018	0.011	<0.01	<0.01
CA Row Crop RLF	6.075	2.668	0.01	0.14
CA Turf RLF	0.977	0.434	<0.01	0.02

CA Wheat RLF (aerial and ground)	3.684	2.351	0.01	0.12
	2.969	2.224	0.01	0.12
CA Wine Grapes RLF	7.485	3.436	0.02	0.18
Aquatic Food Use	2,500	0.577	5.95	0.03
Aquatic Non-Food Use	2,500	2.143	5.95	0.11
+ Units of EECs reported in this table are µg cation/L. They were obtained from Tables 3-3 and 3-5 from the percent cation in technical a.i. (53.9%). * = LOC exceedances (acute RQ ≥ 0.05; chronic RQ ≥ 1.0) are bolded. Acute RQ = use-specific peak EEC / 420 µg cation/L [mysid]. Chronic RQ = use-specific 21-day EEC / 19 µg cation/L [ACR using daphnid and mysid data].				

5.1.1.4 Non-vascular Aquatic Plants

For all scenarios except direct application to water, acute risk to non-vascular plants is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value. For direct application to water, acute risk is based on label target concentrations and the lowest acute toxicity value. Acute risk to aquatic non-vascular plants is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value. Risk quotients are shown in **Table 5-4**. The acute LOC was exceeded for the nursery scenario and direct application to water (food and non-food uses).

Since the LOC is exceeded, there is a potential for indirect effects to those listed species that rely on non-vascular aquatic plants during at least some portion of their life-cycle (*i.e.*, DS).

5.1.1.a Aquatic Vascular Plants

For all scenarios except direct application to water, acute risk to vascular plants is based on 1 in 10 year peak EECs in the standard pond and the lowest acute toxicity value. For direct application to water, acute risk is based on label target concentrations and the lowest acute toxicity value. Risk quotients are shown in **Table 5-4**. The acute LOC was exceeded for all scenarios except citrus, residential, and right of way.

Since the LOC is exceeded, there is a potential for indirect effects to those listed species that rely on vascular aquatic plants during at least some portion of their life-cycle (*i.e.*, DS).

Table 5-4. Summary of Acute RQs for Non-Vascular and Vascular Aquatic Plants.

Modeled Scenario	Peak EEC (µg cation/L)+	Non-vascular Acute RQ*	Vascular Acute RQ**
CA Alfalfa OP (aerial and ground)	2.026	0.22	2.70
	0.973	0.10	1.30
CA Almond STD	2.805	0.30	3.74
CA Avocado RLF	9.113	0.97	12.15
CA Citrus STD	0.652	0.07	0.87

Modeled Scenario	Peak EEC (µg cation/L)+	Non-vascular Acute RQ*	Vascular Acute RQ**
CA Forestry RLF	9.308	0.99	12.41
CA Fruit STD	1.272	0.14	1.70
CA Grape STD	2.653	0.28	3.54
CA Nursery	20.546	2.19	27.40
CA Olive RLF	1.470	0.16	1.96
CA Potato RLF (aerial and ground)	1.869	0.20	2.49
	1.076	0.11	1.44
CA Residential RLF	0.494	0.05	0.66
CA Right Of Way RLF	0.018	<0.01	0.02
CA Row Crop RLF	6.075	0.65	8.10
CA Turf RLF	0.977	0.10	1.30
CA Wheat RLF (aerial and ground)	3.684	0.39	4.91
	2.969	0.32	3.96
CA Wine Grapes RLF	7.485	0.80	9.98
Aquatic Food Use	2,500	266	3333
Aquatic Non-Food Use	2,500	266	3333
+ Units of EECs reported in this table are µg cation/L. They were obtained from Tables 3-3 and 3-5 from the percent cation in technical a.i. (53.9%). *LOC exceedances (RQ ≥ 1) are bolded. RQ = use-specific peak EEC/ 9.4 µg cation/L [<i>Kirchneria ubcapitata</i>]. **LOC exceedances (RQ ≥ 1) are bolded. RQ = use-specific peak EEC/ 0.75 µg cation/L [<i>Giant duckweed (Spirodela punctata)</i>].			

5.1.2 Exposures in the Terrestrial Habitat

5.1.2.1 Terrestrial Plants

Generally, for indirect effects, potential effects on terrestrial vegetation are assessed using RQs from terrestrial plant seedling emergence and vegetative vigor IC₂₅ data as a screen. Risk quotients are shown in **Table 5-5** and **Table 5-6**.

For monocots, the LOC was only exceeded for aerial applications, residential applications, and direct water applications for exposure to spray drift alone. For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone. Since the non-listed plant RQs are exceeded, there is a potential for indirect effects to those listed species that rely on terrestrial plants during at least some portion of their life-cycle (*i.e.*, DS).

Table 5-5. RQs* for Monocots Inhabiting Dry and Semi-Aquatic Areas Exposed to Diquat Dibromide via Runoff and Drift.

Modeled Scenario	Application rate (lbs cation/A)	Drift Value (%)	Spray drift RQ	Dry area RQ	Semi-aquatic area RQ
Aerial Applications					
Alfalfa, Clover, Jojoba	0.50	5	2.27	<0.1	<0.1
Potatoes					
Canola					
Ground Applications					
Alfalfa, Clover, Jojoba	0.50	1	0.45	<0.1	<0.1
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut					
Avocado					
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon, Tangerine					
Forestry					
Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate					
Grapes, Kiwi Fruits					
Olive					
Potatoes					
Artichokes, Asparagus					
Recreation Area Turf, Golf Course					
Canola					
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit					
Right of Way Areas (including Roadsides, CRP acreage)	1.0	1	0.91	<0.1	0.11
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations					
Household/Domestic Dwellings Outdoor Premises, Paved Areas	1.12	1	1.02	<0.1	0.12
Direct Water (food use)	6.0**	2	5.45	NA	NA
Direct Water (non-food)	24.0**	1	21.82	NA	NA
*LOC exceedances (RQ ≥ 1) are bolded. *labeled application rate is 1.0 and 4.0 lbs cation/acre-ft; this analysis assumes water depth of 6 ft. NA – Not Applicable (Chemical treatments would not be expected to run-off from water bodies and potentially impact terrestrial plants).					

