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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

9/29/94

OFFICE OF
PREVENTION, PESTICIDES
AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: EFED Recommendations and Mitigation Measures for Diquat dibromide (Chemical # 032201) Case # 0288

FROM: William R. Schneider, Ph.D.
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THRU: for Evert K. Byington, Chief
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Background

Use Profile

Common name: Diquat

CAS number: 85-00-7

Chemical name: 1,1'-Ethylene-2,2'-bipyridylium ion, dibromide salt; 6,7-dihydrodipyrido[1,2-a:2',1'-c)pyrazdiium ion, dibromide salt.

Formulations: Soluble concentrate or pressurized liquid

CC:\ (with SACS Reregistration Summary Report attached)

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Mode of action: Lipid peroxidation resulting in disruption of cell membrane

Physical/Chemical properties:

Molecular formula:	$C_{12}H_{12}N_2Br_2$.
Molecular weight:	344.0.
Physical state:	Crystalline.
Vapor pressure:	<0.013 mPa.
Solubility at 20 C:	700 g/L in water; slightly soluble in alcohols and hydroxylic solvents, insoluble in nonpolar organic solvents.

Sites: Diquat is a nonselective contact herbicide, desiccant, algicide, and defoliant registered for use in terrestrial noncrop and aquatic areas; as a desiccant for potatoes, carrots, cucumber, cantaloupe, watermelon, tomato, radish, turnip and seed crops of clover, sorghum, soybean. It is also used on residential, industrial and agricultural noncrop land for spot treatment of weeds. It is used on golf courses, turf, and ornamental for desiccation, spot treatment of weeds and pre-renovation. Diquat is used on lakes, ponds, irrigation ditches, reservoirs, rivers, streams, wetlands, shorelines, edging and irrigation systems for submerged, emerged and floating aquatic weed control. Diquat is injected in the water or applied to the surface of the water. Diquat can be applied by aerial or ground application and could be used up to two times a year if needed.

Quantitative Usage: Diquat was applied on 26% of all potato acreage in the US during 1992 (Agricultural Chemical Usage, 1992 Field Crop Summary published by USDA) This would amount to 101,000 pounds on potato. Some major potato production states have diquat applied to a large percentage of the potato crop (ME-93%, MI-53%, MN-43%, NY-43%, PA-70%, WI-71%).

Use Limitations: i) Do not use treated water for drinking or domestic purposes until 14 days after treatment.

ii) Do not graze on treated areas or feed foliage to livestock.

iii) Do not use treated water for animal consumption within 14 days after treatment.

iv) Do not use treated water for spraying or irrigation within 14 days after treatment.

v) Do not apply within 880 yards of potable water intake.

vi) Do not apply through any type of irrigation system.

vii) Do not apply in muddy waters for aquatic weed control.

viii) For aquatic weed control, be careful not to stir sediment in water during application.

Rates of application:

Use Site	Maximum Application Rate lb cation/A	Remarks
Lakes, ponds, reservoirs, agricultural drainage systems	4.0/A - 4.2/A ft	apply when needed via injection, and on water surface
Edging Treatment, Shoreline	2.16	apply when needed
Alfalfa, clover, carrot	0.5	apply for desiccation, seed crop seeding
Cucumber, tomato, Watermelon,	0.375	at post final harvest via ground sprayer
Cantaloupe	0.25	at post final harvest via ground sprayer
Pepper, Squash	0.5	at post final harvest via ground sprayer
Potato, Radish, Turnip	0.5	for desiccation at preharvest
Soybean, Sorghum	0.5	for seed crop
Turf, Golf Course, Ornamental,	0.8923	for desiccation, pre-renovation
Spot Treatment on Turf, Agricultural noncrop land, Industrial Sites, Rights-of Ways, Residences,	see footnote[1]	for weed control

Levels of Concern Exceedances

How Application Rates are Used

The LUIS provided application rates in lb cation/acre.

When estimating exposure to aquatic organisms in aquatic habitat, this rate in lb ai cation was used to model exposure. The resulting concentrations (in ppb cation) were compared to results of aquatic toxicity tests also expressed in ppb cation.

The bird and mammal toxicity data were expressed in a variety of units ranging from ai formulation, cation formulation, 100% ai, and cation ai. All results were extrapolated to cation units to be consistent with the application rate units. Exposure on food items was then calculated in ppm cation.

