US EPA ARCHIVE DOCUMENT

DYNAMAC
CORPORATION

DITHIOPYR

TASK 1: REVIEW AND EVALUATION OF INDIVIDUAL STUDIES

TASK 2: ENVIRONMENTAL FATE ASSESSMENT

February 9, 1990

Final Report

Contract No. 68D90058

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
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Rockville, MD 20852

DATA EVALUATION RECORD

STUDY 1

CHEM 128994 Dithiopyr §162-1

FORMULATION--OO--ACTIVE INGREDIENT

STUDY ID 41001517
Patano, L.K. and Y.L. Sing. 1989. The aerobic soil metabolism of dithiopyr, 3,5-pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethyl ester (MON 7200/15100). Report No. MSL-8551; R.D. No. 900. Unpublished study performed and submitted by Monsanto Agricultural Company, St. Louis, MO.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study can be used to fulfill data requirements.

2. Dithiopyr degraded with half-lives of 523 days in silt loam soil, 625 days in sandy loam soil, 639 days in clay soil, and 1,125 and 2,300 days in two Japanese loam soils incubated in the dark at 25 C and 75% of 0.33 bar moisture for 12-18 months. The degradates normal acid [(2-difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid], reverse acid [6-(difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-2-(trifluoromethyl)-3-pyridinecarboxylic acid], and diacid [2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylic acid] were isolated. At 1 year posttreatment, volatiles

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other than carbon dioxide (identified as dithiopyr in selected samples) comprised 7.29-25.86%.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the aerobic metabolism of dithiopyr in sandy loam, silt loam, and clay soils.

4. No additional data on the aerobic metabolism of dithiopyr in soils are needed at this time.

METHODOLOGY:

Pyridine ring-labeled [$^{13}C/^{14}C$]dithiopyr (radiochemical purity >99%, specific activity 18.32-26.21 mCi/mmol, Monsanto Chemical Company) was applied at approximately 1 ppm to a sandy loam, a silt loam, a clay, and two Japanese loam soils (Table 4) adjusted to 75% of 0.33 bar moisture. The soils were incubated in the dark at 25 C in flasks that were each topped with a column containing Ascarite (sodium hydroxide fused to an inert carrier) to trap $^{14}CO_2$ and foam plugs to trap other volatile compounds (Figure 2). Duplicate flasks containing the five soils were sampled at intervals up to 12-18 months posttreatment.
The Ascarite and foam plug volatile traps were analyzed at 1 week and 1 or 4 week intervals, respectively.

The soils were extracted four times with acetonitrile:water (50:50) (the extracting solution for the clay soil additionally contained 1% sodium chloride). The combined extracts were analyzed for total radioactivity by LSC and for dithiopyr and degradates by HPLC with a mobile phase of pH 3.6 acetic acid buffer and acetonitrile and radioactivity detection. Nonradiolabeled reference standards of dithiopyr, normal acid, reverse acid, and diacid that were cochromatographed with the extracts were located by UV detection. Some of the acetonitrile:water extracts were stored frozen for an unspecified period of time prior to HPLC analysis.

In order to confirm the identities of the degradates, selected acetonitrile:water extracts were partitioned by one of two procedures and then analyzed by HPLC/MS, GC with chemical ionization/MS, or high voltage electrophoresis. In the first procedure, the extracts were partitioned three times with ether. The aqueous fraction was acidified with concentrated hydrochloric acid and re-extracted with ether. All ether fractions were evaporated to near dryness, dissolved in 50% aqueous acetonitrile, and analyzed by HPLC/MS (negative ion mode). In the second procedure (Figure 11), the extracts were partitioned three times with isooctane. The aqueous fraction was partitioned three times with ethyl acetate, acidified to pH 1.0 with hydrochloric acid, and re-extracted three times with ethyl acetate. The isooctane and the first three ethyl acetate fractions, and the following three ethyl acetate fractions were each combined, concentrated, redissolved in aqueous acetonitrile, and analyzed by HPLC/MS, GC with chemical

ionization/MS, or high voltage electrophoresis following derivatization with ethereal diazomethane.

The extracted soils were stored frozen for an unspecified period of time, thawed, and then analyzed for unextractable radioactivity by LSC following combustion. Selected extracted soils were further extracted by refluxing with acidified ethyl acetate:glacial acetic acid (350:2 or 350:3) for approximately 18 hours. The extracts were concentrated, and the remaining residues were dissolved in 50% aqueous acetonitrile and analyzed by HPLC as described.

The foam plugs were analyzed for volatiles by cutting the plugs in half, placing each half in a separate vial containing scintillation cocktail, and analyzing by LSC. The Ascarite was analyzed for CO_2 by mixing it with distilled water in a flask immersed in ice, adding sulfuric acid dropwise, trapping the escaping CO_2 in a phenethylamine solution, and analyzing the phenethylamine solution by LSC.