Table 5-6. RQs* for Dicots Inhabiting Dry and Semi-Aquatic Areas Exposed to Diquat Dibromide via Runoff and Drift.

Modeled Scenario	Application rate (lbs cation/A)	Drift Value (%)	Spray drift RQ	Dry area RQ	Semi-aquatic area RQ
Aerial Applications					
Alfalfa, Clover, Jojoba	0.50	5	5.0	<0.1	<0.1
Potatoes					
Canola					
Ground Applications					
Alfalfa, Clover, Jojoba	0.50	1	1.00	<0.1	<0.1
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut					
Avocado					
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon Tangerine					
Forestry					
Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate					
Grapes, Kiwi Fruits					
Olive					
Potatoes					
Artichokes, Asparagus					
Recreation Area Turf, Golf Course					
Canola					
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit					
Right of Way Areas (including Roadsides, CRP acreage)	1.0	1	2.00	<0.1	0.11
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations					
Household/Domestic Dwellings Outdoor Premises, Paved Areas	1.12	1	2.24	<0.1	0.12
Direct Water (food use)	6.0**	1	12.00	NA	NA
Direct Water (non-food)	24.0**	1	48.00	NA	NA
*LOC exceedances (RQ ≥ 1) are bolded. **labeled application rate is 1.0 and 4.0 lbs cation/acre-ft; this analysis assumes water depth of 6 ft. NA – Not Applicable (Chemical treatments would not be expected to run-off from water bodies and potentially impact terrestrial plants).					

5.1.3 Primary Constituent Elements of Designated Critical Habitat

For diquat dibromide use, the assessment endpoints for designated critical habitat PCEs involve the same endpoints as those being assessed relative to the potential for direct and indirect effects to the listed species assessed here. Therefore, the effects determinations for direct and indirect effects are used as the basis of the effects determination for potential modification to designated critical habitat.

5.2 Risk Description

The risk description synthesizes overall conclusions regarding the likelihood of adverse impacts leading to a preliminary effects determination (*i.e.*, “no effect,” “may affect, but not likely to adversely affect,” or “likely to adversely affect”) for the assessed species and the potential for modification of their designated critical habitat based on analysis of risk quotients and a comparison to the Level of Concern. The final No Effect/May Affect determination is made after the spatial analysis is completed at the end of the risk description, **Section 5.2.3**. In Section 5.2.3, a discussion of any potential overlap between areas where potential usage may result in LAA effects and areas where species are expected to occur (including any designated critical habitat) is presented. If there is no overlap of the species habitat and occurrence sections with the Potential Area of LAA Effects a No Effect determination is made.

If the RQs presented in the Risk Estimation (**Section 5.1**) show no direct or indirect effects for the assessed species, and no modification to PCEs of the designated critical habitat, a preliminary “no effect” determination is made, based on diquat dibromide’s use within the action area. However, if LOCs for direct or indirect effect are exceeded or effects may modify the PCEs of the critical habitat, the Agency concludes a preliminary “may affect” determination for the FIFRA regulatory action regarding diquat dibromide. A summary of the risk estimation results are provided in **Table 5-7** for direct and indirect effects to the listed species assessed here and in **Table 5-8** for the PCEs of their designated critical habitat.

Table 5-7. Risk Estimation Summary for Diquat Dibromide - Direct and Indirect Effects on Delta Smelt

Taxa	LOC Exceedances (Yes/No)	Description of Results of Risk Estimation	Delta Smelt Potentially Affected Via:
Freshwater Fish	Listed Species (Yes)	acute: LOCs for 2 of 21 scenarios are exceeded (direct water application for food and non-food uses) chronic: no exceedances	Direct Effects
Freshwater Invertebrates	Non-listed Species (Yes)	acute: LOCs for 11 of 21 scenarios are exceeded chronic: LOCs for 8 of 21 scenarios are exceeded	Indirect Effects
Estuarine/Marine Invertebrates	Non-listed Species (Yes)	acute: LOCs for 2 of 21 scenarios are exceeded (direct water application for	Indirect Effects

Taxa	LOC Exceedances (Yes/No)	Description of Results of Risk Estimation	Delta Smelt Potentially Affected Via:
		food and non-food uses) chronic: no exceedances	
Non-Vascular Aquatic Plants	Non-listed Species (Yes)	LOC was exceeded for nursery and direct water application scenarios only	Indirect Effects
Vascular Aquatic Plants	Non-listed Species (Yes)	LOCs for 18 of 21 scenarios are exceeded	Indirect Effects
Terrestrial Plants - Monocots	Non-listed Species (Yes)	Spray drift LOCs were exceeded for all aerial applications, residential uses (1.12 lbs cation/acre), and direct water applications.	Indirect Effects
Terrestrial Plants - Dicots	Non-listed Species (Yes)	Spray drift LOCs exceeded for all modeled scenarios	Indirect Effects

Table 5-8. Risk Estimation Summary for Diquat Dibromide – Effects to Designated Critical Habitat for Delta Smelt. (PCEs)

Taxa	LOC Exceedances Yes/No)	Description of Results of Risk Estimation
Freshwater Fish	Listed Species (Yes)	acute: LOCs for 2 of 21 scenarios are exceeded (direct water application for food and non-food uses) chronic: no exceedances
Freshwater Invertebrates	Non-listed Species (Yes)	acute: LOCs for 11 of 21 scenarios are exceeded chronic: LOCs for 8 of 21 scenarios are exceeded
Estuarine/Marine Invertebrates	Non-listed Species (Yes)	acute: LOCs for 2 of 21 scenarios are exceeded (direct water application for food and non-food uses) chronic: no exceedances
Non-Vascular Aquatic Plants	Non-listed Species (Yes)	LOC was exceeded for nursery and direct water application scenarios only
Vascular Aquatic Plants	Non-listed Species (Yes)	LOCs for 18 of 21 scenarios are exceeded
Terrestrial Plants - Monocots	Non-listed Species (Yes) ¹	Spray drift LOCs were exceeded for all aerial applications, residential uses (1.12 lbs cation/acre), and direct water applications.
Terrestrial Plants - Dicots	Non-listed Species (Yes) ¹	Spray drift LOCs exceeded for all modeled scenarios
¹ Only non-listed LOCs were evaluated because none of the assessed species have an obligate relationship with terrestrial monocots and dicots.		

