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

APR 12 1988

MEMORANDUM

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

SUBJECT: EPA Reg. No. 239-2505. Residues of Diquat in Fish and Shellfish. MRID No. 46427601. RCB No. 3508.

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Ortho Agricultural Chemicals Division of Chevron Chemical Company has submitted data reflecting residues of diquat in fish and shellfish to satisfy a requirement cited in the Diquat Registration Standard which was issued 12/27/85.

Tolerances have been established in or on fish or shellfish at 0.1 ppm for residues of the herbicide diquat (6,7-dihydro-ipyrido(1,2-a:2', 1'-c)pyrazidiinium) (calculated as the cation) derived from the application of the dibromide salt to ponds, lakes, reservoirs, marshes, drainage ditches, canals, streams, and rivers which are slow-moving or quiescent in programs of the Corps of Engineers or other Federal or State public agencies and to ponds, lakes and drainage ditches only where there is little or no outflow of water and which are totally under the control of the user [40 CFR 180.226 (b)].

The Diquat Registration Standard issued 12/27/85 concluded that the available residue data for fish was not adequate to determine whether the established tolerance was acceptable. The Registration Standard requested that additional residue studies be generated reflecting fish in water with diquat levels comparable to those expected when treated with diquat at the maximum recommended rates at the time of application.

The following formulations may be applied to drainage ditches, lakes, and ponds at the rates and under the conditions listed: (1) 0.082-2 lb/gal at 1.6-15 lb cation/A and 1.85% and 2.36% SC/L at 20-84 gal product/A, direct water treatment, repeat treatment permitted where necessary; (2) 0.08-2 lb/gal SC/Ls at 0.8-2 lb /gal SC/Ls at 0.8-2 lb cation/A, 0.4 lb/gal SC/L at 8-

12 fl.oz./1000 sq. ft., 0.08 lb/gal SC/L at 12-18 gal product/1000 sq. ft., 2.36% SC/L at 10-15 gal/A, foliar application for control of floating weeds, apply in 150-200 gal water/A by surface, or in 7.5 gal water/surface acre for aerial application to lettuce; (3) 0.08-2 lb/gal SC/Ls at 1.66-2 lb cation/A, 0.1 lb/gal SC/L at 1 part product/5 parts water, 0.4 lb/gal SC/L at 16 fl. oz./1000 sq. ft., and 2.36% SC/L at 20 gal product/A, foliar application in 30-150 gal water/A for control of cattail and duckweed; repeat treatment as needed.

The following formulations may be applied to marshes, streams, rivers, waterways, and canals at the rates and under the conditions listed: (1) 0.083 lb/gal SC/L at 1.66-11.6 lb cation/A, 0.2 lb/gal SC/L at 2-8.4 lb cation/A, and 1.85% SC/L at 20-140 gal/A for control of submerged weeds by direct water treatment; repeat as needed; (2) 0.083 lb/gal SC/L at 0.83-1.24 lb cation/A, 0.2 lb/gal SC/L at 1-1.5 lb cation/A, and 1.85% SC/L at 10-15 gal product/A foliar application for control of floating weeds; apply in 150-200 gal water/A, (3) 0.2 lb/gal SC/L at 2 lb cation/A foliar application for control of cattail and duckweed; apply in 100 gal water/A; repeat as needed.

Do not use treated areas for animal consumption, swimming, spraying, irrigation, or domestic purposes for 14 days after treatment, or until approved analysis shows that the water does not contain more than 0.01 ppm diquat cation [21 CFR 193.160 (a)]. Apply with a surfactant. No treatment will be made where commercial processing of fish resulting in production of fish protein concentrate or fish meal is practiced. Applications to ponds, lakes and drainage ditches where there is little or no outflow of water and which are totally under the control of the use are not permitted in FL [21 CFR 193.160 (b)].

Diquat Residues in Fish and Shellfish

The registrant has submitted the results of a study showing residue accumulation in the edible tissue of four non-target, representative freshwater organisms including two fish species (bluegill sunfish and channel catfish), a bottom dwelling crustacean (Louisiana Red Swamp crayfish), and a freshwater unionid clam exposed to diquat water at concentrations expected following maximum label rate applications.

