Reward®
Landscape and aquatic herbicide

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# Review of the Aquatic Toxicology and Fate of Reward® Herbicide


## Executive Summary

This document reviews the effects and fate of Reward® herbicide (diquat dibromide) in aquatic environments, following its use as an aquatic herbicide, using published literature references and registration documents on file with the EPA.

Diquat dibromide is a herbicide that has been used throughout the United States for over 50 years to control invasive aquatic weeds and algae. Because it is applied directly to water, it can come into contact with fish and other aquatic organisms. For this reason, an extensive database on its environmental safety has been developed. Minimal risk to humans and aquatic organisms following application of Reward has been demonstrated over decades of use, in laboratory studies, and in state and federal registration programs.

Following aquatic application, dissipation of Reward is very rapid. The half-life of Reward in water is typically one to two days (EPA, 2002). This dissipation occurs initially through mixing and dilution in the water column. Reward is subsequently very tightly bound to aquatic plants, sediment, and suspended particles. Once Reward becomes bound to sediment, it is inactivated and biologically unavailable.

The United States EPA has reviewed all of the available data on diquat (Reward) and determined that sufficient information is available regarding the potential for adverse human health effects and potential adverse effects in fish, wildlife, and the environment. The Agency has concluded that labeled uses of diquat products will not pose unreasonable risks or adverse effects to humans or the environment if used according to label instructions (EPA, 1995). A 2002 review under the Food Quality Protection Act further confirmed that diquat is not a mutagen nor carcinogen, poses no dietary risks, and that (EPA 2002a; 2002b):

> "Exposures from diquat dibromide to surface or ground water sources for both terrestrial and aquatic uses are not of concern to the Agency. Diquat dibromide is essentially immobile in the environment, indicating that it will most likely be associated with the soil and sediment instead of water. Significant residues of diquat dibromide are not expected to reach ground or surface water. Therefore, no risk mitigation measures are necessary to address drinking water risks from diquat dibromide use."

In summary, based on over 50 years of data and modern reassessments, the EPA has concluded that Reward applications in accordance with labeled use pose no unreasonable risk to humans or to fish and other aquatic organisms.


## Environmental Fate of Diquat Dibromide/Reward

Before considering the potential effects of Reward in animals and humans, it is useful to consider the fate of the product in aquatic systems. Reward is highly water soluble (700 grams per liter/5.9 pounds per gallon; British Crop Protection Council, 2000) and is relatively stable in pure water (EPA, 2002). Reward will slowly photodegrade (photodegradation half-life of 74 days in laboratory studies with clean water; Tegala and Skidmore, 1987) and is resistant to microbial degradation under most conditions (EPA, 2002). Diquat dibromide is a salt with a very low vapor pressure (British Crop Protection Council, 2000), indicating that diquat does not readily evaporate. The risk of exposure from inhalation is therefore negligible (USEPA, 1995).

Reward in water initially becomes diluted through mixing in the water column, and hot spots near the site of application are quickly eliminated via mixing and binding to organic matter (Coats et al., 1964; Sewell, 1969; Langeland and Warner, 1986; Fujie, 1988). The primary route of dissipation of Reward in water is adsorption. Reward rapidly disappears from water in natural systems by adsorption to sediment, aquatic vegetation, and particulate matter (e.g. EPA, 2002; WHO, 1984). Upon introduction into water, Reward quickly binds to these matrices and is thereby removed from the water column, becoming essentially immobile and inactivated in the environment (EPA, 2002). The aquatic half-life of the product in natural waters is approximately 1–2 days (EPA, 2002). Because of its rapid dissipation, aquatic animal exposure to Reward would be limited to short-term, acute durations (Washington State Department of Ecology, 2002). However, the extensive database currently available on the environmental safety of diquat includes chronic environmental toxicology results. These are discussed on the following pages.

### Potential Toxicity of Diquat to Aquatic Organisms

The Washington State Department of Ecology (2002) and the EPA (EPA 1995; 2002a; 2002b) have concluded that aquatic application of Reward according to label requirements does not pose unacceptable acute or chronic risk to aquatic animals.

Fish and Amphibians

Washington State Department of Ecology (2002) conducted a risk assessment using well-established methods (EPA, 1986; Campbell et al., 2000) that involved comparing expected environmental concentrations with environmental toxicology values and determining if these "risk quotients" exceeded levels of concern.