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[1] Formulation is often in very diluted form, is directly targeted at weed species by hand sprayer and is not applied on an acreage basis.

Risk Summary

1- The Level of Concern (LOC) for acute effects to nonendangered mammals have not been exceeded; acute risk to non endangered mammals is assumed to be minimal.

mammals 2- The LOC for chronic effects to mammals has been exceeded by uses on turf/ornamental (Risk Quotient (RQ)=2.7) and crops treated at 0.5 lb cation/acre (RQ=1.5). This is based on maximum residues on short grass immediately after application. Typical residues on short grass and long grass from turf/ornamental treatment also exceed the NOEL from the rat reproduction study.

3- The LOC for acute effects to nonendangered birds has not been exceeded. Acute risk to birds is assumed to be minimal.

birds 4- However, the LOC for chronic effects to birds has been exceeded. Therefore, a conclusion of minimal risk to birds cannot be made. Both maximum and typical residue levels on a variety of food items exceed the NOEL from the mallard reproductive study. The risk quotients range from 1.7 to 42.8, all of which exceed the LOC of 1.

5- The LOC for acute risk to nonendangered fish and invertebrates, including estuarine organisms, has not been exceeded from treatment of terrestrial sites (turf, ornamental and crop).

Direct application to water (aquatic weed control) may result in risk (RQ=0.6) that exceeds the LOC (0.5) for acute risk to estuarine invertebrates. However, this risk potential is mitigated by the fact that diquat dibromide quickly binds to suspended particulates in water, and would quickly be come unavailable. Ultimately the risk potential appears to be low.

6- The LOC (1) for chronic effects to aquatic organisms is equaled (RQ=1.1), by treatment of terrestrial use sites. However, chronic exposure is unlikely because diquat dibromide is likely to bind rapidly to suspended particles in the water column making it unavailable, biologically. As above, the risk potential appears to be relatively low.

The LOC of chronic effects to aquatic invertebrates may be exceeded by the risk from immediate concentrations occurring after treatment of aquatic use sites (RQ=0.26 [fish] and 5.5 [aquatic invertebrate]). However, chronic exposure is unlikely because of the environmental fate characteristics of diquat dibromide. Diquat dibromide apparently tends to bind rapidly to suspended matter in the water column and becomes biological unavailable.

Therefore, in spite of the risk quotients, chronic risk to aquatic fish and invertebrates is considered to be minimal.

7- The LOC for aquatic plants has been exceeded by both ground and aerial application. The RQ's range from 3.5 to 967. The LOC for plants is 1. However, due to the environmental fate characteristics of diquat dibromide, it is unlikely that hazardous exposure from runoff alone will occur (RQ=967). The route of exposure likely to represent a risk to aquatic plants is drift from aerial spray. Aerial spray of the following terrestrial sites results in the risk quotients shown.

aq. plants

These risk quotients are all from spray drift, which is assumed to be 5% of the applied.

Note that in the case of aquatic weed control, it is not the intent of this risk assessment to address nonendangered plants in the actual target site nor the untreated band between the 40-foot spray swaths, see the discussion in the next paragraph. It is assumed that the treated and untreated swaths will eventually be treated; i.e they are actually the target site. The risk quotient calculated (55.6) is based on 5% of the spray drifting to some other nontarget aquatic habitat adjacent to the treated lake or pond.

But please also note that the drift that occurs from aerial treatment for aquatic weed control may negate the value of leaving the 40-foot untreated swaths. When diquat is applied to weed infested water, the result and intent is that the weeds die. As these weeds decompose, dissolved oxygen is depleted. The dissolved oxygen reduction may become severe enough to kill aquatic organisms (fish and invertebrates) due to lack of oxygen. The purpose of treating in swaths, and leaving 40-foot untreated bands is to provide these organisms a place to go where the dissolved oxygen may be high enough to support them. If drift from aerial application settles on these "untreated" bands and ends up killing the plants there, the dissolved oxygen could be reduced in these areas along with the treated areas. The fish and invertebrates would then have no where to go, and could also be killed. This risk of this potential impact cannot be expressed with quotients.

ter plants 8- The LOC (1) for terrestrial plants is not exceeded by risk from runoff, however, it is exceeded by risk from drift from aerial applications to turf and for aquatic weed control.

