



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

3-26-92

MEMORANDUM

SUBJECT: Dithiopyr Acute Toxicity Testing with Aquatic Invertebrate

FROM: Douglas J. Urban, Chief
Ecological Effects Branch
Environmental Fate and Effects Division (H7507C)

TO: Joan Miller, PM 23
Registration Division (H7505C)

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

Douglas J. Urban

3/25/92

MAR 26 1992

EEB has reviewed the acute toxicity testing results submitted to Monsanto Corporation for the active ingredient dithiopyr. The requirements for 72-2 testing is satisfied by this submission. Further review of registration standard data requirement submitted to date indicates that the following requirements for Dithiopyr remain outstanding.

- 71-4 Avian Reproduction Studies
- 72-4 Invertebrate Full Life Cycle
- 72-3 Estuarine Toxicity Testing with
 - Estuarine Shrimp Species
 - Estuarine Fish Series
 - Estuarine Mollusc Testing
- 122-1 Plant Testing Requirements
 - Seed Germination/Seedling Emergence
 - Vegetative vigor
- 122-2 Aquatic Plant Growth

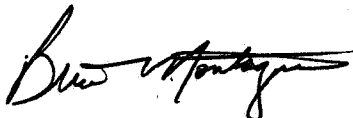
In addition results from Fish Early Life Stage testing would indicate that the Estimated Environmental Concentration of 18.3 ppb from 2% runoff (See Turf Use Review Lee - 1990) is well above 1/10 of the NOEL of early life stage on trout (56ppb) which would be 5.6 ppb. The LOEL for trout larvae was 120 ppb in this study and the EEC is also above 1/10 of this level. In Acute studies the 96 hour LOEL for trout was \leq 320 ppb (20% mortality) and the LOEL for bluegill was \leq 560 ppb. The chemical is extremely persistent with a hydrolysis half-life of over 1053 days in pH-9 and no observed hydrolytic degradation in lower pH waters. This would indicate that dithiopyr may pose risk to reproductive processes and other life stages of fish. 72-5 Full Life Cycle Testing with Freshwater Fish may further indicate whether these affects will be multi-generational. This requirement should be added to data requirements for registration of Dithiopyr on Turf.

For further information regarding this review please contact Brian Montague, 305-6438.

ECOLOGICAL EFFECTS BRANCH
DATA EVALUATION REPORT

1. **Chemical:** Dithiopyr and Mon 15151-Formulation (Dimension Turf Herbicide)
2. **Test Materials:** Dithiopyr technical, 92.6% ai and Mon 15151 Formulated Product
3. **Study Type:** Modified Acute Toxicity Test with *Daphnia magna* 48 Hour duration
4. **Study Identification:**

Study Director: Blasberg, Jennifer W.
Study Laboratory: ABC Laboratories, Columbia, Ms.
Study Dates: June 4-6, 1991, August 13-15, 1991
Study Identification: Project No. AB-90-582/39173 and Project No. AB-90-583 (Mon 15151)
Sponsor: Monsanto Chemical Company
EPA Identification: MRID 420502-01
5. **Reviewed by:**

Brian Montague, Fisheries Biologist
Ecological Effects Branch
Environmental Fate & Effects Division 
6. **Approved by:**

Les Touart, Ph.D., Supervisory Biologist
Ecological Effects Branch
Environmental Fate & Effects Division
7. **Conclusions:** EEB concurs with the results of testing of Mon 7200 (dithiopyr 92.6 ai) and Mon 15151 (dithiopyr 12.8%). Statistical analysis supports the study author's conclusions. The test has followed the specialized protocol agreed upon by the Agency. Dithiopyr EC50 is greater > than 1.7 mg ai/L (the solubility limit for this chemical with solvents) The EC₅₀ with Mon 15151 formulated product is 5.2 mg ai/L.
8. **Recommendation:** The study has fulfilled amended testing requirements for satisfaction of 72-2 testing.

9. **Study Purpose:** The study was repeated to satisfy 72-2 requirements for registration. Earlier studies have failed to achieve sufficient concentrations to produce 50% mortality.

I. **Testing with Dithiopyr Technical**

10. **Study Design and Protocol:** Protocol was specially designed to satisfy EEB requests to test the material with acceptable solvents as the maximum concentration reached without solvents in earlier tests was about 1.3 mg/L (The water solubility limit for dithiopyr). The LC_{50} for this study was expressed simply as > 1.1 mg ai/L (See MRID 41001'5-14, 1988 review by C. Moulton). This was not felt to be adequate data for risk assessment of aquatic invertebrate exposure under varied field conditions. A letter of agreement between Les Touart of EEB and Monsanto Corp established that testing with use of DMF solvent at a maximum permissible limit of 0.5 mg/L with 30 daphnids at maximum water solubility for Dithiopyr would be acceptable in satisfying this guideline requirement.

In addition Mon 15151 formulation was also tested using similar methodology.

Study Methods and Materials: Prior to testing Monsanto established DMF and DMSO to be solvents of greatest effect in reaching higher solubility. Although the increases never exceeded 5.7 mg/L, this was 5 times higher than achieved in earlier testing. Test water used in range and definitive testing was hard blended water with hardness of 160-180 mg/L as $CaCO_3$, alkalinity of 190-194 mg/L $CaCO_3$, pH of 8.2, and conductivity of 340 microohms/cm.

An initial range finding study using 10 daphnia placed in 200 ml of test solution at nominal concentration of 10 mg/L of Dithiopyr.