Following a preliminary “may affect” determination, additional information is considered to refine the potential for exposure at the predicted levels based on the life history characteristics (*i.e.*, habitat range, feeding preferences, *etc.*) of the assessed species. Based on the best available information, the Agency uses the refined evaluation to distinguish those actions that “may affect, but are not likely to adversely affect” from those actions that are “likely to adversely affect” the assessed species and its designated critical habitat.

The criteria used to make determinations that the effects of an action are “not likely to adversely affect” the assessed species or modify its designated critical habitat include the following:

- Significance of Effect: Insignificant effects are those that cannot be meaningfully measured, detected, or evaluated in the context of a level of effect where “take” occurs for even a single individual. “Take” in this context means to harass or harm, defined as the following:
 - Harm includes significant habitat modification or degradation that results in death or injury to listed species by significantly impairing behavioral patterns such as breeding, feeding, or sheltering.
 - Harass is defined as actions that create the likelihood of injury to listed species to such an extent as to significantly disrupt normal behavior patterns which include, but are not limited to, breeding, feeding, or sheltering.
- Likelihood of the Effect Occurring: Discountable effects are those that are extremely unlikely to occur.
- Adverse Nature of Effect: Effects that are wholly beneficial without any adverse effects are not considered adverse.

A description of the risk and effects determination for each of the established assessment endpoints for the assessed species and their designated critical habitat is provided in **Sections 5.2.1 through 5.2.3**. The effects determination section for each listed species assessed will follow a similar pattern. Each will start with a discussion of the potential for direct effects, followed by a discussion of the potential for indirect effects. These discussions do not consider the spatial analysis. For those listed species that have designated critical habitat, the section will end with a discussion on the potential for modification to the critical habitat from the use of diquat dibromide. Finally, in **Section 5.2.3**, a discussion of any potential overlap between areas of concern and the species (including any designated critical habitat) is presented. If there is no overlap of the species habitat and occurrence sections with the Potential Area of LAA Effects a No Effect determination is made.

5.2.1 Delta Smelt

5.2.1.1 Direct Effects

Delta smelt must spend part of their life-cycle in both freshwater and saltwater. Larvae feed on freshwater algae and juveniles and adults feed mainly on zooplankton. These water bodies can receive runoff and spray drift containing diquat dibromide and/or be affected by diquat dibromide effects to terrestrial plants which influence water temperature, water quality, shade, sedimentation and runoff. As shown in **Table 5-1**, acute and chronic RQs based on the highest modeled EECs for diquat dibromide use on nursery (acute EEC = 20.5 µg cation/L, chronic EEC = 8.2 µg cation/L) and the most sensitive freshwater fish data are well below the Agency’s acute and chronic risk LOCs.

Diquat dibromide is not included as a measured analyte in the majority of surface water and ground water monitoring programs. The monitoring data reported by CDPR in Tulare County surface waters were non-detections (sampling occurred 01/03/2006). The CA monitoring data in

STORET consisted of seven samples from the Zanja de Cota Creek in 2009; all resulted in ‘less than the limit of detection.’ Because there were so few surface water samples and no ground water samples, it cannot be concluded that diquat dibromide will not be found in surface or ground waters. Given the lack of adequate monitoring data, it is assumed that the modeled EECs provide an adequate conservative measure of diquat dibromide exposures for DS.

Since DS inhabit both freshwater and saltwater, the most sensitive toxicity endpoints among freshwater and saltwater fish toxicity data are used to assess risk to DS from direct effects of diquat dibromide. Except for the direct application to water, acute RQs (**Table 5-2**) based on the modeled EECs and the most sensitive freshwater fish data (walleye $LC_{50} = 750 \mu\text{g cation/L}$ and fathead minnow $NOAEC = 122 \mu\text{g cation/L}$, **Table 4-1**) are well below the Agency’s acute and chronic risk LOCs. For the direct application to water scenario, the acute RQ was 3.33, exceeding the Agency’s listed species LOC of 0.05. The chronic LOC was not exceeded for any of the modeled scenarios.

Because raw data were not provided as part of the acute toxicity study for the walleye used as a surrogate for the DS, information is unavailable to estimate a slope for the dose response curve. Therefore, the probability of an individual effect to DS was calculated based on a default assumption of 4.5 (with lower and upper bounds of 2 and 9) (Urban and Cook, 1986). The corresponding estimated chance of an individual acute mortality to the DS at an RQ level of 0.03 (nursery, the highest RQ that did not exceed the listed species LOC) is 1 in $2.76\text{E}+11$ (with respective upper and lower bounds of 1 in 862 to 1 in $2.14\text{E}+42$). The corresponding estimated chance of an individual acute mortality to the DS at an RQ of 3.33 (direct application to water) is 1 in 1.1 (with respective upper and lower bounds of 1 in 1.0 to 1 in 1.17). Given the low probability of an individual mortality occurrence and acute and chronic RQs that are well below LOCs, diquat dibromide is not likely to cause direct adverse effects to the DS for applications that are not directly applied to water. For applications in which diquat dibromide is directly applied to water at the maximum target concentration, the probability of an individual mortality occurrence is high and diquat dibromide is likely to cause direct adverse effects to the DS.

Seven aquatic incidents classified as ‘possible,’ ‘probable,’ or ‘highly probable’ were reported in EIIS. All seven incidents were as a result of direct application of diquat dibromide to a water body. Reported effects for all incidents were mortality, with species ranging from clams to fish to frogs. Of these seven reported incidents, two were misuses, three were registered uses, and two were of unknown legality of use. For two of the incidents that were registered uses, the cause of death was reported as likely to be due to low dissolved oxygen following the large algae kill. No further information regarding cause of mortality was provided for the third registered use incident or the two unknown use incidents. A complete list of all the aquatic incidents involving diquat dibromide is included in Appendix I.

Using a weight-of-evidence approach, the following pieces of evidence were weighed:

- the LOC is exceeded for fish for the direct application to water scenarios
- for direct application to water, at the water concentration of 2.5 mg cation/L , the likelihood of an individual effect (mortality) is 1 in 1.1, and
- all reported incidents for aquatic animals were as a result of direct application to water.

From these lines of evidence, there **is** a potential for direct effects to the Delta smelt from the registered use of direct application to water of diquat dibromide.