	Cantaloupe	Soybeans, etc	Turf	Aquatic weed control
Applied:	0.25 lb cation/Acre	0.5 lb cation/A	0.89 lb cation/A	4 lb cation/A
Risk Quotient::	2.7	5.3	9.5	42.5

Discussion of Certainty

Chronic risk to Mammals

The chronic risk to mammals was based on a comparison of immediate residues with the NOEL from a 2-generation reproduction study. It is possible that very short (i.e. immediate) exposures could cause chronic responses; no data is provided to negate this possibility. Furthermore, there is no way of knowing if wild mammals may be more sensitive to diquat dibromide than laboratory rats. However, there is high degree of uncertainty in concluding that adverse effects to mammals would actually occur because of the following factors.

Residues may decline over time to levels lower than the NOEL.

Typical and even maximum residues do not exceed the LOEL (453 ppm).

The residues used to calculate the risk quotients were from food items (short grass) having the highest estimated levels. Other food items would have lower residue levels.

Chronic risk to Birds

Note that the risk quotients for chronic risk to birds were based on both maximum and typical residues expected to occur immediately after treatment. Diquat is extremely persistent, but neither the rate of decline on food items, nor rate at which diquat becomes "biologically unavailable" to birds is known.

Based on available data, there is moderate to high certainty that some reproductive effects will occur to birds. The likelihood that this impact will occur frequently, or be of ecological significance is less certain.

Risk to aquatic organisms

Except for aquatic plants, which are assumed to be at considerable risk from drift from any aerial treatment, most aquatic risk was assumed to be low. This conclusion was made despite the fact that LOC's were exceeded. There is some uncertainty with this conclusion in that diquat dibromide is extremely persistent. It "dissipates" from the water column quickly, however, once bound to sediment, there is no data showing that it degrades. The current assumption is that once bound it is unavailable to exert adverse effects on aquatic plants and animals. It is unknown what the long term exposure concentrations might be to aquatic life living in the sediment. It is also unknown what affects this long-term exposure might have on aquatic life, especially plants.

Risk to terrestrial plants

There is relatively high certainty that drift from aerial spraying of diquat dibromide will result in adverse effects to plants. There is an element of uncertainty in the terrestrial plant risk assessment because data from the more sensitive plant species is probably not available. It is considered likely that sweet corn and wheat would yield lower EC25's. Failing to have this data does not preclude doing a risk assessment, since other data indicate the LOC is exceeded. However:

1-It is not possible to determine the full extent of risk as would be valuable in comparisons with other herbicides; and

2-EFED would be unable to fully evaluate the effectiveness of risk reduction measures.

Endangered Species

1- Endangered species of mammals and birds may be affected by terrestrial uses of diquat dibromide.

2- Endangered species of aquatic fish and invertebrates may be affected, acutely, by the aquatic weed control use. While RQ's for chronic effects exceed the chronic LOC, chronic exposure in aquatic habitats is not expected and thus potential for chronic effects to endangered aquatic animals is considered unlikely.

3- Endangered species of aquatic plants may be affected from aerial application of terrestrial use sites and from both aerial and nonaerial treatment of aquatic use sites.

4- Endangered species of terrestrial plants may be affected from aerial treatment of all use sites. In the case of the aquatic weed control, it is assumed that 5% of what is sprayed aerially could drift to adjacent terrestrial habitats.

Risk Reduction Measures

Suggestion 1: Reduce or eliminate aerial application

The primary route of hazardous exposure appears to be via aerial spray drift. Elimination of aerial application would reduce to minimal, in most cases, risk to aquatic organisms and terrestrial plants.

Suggestion 2: Modify treatment of water bodies.

According to the current label for aquatic weed control, Diquat is to be applied in 40 foot strips throughout the lake or water body. As was mentioned earlier, this is to avoid a condition that may result in acute reduction of dissolved oxygen throughout a water body. The following suggestion may provide the registrants with alternative labeling practices if the current method has been suspected of causing fish kills or other adverse effects. An alternative practice is to have blocks of the body of water, usually a third of the surface, treated; thereby the fish will be able to avoid the lowered dissolved oxygen areas. After a period of time, usually about 2 weeks, the dissolved oxygen content would return to regular levels. Then another third of the lake can then be treated, etc. This method of application may reduce the potential for fish kills due to depleted oxygen.