Laboratory studies in exposure vessels without sediment have demonstrated that 96-h acute LC50 toxicity values for all verified studies on fish are greater than 0.5 mg/L c.e. (cation equivalents; Washington State Department of Ecology, 2002). Based on the short-term expected environmental exposure concentration of 0.021 mg/L (Washington State Department of Ecology, 2002), the acute Risk Quotient for Reward with early-life stage largemouth bass and striped bass is [0.021 mg/L/0.5 mg/L] = 0.04. This acute RQ is well below the acute levels of concern (0.1) for these sensitive species and life stages. Field studies have confirmed the low potential for acute and chronic toxicity of Reward to fish (EPA, 1995).

The low toxicity of Reward to fish has been recognized by the FDA, USGS, and US Fish and Wildlife Service in treatment trials for control of bacterial gill disease and columnaris infections in salmon. While not yet approved by the U.S. Food and Drug Administration for disease control in food fishes, a 10-year, ongoing program in which hatchery salmon, and other fish species, can be exposed to 2–28 mg diquat cation/L for treatment of bacterial diseases (US Fish and Wildlife Service, 2004; USGS, 1990) is being conducted. This hatchery treatment rate is 75 times greater than the highest labeled use rates for aquatic applications of diquat at a MCL of 0.37 ppm.

Applications of Reward could result in exposure of amphibians as eggs, larvae, and adults, and environmental toxicity data are available for the potential toxicity of the product to several species of amphibians. Bimber and Michell (1976) exposed eggs of *Rana pipiens* (Northern leopard frog) to 100 mg diquat/L and reported no effects on hatching, but larval development and survival was adversely affected at this level. The relevance of these data is questionable, however, as exposure concentrations were 1000x expected field concentrations 24 hours after application. The most sensitive amphibian tested appears to be *Xenopus laevis* (African Clawed Frog), with a 96-h LC50 of approximately 0.75 mg/L, which is of similar sensitivity to the most sensitive fish (Anderson and Prahlad, 1976). However, dissipation data demonstrate that amphibians, like fish, will not be exposed in the field to even 0.5 mg/L for as long as 24 hours.

As discussed above, because of the rapid dissipation of Reward in water and the low application rates for this herbicide, calculation of risk from chronic exposure is not necessary (Campbell et al., 2000; Washington State Department of Ecology, 2002). However, chronic laboratory and field studies have confirmed the low potential for long-term toxicity of diquat to aquatic organisms (EPA, 1995; Washington State Department of Ecology, 2002), and confirmed that using diquat according to the label poses no significant acute or chronic risk to aquatic animals (Washington State Department of Ecology, 2002).

Invertebrates

Invertebrates are more sensitive to diquat than fish. The most sensitive invertebrate studied is the amphipod, *Hyalella azteca.* Testing in vessels containing only water and no sediment resulted in Acute Risk Quotients for *H. azteca* of 0.38 (i.e., 0.021 mg/L/0.048 mg/L), which is greater than the level of concern of 0.1. However, when considering studies in which sediment was added to vessels to improve environmental realism, the risk quotient drops significantly to an acceptable level of 0.003 (i.e., 0.021 mg/L/6.8 mg/L) (Washington State Department of Ecology, 2002). Wilson and Bond (1969) demonstrated that the addition of sediment to the system could increase the 96-h LC50 for *H. azteca* by ~140x, from 0.048 mg/L to 6.8 mg/L. The practical level of concern of 0.1 for protection of biota is therefore not exceeded, and no acute risk to invertebrates is expected (Washington State Department of Ecology, 2002). Inactivation of Reward following sorption to sediments was further demonstrated in a study with the aquatic invertebrate *Chironomus riparius* (Ashwell, 1999). Diquat spiked into sediment at 100 mg/kg (dry sediment weight) had no effect on the survival or development of *C. riparius* in a chronic study (Ashwell, 1999).

Field studies have confirmed that *H. azteca* can be sensitive to Reward (Wilson and Bond, 1967), although it is unclear whether these effects were due to acute or chronic exposure. Hilsenhoff subsequently demonstrated that reductions in invertebrate densities, including *H. azteca* populations, may be due to the loss of habitat as the nuisance plant species were eliminated following Reward treatment (Hilsenhoff, 1966).