5.2.1.2 Indirect Effects

5.2.1.2.1 Potential Loss of Prey

Algae (Aquatic Non-Vascular Plants)

As discussed in **Section 2.5**, the diet of DS larvae is composed primarily of unicellular aquatic plants (i.e., algae and diatoms) and detritus. Based on RQs for algae (**Table 5-3**) applications of diquat dibromide to water bodies and in nurseries may affect this food source. RQs for non-vascular plants were based on the most sensitive IC₅₀ value of 9.4 µg cation/L for freshwater green algae (*Kirchneria subcapitata*). Further examination of toxicity data submitted to the Agency for other non-vascular plants indicates that they are considerably less sensitive to diquat dibromide than *Kirchneria subcapitata* with IC₅₀ values ranging from 7.6 to 100 mg cation/L. There is considerable uncertainty in these values as no raw data were available for review and the study was conducted for 240 hours instead of the recommended 96-120 hours. Review of open literature data for diquat dibromide indicated all tested non-vascular aquatic plants species were less sensitive than *Kirchneria subcapitata* (MRID 43532703).

Based on applications of diquat dibromide to water bodies and nurseries, diquat dibromide **does** have the potential to indirectly affect the delta smelt by impacting aquatic non-vascular plants. According to the 1999-2008 CA PUR data described in **Section 2.4.3** and summarized in **Table 2-4**, some of the highest diquat dibromide usage categories were landscape maintenance and nurseries in California. Other crops with high reported diquat dibromide usage are alfalfa and rights of way, which are not expected to cause effects to non-vascular plants as food for DS larvae.

Aquatic Invertebrates

Since DS inhabit both freshwater and saltwater, the most sensitive toxicity endpoints from both freshwater and saltwater invertebrate toxicity data are used to assess risk to DS from indirect effects of diquat dibromide through reduction in prey. DS juveniles and adults feed on zooplankton, primarily consuming planktonic copepods, cladocerans, amphipods, and insect larvae. The daphnid and hyalella data described above is likely a good representative toxicity estimate for freshwater food items and mysids are good representative toxicity estimate for estuarine/marine food items since most of the mentioned taxa are crustacea. For freshwater invertebrates, acute LOCs were exceeded for 11 of 21 scenarios, and chronic LOCs were exceeded for 8 of 21 scenarios. For estuarine/marine invertebrates, acute LOCs are exceeded for direct applications to water, and all remaining acute and chronic RQs are well below the Agency's acute and chronic risk LOCs.

As previously discussed in **Section 5.1.1.b**, acute RQs (**Table 5-2**) calculated using modeled peak aquatic EECs and the 48-hour LC₅₀ for the *Hyalella* did exceed the endangered species LOC for 11 of 21 scenarios. Raw data was not provided as part of the acute toxicity study for

Hyalella; therefore, the probability of an individual effect to freshwater invertebrates was calculated based on a default assumption of a slope of 4.5 (with lower and upper bounds of 2 and 9) (Urban and Cook, 1986) (**Table 5-9**). The corresponding estimated chance of an individual acute mortality/immobilization to a freshwater invertebrate at the endangered species LOC of 0.05 is 1 in 4.18E+08 (with respective upper and lower bounds of 1 in 216 and 1 in 1.75E+31).

Table 5-9. Likelihood of Individual Effect on Freshwater Invertebrates for Each Use of Diquat Dibromide for the Delta Smelt (scenarios with LOC exceedances).

Modeled Scenario	Acute RQ*	Likelihood of individual acute effect (1 in....)	95% upper and lower bounds (1 in ...)
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	0.06	5.22E+07	(138, 5.04E+27)
Avocado	0.19	1710	(13.4, 2.35E+10)
Forestry	0.19	1710	(13.4, 2.35E+10)
Grapes, Kiwi Fruits	0.06	5.22E+07	(138, 5.04E+27)
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	0.43	20	(4.3, 2060)
Artichokes, Asparagus	0.13	2.99E+04	(26.2, 1.31E+15)
Canola (aerial and ground)	0.08	2.51E+06	(70.8, 3.64E+22)
	0.06	5.22E+07	(138, 5.04E+27)
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	0.16	5850	(17.9, 2.53E+12)
Aquatic food and non-food use	52.1	1	(1, 1)
* = LOC exceedances (acute RQ ≥ 0.05; chronic RQ ≥ 1.0) are bolded. Acute RQ = use-specific peak EEC / 48 µg cation/L [<i>Hyalella</i>]. Chronic RQ = use-specific 21-day EEC / 2 µg cation/L [ACR using daphnid and <i>Hyalella</i> data].			

A chronic toxicity value was estimated for the *Hyalella*, the most acutely sensitive freshwater invertebrate using acute and chronic values from the daphnids. Daphnids had an acute LC₅₀ of 0.77 mg cation/L (MRID 00115577) and a chronic NOAEC of 0.036 mg cation/L (MRID 403807-02 and D155699) resulting in an Acute to Chronic Ratio (ACR) of 21.4. This ratio was applied to the acute *Hyalella* LC₅₀, resulting in an estimated NOAEC = 0.002 mg cation/L. This estimated NOAEC for *Hyalella* will be used for risk estimation. Uncertainty is introduced into the assessment by calculating an estimated NOAEC for *Hyalella*; however, this added uncertainty is a consequence of addressing uncertainty in risk estimation by assuming the most sensitive species for acute data is not the same as the most sensitive species for chronic data.

Based on acute and chronic LOC exceedances, likelihood of individual mortality analysis and genus sensitivity distribution information for aquatic invertebrates, diquat dibromide **does** have the potential for indirect effects to the DS from loss of prey items due to applications in almond, avocado, forestry, grape, nursery, row crop, wheat, wine grapes, and applications directly to water.

5.2.1.2.2 Potential Modification of Habitat

Aquatic plants serve several important functions in aquatic ecosystems. Non-vascular aquatic plants are primary producers and provide the autochthonous energy base for aquatic ecosystems. Vascular plants provide structure, rather than energy, to the system, as attachment sites for many aquatic invertebrates, and refugia for juvenile organisms, such as fish and frogs. Emergent plants help reduce sediment loading and provide stability to nearshore areas and lower streambanks. In addition, vascular aquatic plants are important as attachment sites for egg masses of aquatic species.