Endangered Species

Labeling and use restrictions to protect endangered species are being developed as part of the EFED Endangered Species Protection Program.

Value of the Additional Information

GDLN NO.	TYPE OF TEST	MRID OR ID. NO.	REPLACEMENT VALUE
123-1(b)	Vegetative Vigor, two more grass species (wheat & sweet corn)	41883001	medium to high
123-2	Unicellular Aquatic plants	41883002	medium to high

A low replacement value is assigned when there is a low probability that a new test will effectively challenge/change significantly previous assumptions, previously-determined levels of risk and/or decrease the overall level of uncertainty of adverse effects when other, core, scientifically sound and similar type of tests to the one under consideration are in the data base.

A medium replacement value is given to a test when the new results have some probability of altering previous assumptions or levels of risk and/or because it is likely to have a higher value in completing a toxicological data base that would otherwise be somehow incomplete for this type of test and, therefore, vulnerable to sound scientific challenge.

A high replacement value is given to a test when without a new test it would be impossible and scientifically incorrect to make assumptions and a determination of the level of risk involved. Furthermore, without a replacement test the level of uncertainty will remain high and the ecotoxicological data base will be incomplete and totally vulnerable to scientific challenge.

EFED recommends additional vegetative vigor nontarget plant testing (tier II) because only one grass species (corn) was tested. According to an earlier study (40165102) which was, sweet corn and wheat were found to be sensitive to diquat dibromide. It is recommended that two more grass species. Attempts should be made to use seed that has not been treated with fungicide. The value of this additional testing would be medium to high.

EFED recommends additional aquatic plant testing (tier II) because only vascular aquatic plants were tested and therefore only the vascular plant requirement (*Lemna gibba*) was satisfied. An EC_{50} was determined for different species of vascular plants in a dose response study. No unicellular plants (algae and diatoms) were tested. *Skeletonema costatum, Anabaena flos-aquae, Selenastrum capricornutum*, and a freshwater diatom needs to be tested to satisfy the requirements under 123-2 and for EFED to provide a complete risk assessment of diquat to nontarget aquatic plants. The added value of this additional testing is medium to high.

Although eco-toxicity data is lacking on algae and grasses, EFED is able to provide a risk assessment for plants. The certainty of such assessment is moderate to low. Additional data may confirm the risk assessment with increased certainty plus more understanding of eco-system wide affects from the labeled use of diquat. Data on the grasses would provide information on the conditions in which endangered species of grasses may be affected. Such data may also help EFED to evaluate risk reduction measures. For this risk assessment, EFED is assuming that grasses would be affected.

Labeling Requirements for Manufacturing- Use Products

The following statements must be on the label: "This pesticide is toxic to aquatic invertebrates. Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or public waters unless in accordance with the requirements of a National Pollutant Discharge Elimination System permit and the permitting authority has been notified in writing prior to discharge. Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact your State Water Board or Regional Office of the EPA."

Labeling Requirements for End-Use Products

Environmental hazard requires the following labeling statements:

a. For products that are for terrestrial nonfood site, use this precautionary statement: "This pesticide is toxic to aquatic invertebrates. Do not apply directly to water, or to areas where surface water is present or to intertidal areas below the mean high water mark. Do not contaminate water when disposing of equipment washwater or rinsate."

For products that are for outdoor residential site, use this precautionary statement: "This pesticide is toxic to aquatic invertebrates. Do not apply directly to water."

b. Restricted Use: The criteria for restricted use have been exceeded for aquatic weed control and turf use sites. The risk is to bird and aquatic invertebrate species.

Labeling for Endangered Species

No use limitations to protect endangered plant species will be suggested until the OPP Endangered Species Protection Program is complete.

Additional Study:

Note that EFGWB used an hydrolysis study that was not assigned an MRID number: The citation is Upton, Hendley & Skidmore, 1985. Diquat: hydrolytic stability in water at pH 5,7, and 9. ICI Plant Protection Division, Jealotts' Hill Research Station, Bracknell, Berkshire, UK Accession #'s 259950 & 259951.