DATA SUMMARY:

Pyridine ring-labeled [$^{13}C/^{14}C$]dithiopyr (radiochemical purity >99%), at approximately 1 ppm, degraded with registrant-calculated half-lives of 523 days in silt loam soil, 625 days in sandy loam soil, 639 days in clay soil, and 1,125 and 2,300 days in two Japanese loam soils incubated in the dark at 25 C and 75% of 0.33 bar moisture for 12-18 months. At 1 year posttreatment, dithiopyr comprised 51.0-73.1% of the applied radioactivity in the five soils (Tables 10 to 14). The degradates . . .

normal acid,

reverse acid, and

diacid

were isolated at maximum concentrations of 6.3%, 5.0%, and 7.3% of the applied, respectively. The highest concentrations of all three degradates were isolated from the silt loam soil; and, in general, maximum concentrations of the degradates in all five soils were reached at 6-12 months posttreatment. Throughout the study, an unidentified degradate comprised up to 2.0% of the applied radioactivity. At 1 year posttreatment, unextractable radioactivity comprised 3.48-19.08% of the applied, $^{14}CO_2$ comprised 0.11-1.33%, and other volatiles (identified as dithiopyr in selected samples) comprised 7.29-25.86% (Tables 5-9). Material balances ranged from 85.63 to 102.6% of the applied, with the exception of the immediate posttreatment silt loam soil sample, which had a material balance of 51.63%.

COMMENTS:

1. An unidentified degradate was isolated at up to 2.0% of the applied (0.02 ppm); however, this degradate only comprised 0.4% of the applied (0.004 ppm) in the clay soil. Although Subdivision N guidelines specify that all degradates isolated at ≥0.01 ppm must be identified, the registrant is only required to submit aerobic soil metabolism data for one soil. Therefore, since the unidentified degradate was isolated at <0.01 ppm in the clay soil, characterization of this degradate is not required.

2. The two Japanese soils are not typical of soils in the United States. Unlike typical soils in the United States, these soils contain volcanic ash, and the clay fractions of the soils do not contain any montmorillonite (smectite). Therefore, data concerning the aerobic soil metabolism of the two Japanese soils provide supplemental information, but cannot be used to fulfill data requirements.

3. The registrant reported that Soxhlet extraction of selected extracted Japanese loam (paddy) and clay soils indicated that these unextractable [^{14}C]residues in the soxhlet extracts (which were unextractable using acetonitrile:water) were comprised of parent dithiopyr and the same degradates isolated from the soil by extraction with acetonitrile:water.

4. The statistical estimations of the degradation half-lives of dithiopyr reported in this study are of limited value because the calculations involve extrapolation considerably beyond the experimental time limits of the study. Data are often incapable of accurately predicting trends outside of their range because small differences are magnified and reactions which appear to be linear may, in fact, be curvilinear.

Dithiopyr Science Review

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Pages _14__ through _35__ are not included in this copy.

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_____ Identity of product inert ingredients.

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_____ Description of the product manufacturing process.

_____ Description of product quality control procedures.

_____ Identity of the source of product ingredients.

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_____ A draft product label.

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__X__ FIFRA registration data.

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

STUDY 2

CHEM 128994 Dithiopyr §163-1

FORMULATION--00--ACTIVE INGREDIENT

STUDY ID 41135601
Sing, Y.L. and C. George. 1989. Adsorption/desorption studies on metabolites of MON 7200/15100 (Dithiopyr): Monoacid-I, Monoacid-II, and Diacid. Laboratory Project No. 204400/MSL-8243; R.D. No. 932. Unpublished study performed and submitted by Monsanto Agricultural Company, St. Louis, MO.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study can be used to fulfill data requirements.

2. Based on batch equilibrium experiments, the dithiopyr degradates normal acid [(2-difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid], reverse acid [6-(difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-2-(trifluoromethyl)-3-pyridinecarboxylic acid], and diacid [2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylic acid] were determined to be very mobile in a sandy loam, clay and two silt loam soils.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the mobility of

the normal acid, reverse acid, and diacid degradates of dithiopyr in a sandy loam, two silt loams, and a clay soil.

4. No additional data on the mobility of dithiopyr degradates in soil are needed at this time.

METHODOLOGY:

A sandy loam, two silt loams, and a clay soil (Table 5) were air-dried for 1-2 days and sieved through a 2-mm mesh sieve. A preliminary equilibrium test was conducted to determine a valid shaking time for conducting the adsorption experiment. Sixteen hours was selected for all subsequent experiments based on the equilibria data obtained (Tables 6-8). The results of a chemical stability test indicated that little degradation of the test compounds would occur during the 16-hour equilibration period (Table 9).