Terrestrial plants serve several important habitat-related functions for the DS. Riparian vegetation helps to maintain the integrity of aquatic systems by providing bank and thermal stability, serving as a buffer to filter out sediment, nutrients, and contaminants before they reach the watershed.

Herbicides can adversely impact habitat in a number of ways. In the most extreme case, herbicides in spray drift and runoff from the site of application have the potential to kill (or reduce growth and/or biomass in) all or a substantial amount of the vegetation, thus removing or impacting structures which define the habitat, and reducing the functions (*e.g.*, cover, food supply for prey base) provided by the vegetation.

Diquat dibromide is a member of a group of herbicides that are known as Cell Membrane Destroyers (<http://www.ces.purdue.edu/extmedia/ws/ws-23-w.html>). Exposure to compounds in this group results in rapid disruption of cell membranes and very rapid kill. More specifically, diquat dibromide, along with paraquat dichloride, is in the smaller class of bipyridyliums. The bipyridyliums penetrate into the cytoplasm and cause the formation of peroxides and free electrons that destroy the cell membranes almost immediately. Rapid destruction of cell membranes prevents translocation to other regions of the plant. Severe injury is evident hours after application, first as water-soaked areas which later turn yellow or brown. Maximum kill is attained in a week or less. Partial coverage of a plant with spray results in spotting and/or partial shoot kill. New growth on surviving plants will be normal in appearance.

The bipyridyliums are foliar applied, strongly cationic, relatively toxic herbicides that are used postemergence only. Extremely strong binding to clay prevents activity for weed control or leaching in the soil. Only shoot kill can be expected. Liquids with suspended colloids (muddy water, slurry fertilizers) can cause inactivation.

Based on the available toxicity data for terrestrial plants, it appears monocots and dicots in the vegetative vigor test are more sensitive to diquat dibromide than monocots and dicots in the seedling emergence test. This is demonstrated by the difference in response to the two guideline studies. The dicot IC_{25} values for the seedling emergence is >4.65 lbs cation/acre and ranges from 0.005 to 0.141 lbs cation/acre for the vegetative vigor test. The monocot IC_{25} values for the seedling emergence is >4.65 lbs cation/acre and ranges from 0.011 to 0.177 lbs cation/acre for the vegetative vigor test. In the vegetative vigor studies, dicots appear to be somewhat more sensitive to diquat dibromide than monocots.

Riparian vegetation typically consists of three tiers of vegetation, which include a groundcover of grasses and forbs, an understory of shrubs and young trees, and an overstory of mature trees. While no guideline data are available on the toxicity of diquat dibromide to woody plants, the available incident data indicate that woody plants may be susceptible to diquat dibromide. Diquat dibromide is labeled for numerous forestry and nursery uses, suggesting that woody species are less susceptible than herbaceous plants. However, in one incident (I014404-020) ornamentals and trees were impacted following an application in a potato field. Woody trees and shrubs in both upland and riparian habitats are expected to intercept some of the diquat dibromide that might otherwise be deposited on the more sensitive herbaceous species. Additionally, in natural systems, older plants, fallen leaves, and other debris often provide a litter layer, which may serve to protect newly emerging herbaceous plants.

For monocots, the LOC was only exceeded in semi-aquatic areas for applications directly to water (non-food) (**Table 5-5**). For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone, dry areas, and semi-aquatic areas (**Table 5-6**).

In order to estimate buffer distances that are protective of plant species that the terrestrial-phase DS or its prey may depend on for cover, AgDRIFT (2.01) was used to model the dissipation distance to the IC₂₅ levels for terrestrial plants. Because diquat dibromide is used as a post-emergent herbicide, buffer distances were calculated for the most sensitive endpoints for both monocots and dicots in the vegetative vigor studies. Spray drift RQ values did not exceed LOCs for ground application when rates were 1.0 lbs cation/acre or less. For monocots, the calculated buffer distances ranged from 243 to >1000 ft, and for dicots, the calculated buffer distances ranged from 236 to >1000 ft (**Table 5-10**).

Table 5-10 Estimation of Buffer Distance Required to Eliminate LOC Exceedances (only spray drift exposure considered) for Terrestrial Plants Based on AgDRIFT*

App. Rate (lb cation/ acre)	Method (Boom Height for Ground)	Tier	Parameters***	Vegetative Vigor Required Buffer Distance (ft)	
				Monocot	Dicot
0.5*	Aerial	I	DSD = ASAE very fine to fine	>1000	>1000
0.5*	Ground (high)	I	DSD = ASAE very fine to fine	LOC not exceeded	236
1.0*	Ground (high)	I	DSD = ASAE very fine to fine	LOC not exceeded	417
1.12*	Ground (high)	I	DSD = ASAE very fine to fine	243	453
6.0**	Aerial (aquatic application)	I	DSD = ASAE very fine to fine	>1000	>1000
* Rates and input parameters based on the Reglone label (EPA Reg. No. 100-1061) ** Rates and input parameters based on the Reward label (EPA Reg. No. 100-1091) ***Fraction of applied input values for AGDRIFT: For vegetative vigor (monocot) IC ₂₅ = 0.011 lbs cation/acre; Fraction of the applied = IC ₂₅ ÷ Rate For vegetative vigor (dicot) IC ₂₅ = 0.005 lbs cation/acre; Fraction of the applied = IC ₂₅ ÷ Rate					

In one incident (I014404-020) ornamentals and trees were impacted following an application in a potato field. Field crops and wildflowers were negatively impacted in six other reported incidents in the EIIS database. In addition, there were 43 plant incidents reported in the Aggregate Incident Reports database. Although the reported number of diquat dibromide incidents for terrestrial plants is low, an absence of reports does not necessarily provide evidence of an absence of incidents. The only plant incidents that are reported are those that are alleged to occur on more than 45 percent of the acreage exposed to the pesticide. Therefore, an incident could impact 40% of an exposed crop and not be included in the EIIS database (unless it is reported by a non-registrant, such as a state agency, where data are not systemically collected).

Based on exceedance of the dicot terrestrial plant LOCs for all diquat dibromide use patterns considering spray drift exposure, it can be concluded that diquat dibromide may enter riparian areas via spray drift where it contacts the leaves and stems of sensitive plants.