The exposure system consisted of six interconnected and recirculating 1500 liter pools measuring 2 meters in diameter and 0.6 meters in height each containing dilution water and sandy loam substrate. A seventh pool identical to the exposure pools, but independent from the recirculating pool system, served as the control pool. Water was internally recirculated within this pool to simulate the conditions in the exposure pools.

The test system (water and sediment substrate) was allowed to operate for four days prior to introducing the test organisms to allow for the establishment of a natural equilibrium of the

sediment/water interface. Four days after system equilibration and water renewal, 25 clams were placed in each pool. One day later 40 bluegill sunfish and 52 channel catfish were added to each of the seven pools while 38 crayfish were added to each exposure pool and 49 crayfish were added to the control pool.

The test animals were acclimated for four days to the system, held under alternating photoperiods of 16 hrs light and 8 hrs darkness, and were fed daily ad libitum a dry pelleted food. Clams were not fed prior to and during the study.

On the initial day of treatment, preweighed aliquots of DIQUAT Concentrate were added to 3-liter volumes of dilution water. The volume of DIQUAT Concentrate added to each mixing pool was calculated based on the exact volume of each individual pool. These diquat solutions were subsequently poured over the water surface of the six mixing pools to obtain stock solutions containing 1.76 mg/L of diquat cation. Each pool was first mixed manually with a length of PVC pipe, and subsequently mixed a minimum of 1.5 hours with a high volume magnetic drive pump before the renewal water was sampled for analytical confirmation of the diquat concentration. On Day 0 and Day 14, 80% of the water from each of the exposure pools and the control pool was pumped out (one pool at a time) and into an effluent lagoon; and the test or control solution replenished with an equal volume of the appropriate renewal solution. Following dilution of the diquat stock solution with the remaining water in the treatment pools, a nominal exposure concentration of 1.4 mg/L diquat cation was obtained.

Total time required for renewal of all test and control solutions was approximately three hours. The order in which the test or control solution were first added to the respective was maintained throughout the experiment for all subsequent test solution renewals and organism sampling. Exposure times of test organisms in the various pools were as uniform as possible.

Water and test animals were sampled Day 0, Day 0 (four hours after replacing the pre-exposure water with test or control solution) Day 1, Day 3, Day 7, and Day 14 after the first exposure and Day 0, Day 0 (four hours after renewal of the test or control solution), Day 1, Day 3, Day 7, and Day 14 after the second exposure. Collection of organisms from the control pool occurred on days 0, 14 and 28 of the study. Tissue samples of crayfish were collected from each pool on days 0, 1, 3, 7, 14, 15, and 17. Up to 13 bluegills, up to 16 channel catfish, up to 7 crayfish and up to 16 clams were taken from each exposure pool at each sampling interval. On day 17 of the study it was noted that an insufficient number of crayfish were present in the exposure pools for subsequent sampling. Three of the six pools were drained on day 21 to see if the crayfish had burrowed into the sediment layer, thus escaping retrieval by netting. Drainage of the three pools did not produce the desired number of crayfish, and subsequent crayfish sampling resulted in limited

sample size. Test animals not required for the 21 day sampling were placed in the remaining three pools for use at a subsequent sampling interval. Water samples from the exposure pools were taken concurrently with the organism sampling alternately from three of the six pools and from the control pool. Water samples from each of the mixing pools were taken before refilling the exposure pools. At test termination (day 28), all remaining pools were drained and all organisms were retrieved and processed. A proportional number of organisms were removed from the control pool at each sampling interval. Sediment samples were collected on day 28 at the conclusion of the study.

The bluegill sunfish and channel catfish were dissected into edible and nonedible tissue. The flesh from the tails of each crayfish was removed and all soft tissue from the clam was collected. Each tissue type was wrapped in tared aluminum foil, weighed and frozen.