Following this test a definitive study was initiated using only one test level of approximately 1.5 mg/L of Dithiopyr technical (the maximum concentration achievable with 0.5 ml of DMF solvent/L). This solution was magnetically stirred for 20 hours and allowed to settle for 4 hours before addition to three 250 ml glass test beakers. Daphnid instars < 24 hours old were then added within 30 minutes and observed for mortality or aberrant behavioral signs at 3, 24, and 48 hour intervals. Test water samples were taken at 0 and 48 hours for analysis of dithiopyr concentration using gas liquid chromatography. Temperature was maintained at $20 \pm 1^\circ C$ by use of temperature controlled water bath. Lighting was 37-74 footcandle intensity at 6D/8N photoperiod. Temperature, pH, and D.O. were measured in each replicate at 0 and 48 hours.

11. **Reported Test Results:** The initial range finding test produced no mortality following 48 hours of exposure to 20 mg ai/L concentration using DMF as the solvent. Two of the 10 daphnids were displaying abnormal swimming behavior. A precipitate and surface film were present.

The results of definitive testing residue analysis indicate that a maximum concentration of 1.5 mg of Dithiopyr/L was achieved consistently for the 48 hour period. Analyses yielded 1.7 mg ai/L measurements or 113% of the nominal concentration. Test solutions were clear with a precipitate. Dissolved O₂ ranged from 7.9 to 8.3 mg/L and pH range was 8.2-8.3 during the test period. EC₅₀ and NOEL were not determined as only 10% immobility was observed at maximum solubility. Earlier study established the NOEL at approximately 0.45 mg ai/L. Controls and vehicle blanks suffered no immobility. Thus the EC₅₀ is established to be > than 1.7 mg ai/L.

12. **Study Author's Conclusions:** Test I the mean measured concentration at 0 and 48 hours for the study was 1.7 mg ai/L which represented the maximum amount of MON 7200 that could be dissolved in water...When tested up to its limits of solubility, MON 7200 exposure resulted in 10% immobility...Based on this result the EC₅₀ is greater than 1.7 mg ai/L."

II. **Testing with MON 15151 formulated product - study No. AB-90-583**

1.-8 Same as page 1.

9. **Study Purpose:** To achieve greater concentration of the active ingredient the formulated product was also tested using no solvents. Concentrations of MON 15151 were measured at 0.70, 1.4, 2.0, 4.6, and 6.7 mg/L of formulated product. Formulation blanks containing no active ingredient were also tested.

10. **Study Design and Protocol:** Test design was generally similar to protocol used for testing the technical material. Water quality, organisms, test vessels, and methods of analysis were nearly identical to those used for testing of technical ingredient.

The use of MON 15151 achieved 5 concentrations levels instead of one. Mean measured concentrations after 48 hours were 0.70 to 6.7 mg of MON 15151/L. Two replicates, 10 daphnids per replicate, were used for controls and the 5 test concentration groups. In addition 5 concentrations and a control level were tested using MON 15151 formulation blanks (no ai added) to test possible toxicity affects of inert ingredients. Nominal concentrations were 1.0, 1.8, 3.2, 5.6 and 10.0 mg/L of non activated formulation.

11. **Reported Results:** Temperature and D.O. remained at acceptable levels. Temperature did drop from 21 to 19°C during the 48 hour study period but this is not felt to have affected the results. pH of the test water ranged from 8.1 - 8.4 for both tests. Some mortality occurred in the formulation blank test vessels indicating that inert ingredients had some effect on the survival. All daphnids were observed on the bottom in the 10 mg/L concentration test vessels after 24 hours and 4 mortalities (20%) occurred after 48 hours exposure.

Mortality in MON 15151 test vessels was 75% in the 6.7 mg/L test concentration after 24 hours of exposure. After 48 hours exposure the 4.6 mg/L test group experienced 15% mortality and the 6.7 mg/L group - 100% mortality. All other daphnids appeared normal.

12. **Study Authors Conclusions:** "The mean measured concentrations of MON 15151 were 0.70, 1.4, 2.0, 4.6, and 6.7 mg/L. The 48-hour EC₅₀ for Mon 15151 was 5.2 mg/L and the no-effect level was 2.0 mg/L.

13. **Reviewers Discussion:**

Test I

Deviation from protocol and/or acceptable guidelines noted by the study director was that mid-study observations were made at 26 hours not 24 ± 1 hour. Range testing was conducted on 1 concentration not 2 or 3 suggested in protocol. This is based on the fact that earlier studies conducted by Monsanto had used lower concentrations and established an NOEL and subsequent agreements with the Agency had negated the requirement for multiple concentration testing and achievement of 50% mortality due to relative insolvent characteristics of dithiopyr. Results would indicate that EC₅₀ of dithiopyr to be greater than 1.7 mg ai/L which is the maximum amount of dithiopyr soluble in 8.0 pH water with hardness of 160-180 mg CaCO₃/L using 0.5 mg DMF/L.

Reviewers Discussion: Test II

Testing with MON 15151 formulation produced mortalities at the two highest concentrations and an NOEL was established for this study. The formulation acted quickly, obtaining 75% mortality in the 6.7 mg/L test level within 24 hours. The study author's statistical estimate of 5.2 mg ai/L as the EC₅₀ is confirmed by EEB's recalculations.

Adequacy of Study:

Classification: Core

Rationale: Study results support author's conclusions and meet modified test requirements agreed to by the Agency.

Repairability: N/A