In summary, terrestrial plant RQs are above LOCs; therefore, riparian vegetation **may** be affected. Given that riparian areas are comprised of a mixture of both non-sensitive woody (trees and shrubs) and sensitive grassy herbaceous vegetation, the DS may be indirectly affected by adverse effects to herbaceous vegetation.

5.2.2 Modification of Designated Critical Habitat

Based on the weight-of-evidence there is a potential for the modification of designated critical habitat based on the potential effects on prey base and aquatic and terrestrial plants.

5.2.3 Spatial Extent of Potential Effects

Since LOCs are exceeded, analysis of the spatial extent of potential LAA effects is needed to determine where effects may occur in relation to the treated site. If the potential area of usage and subsequent Potential Area of LAA Effects overlaps with DS habitat or areas of occurrence and/or critical habitat, a likely to adversely affect determination is made. If the Potential Area of LAA Effects and the DS habitat and areas of occurrence and/or critical habitat do not overlap, a no effect determination is made.

To determine this area, the footprint of diquat dibromide's use pattern is identified, using corresponding land cover data (see **Section 2.8**). Because of the broad spectrum of uses it is expected that the footprint of diquat dibromide's use could include the entire state of California. Therefore, no GIS mapping has been conducted. Actual usage is expected to occur in a smaller area as the chemical is only expected to be used on a portion of the identified area. The spatial extent of the effects determination also includes areas beyond the initial area of concern that may be impacted by runoff and/or spray drift (use footprint + distance downstream or downwind from use sites where organisms relevant to the assessed species may be affected). Because of the spatial extent of the use patterns of diquat dibromide, essentially all DS habitat could be affected by the pesticide.

5.3 Effects Determinations

5.3.1 Assessed Species

The Agency makes a “**may affect, and likely to adversely affect**” determination for the Delta smelt and a **habitat modification determination** for their designated critical habitat based on the potential for indirect effects and effects to the PCEs of critical habitat.

5.3.2 Addressing the Risk Hypotheses

In order to conclude this risk assessment, it is necessary to address the risk hypotheses defined in **Section 2.9.1**. Based on the conclusions of this assessment, only one of the hypotheses can be rejected, the hypothesis that labeled uses of diquat dibromide may directly affect the DS by causing mortality or by adversely affecting growth or fecundity. The other four stated hypotheses represent concerns in terms of direct and indirect effects of diquat dibromide on the DS and its designated critical habitat.

The labeled use of diquat dibromide may:

- indirectly affect DS and modify their designated critical habitat by reducing or changing the composition of food supply;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing the composition of the aquatic non-vascular plant community in the species’ current range, thus affecting primary productivity and larval food supply;
- indirectly affect DS and/or modify their designated critical habitat by reducing or changing aquatic habitat in their current range (via modification of water quality parameters, habitat morphology, and/or sedimentation); and
- indirectly affect DS and/or modify their habitat by reducing or changing the composition of the terrestrial plant community in riparian zones and, thus, affecting sedimentation, water quality and runoff.

6 Uncertainties

Uncertainties that apply to most assessments completed for the San Francisco Bay Species Litigation are discussed in Attachment I. This section describes additional uncertainties specific to this assessment.

6.1 Exposure Assessment Uncertainties

6.1.1 Aquatic Exposure Modeling Uncertainties

The 21- and 60-day average concentration of diquat cation in water due to direct application was estimated using the rice model (EFED, 2007) rather than PRZM and EXAMS as these models cannot simulate the flooding and release of water on an agricultural field. The rice model simulates the concentration in water as it released from the paddy. It considers partitioning of the pesticide to the paddy soil. The model does not consider degradation; however, for diquat dibromide this is a minor uncertainty since the chemical has been shown to be stable.

6.1.2 Exposure in Estuarine/marine Environments

PRZM-EXAMS modeled EECs are intended to represent exposure of aquatic organisms in relatively small ponds and low-order streams. Therefore it is likely that EECs generated from the PRZM-EXAMS model will over-estimate potential concentrations in larger receiving water bodies such as estuaries, embayments, and coastal marine areas because chemicals in runoff water (or spray drift, etc.) should be diluted by a much larger volume of water than would be found in the ‘typical’ EXAMS pond. However, as chemical constituents in water draining from freshwater streams encounter brackish or other near-marine-associated conditions, there is potential for important chemical transformations to occur. Many chemical compounds can undergo changes in mobility, toxicity, or persistence when changes in pH, Eh (redox potential), salinity, dissolved oxygen (DO) content, or temperature are encountered. For example, desorption and re-mobilization of some chemicals from sediments can occur with changes in salinity (Jordan *et al.*, 2008; Means, 1995; Swarzenski *et al.*, 2003), changes in pH (*e.g.*, Wood and Baptista 1993; Parikh *et al.* 2004; Fernandez *et al.* 2005), Eh changes (Velde and Church, 1999; Wood and Baptista, 1993), and other factors. Thus, although chemicals in discharging rivers may be diluted by large volumes of water within receiving estuaries and embayments, the hydrochemistry of the marine-influenced water may negate some of the attenuating impact of the greater water volume; for example, the effect of dilution may be confounded by changes in chemical mobility (and/or bioavailability) in brackish water. In addition, freshwater contributions from discharging streams and rivers do not instantaneously mix with more saline water bodies. In these settings, water will commonly remain highly stratified, with fresh water lying atop denser, heavier saline water – meaning that exposure to concentrations found in discharging stream water may propagate some distance beyond the outflow point of the stream (especially near the water surface). Therefore, it is not assumed that discharging water will be rapidly diluted by the entire water volume within an estuary, embayment, or other coastal aquatic environment. PRZM-EXAMS model results should be considered consistent with concentrations that might be found near the head of an estuary unless there is specific information – such as monitoring data – to indicate otherwise. Conditions nearer to the mouth of a bay or estuary, however, may be closer to a marine-type system, and thus more subject to the notable buffering, mixing, and diluting capacities of an open marine environment. Conversely, tidal effects (pressure waves) can propagate much further upstream than the actual estuarine water, so discharging river water may become temporarily partially impounded near the mouth (discharge point) of a channel, and resistant to mixing until tidal forces are reversed.