On Day 28 (test termination) all remaining clam tissue from the exposure pools was separated into three parts: the hard muscle tissue of the foot; the remaining soft tissue; and the extrapallial fluid. The tissue types were stored frozen in separate aluminum foil wrappings, while the extrapallial fluid was frozen in glass jars. This exercise was to allow differentiation between diquat associated with the digestive tract of the clams (i.e., the fraction of non-assimilated diquat) vs. the diquat assimilated by the clams.

The maximum diquat residue reported in the blue gill (whole fish) was 0.22 ppm occurring 4 hours after the second exposure. The maximum residue reported for the catfish (whole fish) was 1.2 ppm found 1 day after the second exposure. Maximum residues in the edible tissues of the bluegill and catfish were 0.04 ppm and 0.08 ppm, respectively. Diquat residues were higher in nonedible portions: 0.51 ppm in the bluegill and 2.2 ppm in the catfish.

The maximum diquat residue reported for crayfish was 0.56 ppm sampled 4 hrs after the second exposure. The maximum residue reported for clams was 14 ppm sampled 4 hrs after the first exposure.

From the above study, RCB concludes that residues of diquat in fish and shellfish will exceed the established tolerance of 0.1 ppm. Considering that approximately 75% of the stored residues were recovered at the time of analysis (See Storage Stability Studies below) the registrant should be advised to submit a petition requesting a tolerance of 2 ppm for fish and 20 ppm for shellfish to cover all residues of diquat (calculated as the cation) which may occur from the currently registered uses.

Storage Stability Studies

On days 0, 14 and 28 of the study, duplicate samples of control pool were fortified at 0.5 ug/ml with diquat cation, acidified and stored along with samples from the exposure pools. These samples were taken to document stability of diquat in water under the storage and shipping conditions used for this study. All samples were stored at -20°C following collection until extraction for analysis. For water, storage interval ranged from 3 to 13 days. Three water samples were reanalyzed 59 days after the initial analysis. Reanalysis of all three water samples recovered 106% of the initial diquat concentration.

For tissues, subsamples of the extra untreated controls collected from the test population at the beginning of the study were fortified with 0.10 ppm diquat and stored at -20° C. Tissue samples from the exposure tanks were stored for 22-48 days prior to extraction for analysis. The fortified storage stability samples were extracted for analysis following storage for 49-55 days. Recoveries of the fortified tissue ranged from 73-89%.

From these storage stability studies, we conclude that approximately 75% of the stored residues were recovered at the time of analysis.

Analytical Methodology

Water samples were analyzed using a modified version of method RM-5W-3. Briefly, the method involves pH adjustment, cleanup and concentration by ion exchange chromatography, alkaline reduction with sodium dithionite and spectrophotometric measurement of the diquat reduction product. Control or deionized water was fortified at 0.01 ug/ml with diquat cation. Recoveries ranged from 69.6-115%.

Tissue analyses were conducted using method RM-5B-1. This method involves extraction by acid hydrolysis, cleanup and concentration by ion exchange chromatography followed by reduction with sodium borohydride and measurement of the diquat reduction product by gas chromatography using a nitrogen/ phosphorous-flame ionization detector. Tissue samples fortified with 0.1 ppm diquat showed recoveries ranging from 66.2-89.9%. This method underwent a successful method tryout (G.P.Makhijani, EPA internal memorandum dated 12/5/75 regarding PP#5E1648, "Method Tryout for Diquat on Fish"). While this method is adequate for data collecting, RCB does not consider the method suitable for enforcement purposes, since the method cannot distinguish between diquat and paraquat.

Conclusions and Recommendations

The above study fills the data gap cited in the Diquat Registration Standard issued 12/27/85 which concluded that the

available residue data for fish was not adequate to determine whether the established tolerance was acceptable.

RCB concludes from the above studies that residues of diquat occurring in fish and shellfish from currently registered uses will exceed the established tolerance of 0.1 ppm. The registrant should be advised to submit a petition requesting tolerances of 2.0 ppm for fish and 20 ppm for shellfish to cover all residues of diquat (calculated as the cation) which may occur as a result of the currently registered uses.

cc: Reading File, Circulation, Diquat Registration Std. File, Reviewer, TAS, PMSD/ISB
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