### Lack of Bioaccumulation of Reward in Aquatic Animals

The physical and chemical properties of Reward are not conducive to accumulation in animal tissues, and the bioaccumulation of diquat has not been seen in fish or other animals (EPA, 2002; Washington State Department of Ecology, 2002; WHO, 1984). Bioaccumulation is the process by which a contaminant accumulates in the tissues of an individual organism via all exposure routes (inhalation, diet, and across the skin and other tissues). There are a number of factors that will determine a chemical's potential to bioaccumulate, including its solubility in water and in fat. Generally, only chemicals that can dissolve in fat or fat-like matrices, "lipophilic" compounds, will have significant potential for bioaccumulation. Diquat is a polar molecule that is non-lipophilic and highly water soluble (British Crop Protection Council, 2000), and therefore has a very low propensity to bioaccumulate (EPA, 2002). Furthermore, Reward is not readily bioavailable once bound to organic matter, soil, or sediments (EPA, 2002; Washington State Department of Ecology, 2002; WHO, 1984).

Laboratory and field experiments demonstrate that the bioconcentration factor of Reward is generally 1000 times less than the trigger limit that would categorize a compound as bioaccumulative under the EPA classification system (EPA, 1999). The very low bioaccumulation potential of Reward has been demonstrated in a number of laboratory studies using benchtop methods (e.g. British Crop Protection Council, 2000), and in laboratory and field studies with fish. A standardized laboratory study with bluegill sunfish conducted in support of the registration of Reward found that diquat does not bioconcentrate (Hamer et al., 1987). Schultz et al. (1995) exposed catfish to 0.005 and 0.020 ppm Reward in water and did not observe bioconcentration in any tissues (BCF <1.0). In a field study with bluegill in a pond initially treated at 1 ppm Reward, the BCF values never exceeded 0.5 at 10 days after treatment and were below detection limits (<0.01) after 12 weeks (Gilderhaus, 1967). When treated at an exaggerated dose of 3 ppm, the fish BCF values were as high as 1.5 mg diquat/kg fish after 10 days (BCF = 0.5), but completely dissipated below the levels of detection within 12 weeks (Guilderhaus, 1967), further demonstrating the low bioaccumulation potential and rapid depuration of Reward in fish.

**Elimination of Reward from Fish**

Depuration (elimination) of Reward from fish in clean water is very rapid. In edible species, half of the Reward present is eliminated within 1.5–3 days (Washington State Department of Ecology, 2002). Because depuration is so rapid, magnification of Reward up trophic levels (i.e. biomagnification) is not likely (Washington State Department of Ecology, 2002). Mammalian toxicology results clearly demonstrate that diquat is rapidly excreted in urine (EPA, 1995).

**Human Exposure to Diquat**

Based on the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) regulations, EPA only reregisters pesticides that can be used without posing unreasonable risk to human health or the environment. EPA critically analyzed all available studies of Reward and concluded that the product poses no unreasonable risks for adverse effects to humans or the environment (USEPA, 1995) when used according to the label instructions.

In 2002 (EPA 2002a; 2002b), the EPA again considered the toxicology and fate information on Reward and confirmed that diquat is not a mutagen or carcinogen, poses no dietary risks, and that:

> "Exposures from diquat dibromide to surface or ground water sources for both terrestrial and aquatic uses are not of concern to the Agency. Diquat dibromide is essentially immobile in the environment, indicating that it will most likely be associated with the soil and sediment instead of water. Significant residues of diquat dibromide are not expected to reach ground or surface water. Therefore, no risk mitigation measures are necessary to address drinking water risks from diquat dibromide use."

**Swimming, Fishing, and Other Uses**

Based on the rapid dissipation of Reward, detailed risk assessments by the EPA concluded that fishing and swimming are allowed on the same day of application of Reward, pond water may be used for drinking within one to three days of application, pond water may be used for livestock consumption one day after application, and pond water may be used for irrigation of turf and food crops within one to five days following application.

**Conclusions**

The minimal risk that Reward poses to humans and aquatic organisms following application according to label instructions has been demonstrated in field and laboratory studies reflecting decades of use, and has been recognized in state and federal registration programs for this herbicide. Reward applied to water rapidly dissipates and becomes inactivated by organic matter, soil, and sediments. Expected environmental concentrations of Reward do not pose acute risks to aquatic animals, and the rapid dissipation of the product via adsorption indicates that chronic exposures are not likely. Reward does not bioaccumulate or biomagnify along trophic levels, and the risk to humans swimming in or consuming fish from treated waters is negligible.

Additional information on the environmental safety of diquat dibromide/Reward is available from the Environmental Protection Agency's website (www.epa.gov), or from Syngenta.

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