The Agency does not currently have sufficient information regarding the hydrology and hydrochemistry of estuarine aquatic habitats to develop alternate scenarios for assessed listed species that inhabit these types of ecosystems. The Agency acknowledges that there are unique brackish and estuarine habitats that may not be accurately captured by PRZM-EXAMS modeling results, and may, therefore, under- or over-estimate exposure, depending on the aforementioned variables.

6.2 Effects Assessment Uncertainties

6.2.1 Data Gaps and Uncertainties

- There are no estuarine/marine fish data for evaluation of chronic toxicity of diquat dibromide. For chronic toxicity, the acute-to-chronic ratio (ACR) calculations are conducted using freshwater fish toxicity data and applying to the acute sheepshead minnow (*Cyprinodon variegates*) data.
- There are no estuarine/marine invertebrate data for evaluation of chronic toxicity of diquat dibromide. For chronic toxicity, the acute-to-chronic ratio (ACR) calculations are conducted using daphnid toxicity data and applying to the acute Crustacean amphipod (*Hyalella* spp.) data.
- There are no acute or chronic data for benthic invertebrates. This is of concern for diquat dibromide as it sorbs strongly to sediment and pore water concentrations are expected to be higher than in the water column.

6.2.2 Sublethal Effects

When assessing acute risk, the screening risk assessment relies on the acute mortality endpoint as well as a suite of sublethal responses to the pesticide, as determined by the testing of species response to chronic exposure conditions and subsequent chronic risk assessment. Consideration of additional sublethal data in the effects determination is exercised on a case-by-case basis and only after careful consideration of the nature of the sublethal effect measured and the extent and quality of available data to support establishing a plausible relationship between the measure of effect (sublethal endpoint) and the assessment endpoints. However, the full suite of sublethal effects from valid open literature studies is considered for the characterization purposes.

7 Risk Conclusions

In fulfilling its obligations under Section 7(a)(2) of the Endangered Species Act, the information presented in this endangered species risk assessment represents the best data currently available to assess the potential risks of diquat dibromide to the DS and their designated habitat.

Based on the best available information, the Agency makes a Likely to Adversely Affect determination for the DS. Additionally, the Agency has determined that there is the potential for modification of the designated critical habitat for the DS from the use of the chemical. Given the LAA determination for DS and potential modification of designated critical habitat for DS, a description of the baseline status and cumulative effects is provided in Attachment III.

A summary of the risk conclusions and effects determinations for the DS and their critical habitat, given the uncertainties discussed in **Section 6** and Attachment I, is presented in **Tables 7-1** and **7-2**. Use specific effects determinations are provided in **Tables 7-3** and **7-4**.

Table 7-1. Effects Determination Summary for Effects of Diquat Dibromide on the DS

Species	Effects Determination	Basis for Determination
Delta Smelt <i>(Hypomesus transpacificus)</i>	May Affect, Likely to Adversely Affect (LAA)	Potential for Direct Effects
		<i>Aquatic-phase (Eggs, Larvae, and Adults):</i> Acute RQs exceeded the LOC for direct water applications. No chronic LOCs were exceeded. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater fish). In addition, several fish incidents were reported in EIIS. For some incidents, it was unclear if mortality was due toxicity of diquat dibromide or if mortality was a result of reduced dissolved oxygen from the high rate of plant mortality after diquat dibromide application.
		Potential for Indirect Effects
		<i>Aquatic prey items, aquatic habitat, cover and/or primary productivity</i> Freshwater invertebrates: Acute RQs exceeded the LOC for 11 of 21 scenarios; chronic RQs exceeded the LOC for 8 of 21 scenarios. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater invertebrates). Likelihood of an individual effect for other scenarios with LOC exceedences ranged from 1 in 20 to 1 in 5E+7. Estuarine/marine invertebrates: Acute LOC was exceeded for the two direct water applications; chronic LOC was not exceeded. Non-vascular plants: LOC was exceeded for nursery scenario and direct water applications. According to the 1999-2008 CA PUR data, the some of the highest diquat dibromide usage categories were landscape maintenance and nurseries in California. Direct application to water was also reported with moderate usage. Vascular plants: Acute RQs exceeded the LOC for 18 of 21 scenarios
		<i>Riparian habitat</i> For monocots, the LOC was only exceeded for aerial applications, residential applications, and direct water applications for exposure to spray drift alone. For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone. All RQ exceedences were based on vegetative vigor endpoints, as greenhouse toxicity tests indicated that diquat dibromide has a minimal effect on seedling emergence of the tested species. Multiple lines of evidence, including incidents of plant damage, support the conclusion of risk to plants.

Table 7-2. Effects Determination Summary for the Critical Habitat Impact Analysis

Designated Critical Habitat for:	Effects Determination	Basis for Determination
Delta Smelt <i>(Hypomesus transpacificus)</i>	Habitat Modification	Freshwater fish: Acute RQs exceeded the LOC for direct water applications. No chronic LOCs were exceeded. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater fish). In addition, several fish incidents were reported in EIIS. For some incidents, it was unclear if mortality was due to toxicity of diquat dibromide or if mortality was a result of reduced dissolved oxygen from the high rate of plant mortality after diquat dibromide application. Freshwater invertebrates: Acute RQs exceeded the LOC for 11 of 21 scenarios; chronic RQs exceeded the LOC for 8 of 21 scenarios. For direct water applications, probit analysis suggested that the likelihood of an individual effect is high (1 in 1 for freshwater invertebrates). Likelihood of an individual effect for other scenarios with LOC exceedences ranged from 1 in 20 to 1 in 5E+7. Estuarine/marine invertebrates: Acute LOC was exceeded for the two direct water applications; chronic LOC was not exceeded. Non-vascular plants: LOC was exceeded for nursery scenario and direct water applications. According to the 1999-2008 CA PUR data, some of the highest diquat dibromide usage categories were landscape maintenance and nurseries in California. Direct application to water was also reported with moderate usage. Vascular plants: Acute RQs exceeded the LOC for 18 of 21 scenarios Terrestrial plants: For monocots, the LOC was only exceeded for aerial applications, residential applications, and direct water applications for exposure to spray drift alone. For dicots, the LOC was exceeded for all modeled scenarios for spray drift alone. All RQ exceedences were based on vegetative vigor endpoints, as greenhouse toxicity tests indicated that diquat dibromide has a minimal effect on seedling emergence of the tested species.

Table 7-3. Use Specific Summary of the Potential for Adverse Effects to Aquatic Taxa

Uses	Potential for Effects to Identified Taxa Found in the Aquatic Environment:							
	DS (direct effects) ¹		Freshwater Invertebrates ²		Estuarine/Marine Invertebrates ²		Non-Vascular Plants ²	Vascular Plants ²
	Acute	Chronic	Acute	Chronic	Acute	Chronic		
Alfalfa, Clover, Jojoba (aerial and ground)	No	No	No	No	No	No	No	Yes
	No	No	No	No	No	No	No	Yes
Almond, Filbert (Hazelnut), Macadamia Nut, Pecan, Pistachios, Walnut	No	No	Yes	No	No	No	No	Yes
Avocado	No	No	Yes	Yes	No	No	No	Yes
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon, Tangerine	No	No	No	No	No	No	No	No
Forestry	No	No	Yes	Yes	No	No	No	Yes
Acerola, Apples, Apricots, Cherries,	No	No	No	No	No	No	No	Yes

Uses	Potential for Effects to Identified Taxa Found in the Aquatic Environment:							
	DS (direct effects) ¹		Freshwater Invertebrates ²		Estuarine/Marine Invertebrates ²		Non- Vascular Plants ²	Vascular Plants ²
	Acute	Chronic	Acute	Chronic	Acute	Chronic		
Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate								
Grapes, Kiwi Fruits	No	No	Yes	No	No	No	No	Yes
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	No	No	Yes	Yes	No	No	Yes	Yes
Olive	No	No	No	No	No	No	No	Yes
Potatoes (aerial and ground)	No	No	No	No	No	No	No	Yes
	No	No	No	No	No	No	No	Yes
Household/Domestic Dwellings Outdoor Premises, Paved Areas	No	No	No	No	No	No	No	No
Right of Way Areas (including Roadsides, CRP acreage)	No	No	No	No	No	No	No	No
Artichokes, Asparagus	No	No	Yes	Yes	No	No	No	Yes
Recreation Area Turf, Golf Course	No	No	No	No	No	No	No	Yes
Canola (aerial and ground)	No	No	Yes	Yes	No	No	No	Yes
	No	No	Yes	Yes	No	No	No	Yes
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	No	No	Yes	Yes	No	No	No	Yes
Aquatic Food Use	Yes	No	Yes	No	Yes	No	Yes	Yes
Aquatic Non-Food Use	Yes	No	Yes	Yes	Yes	No	Yes	Yes
1 A yes in this column indicates a potential for direct effects to DS.								
2 A yes in this column indicates a potential for indirect effects to DS.								

Table 7-4. Use Specific Summary of the Potential for Adverse Effects to Terrestrial Taxa

Uses	Potential for Effects to Identified Taxa Found in the Terrestrial Environment:	
	Dicots ¹	Monocots ¹
Aerial Applications		
Alfalfa, Clover, Jojoba	Yes	Yes
Potatoes	Yes	Yes
Canola	Yes	Yes
Ground Applications		
Alfalfa, Clover, Jojoba	Yes	No
Almond, Filbert (Hazelnut), Macadamia	Yes	No

Nut, Pecan, Pistachios, Walnut		
Avocado	Yes	No
Grapefruit, Guava, Lemon, Lime, Mango, Orange, Papaya, Persimmon Tangerine	Yes	No
Forestry	Yes	No
Acerola, Apples, Apricots, Cherries, Fig, Nectarines, Pears, Peaches, Plums, Prune, Pomegranate	Yes	No
Grapes, Kiwi Fruits	Yes	No
Olive	Yes	No
Potatoes	Yes	No
Artichokes, Asparagus	Yes	No
Recreation Area Turf, Golf Course	Yes	No
Canola	Yes	No
Black Berries, Blue Berries, Dewberries, Elderberries, Gooseberries, Huckleberries, Boysenberries, Loganberries, Grapes, Passion Fruit	Yes	No
Right of Way Areas (including Roadsides, CRP acreage)	Yes	No
Nonbearing Fruit, Nursery Stock, Outdoor Nursery Operations	Yes	No
Household/Domestic Dwellings Outdoor Premises Paved Areas	Yes	Yes
Direct Water (food use)	Yes	Yes
Direct Water (non-food)	Yes	Yes
1- A yes in this column indicates a potential for indirect effects to DS.		

Based on the conclusions of this assessment, a formal consultation with the U. S. Fish and Wildlife Service under Section 7 of the Endangered Species Act should be initiated.

When evaluating the significance of this risk assessment's direct/indirect and adverse habitat modification effects determinations, it is important to note that pesticide exposures and predicted risks to the listed species and its resources (*i.e.*, food and habitat) are not expected to be uniform across the action area. In fact, given the assumptions of drift and downstream transport (*i.e.*, attenuation with distance), pesticide exposure and associated risks to the species and its resources are expected to decrease with increasing distance away from the treated field or site of application. Evaluation of the implication of this non-uniform distribution of risk to the species would require information and assessment techniques that are not currently available.

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- Enhanced information on the density and distribution of DS life stages within the action area and/or applicable designated critical habitat. This information would allow for quantitative extrapolation of the present risk assessment's predictions of individual effects to the proportion of the population extant within geographical areas where those effects are predicted. Furthermore, such population information would allow for a more comprehensive evaluation of the significance of potential resource impairment to individuals of the assessed species.
- Quantitative information on prey base requirements for the assessed species. While existing information provides a preliminary picture of the types of food sources utilized by the assessed species, it does not establish minimal requirements to sustain healthy individuals at varying life stages. Such information could be used to establish biologically relevant thresholds of effects on the prey base, and ultimately establish geographical limits to those effects. This information could be used together with the density data discussed above to characterize the likelihood of adverse effects to individuals.
- Information on population responses of prey base organisms to the pesticide. Currently, methodologies are limited to predicting exposures and likely levels of direct mortality, growth or reproductive impairment immediately following exposure to the pesticide. The degree to which repeated exposure events and the inherent demographic characteristics of the prey population play into the extent to which prey resources may recover is not predictable. An enhanced understanding of long-term prey responses to pesticide exposure would allow for a more refined determination of the magnitude and duration of resource impairment, and together with the information described above, a more complete prediction of effects to individual species and potential modification to critical habitat.

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