The adsorption experiments were conducted separately using the three pyrimidine-labeled [^{14}C]dithiopyr degradates, normal acid (Monoacid II), reverse acid (Monoacid I), or diacid (radiochemical purities >98%, specific activities 27.23-29.16 mCi/mmol, Monsanto). Duplicate samples of each soil were shaken for 16 hours at 22-23 C with 0.01 M calcium sulfate solutions (1 g soil:5 g solution) containing the test substance at 0.01, 0.05, 0.1, and 0.3 ug/mL. After the shaking period, the soil:solution slurries were centrifuged. Aliquots of the supernatant were analyzed for total radioactivity by LSC.

Desorption was studied by removing the remaining supernatant from each sample and replacing it with an equal volume of 0.01 M calcium sulfate solution. The soil:solution slurries were shaken for 16 hours and then analyzed as described. The desorption procedure was repeated again. Following the second desorption step, soils from soil:solution slurries initially treated at 0.3 ug/mL were analyzed by LSC following combustion, and recoveries were totaled to determine mass balances.

DATA SUMMARY:

Based on batch equilibrium experiments, the pyrimidine ring-labeled [^{14}C]dithiopyr degradates normal acid (Monoacid II), reverse acid (Monoacid I), and diacid (radiochemical purities >98%), at 0.01-0.3 ug/mL, were very mobile in sandy loam, clay, and two silt loam soils equilibrated at 22-23 C in soil:0.01 M calcium sulfate solution slurries. Freundlich K_{ads} values were 0.064-0.196 for the normal acid, 0-0.197 for the reverse acid, and 0 for the diacid (Tables 10-12). In the desorption phase of the study, 65-90% of the dithiopyr degradates adsorbed by soil from soil:solution slurries initially treated at 0.3 ug/mL were desorbed.

COMMENTS:

1. In addition to calculating Freundlich K_{ads} values (referred to as "K" in the original document), the registrant calculated adsorption distribution coefficients (K_d) and adsorption distribution coefficients corrected for soil organic matter content (K_{oc}).

2. The percentages of dithiopyr degradates desorbed from the soil during the desorption phase of the study were calculated by the Dynamac reviewer from data presented in Tables 13-15 using the following equation:

   % Desorbed = ug removed by desorption/(ug removed by desorption + ug remaining in soil following desorption).

3. For stability tests, soil:solution slurries were shaken for two weeks, and then the test solutions were analyzed for dithiopyr degradates by HPLC with a mobile phase of acetonitrile and water:-trifluoroacetic acid (99:1) and radioactivity and MS detection.

Dithiopyr Science Review

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Pages _39__ through _57__ are not included in this copy.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

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_____ Description of the product manufacturing process.

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_____ Identity of the source of product ingredients.

_____ Sales or other commercial/financial information.

_____ A draft product label.

_____ The product confidential statement of formula.

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__X__ FIFRA registration data.

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

STUDY 3

CHEM 128994 Dithiopyr §164-1

FORMULATIONS--12--EMULSIFIABLE CONCENTRATE,
09--MICROENCAPSULATED, and
04--GRANULAR

STUDY ID 41001519
Adams, A. 1989. Terrestrial field dissipation study for the determination of MON-15100 and its major soil metabolites following broadcast application of MON-15126, MON-15120, and MON-15172. Unpublished study performed and submitted by Monsanto Agricultural Co., St. Louis, MO.

DIRECT REVIEW TIME = 80

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CONCLUSIONS:

Dissipation - Terrestrial Field

1. These data may be used to fulfill data requirements.

2. Dithiopyr was applied as emulsifiable concentrate (EC), microencapsulated (Mcap), and granular (G) formulations to turf plots of soils ranging in texture from sand to clay loam in 13 states. At sites treated at approximately ≥0.88 lb ai/A, dithiopyr dissipated from the upper 6 or 3 inches of soil with half-lives of 0.6-7.99 days (EC, 3 sites), 14.03-58.85 days (Mcap, 4 sites), and 3.87-96.70 days (G, 10 sites). The degradates normal acid [(2-difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid], diacid [2-(difluoromethyl)-4-(2-methylpropyl)-6-

(trifluoromethyl)-3,5-pyridinedicarboxylic acid] and reverse acid [6-(difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-2-(trifluoromethyl)-3-pyridinecarboxylic acid] were isolated. In general, dithiopyr and its degradates were not detected below the 0- to 6-inch soil depth; however, dithiopyr and its degradates were isolated in a few soil samples taken below the 6-inch depth at several sites.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the terrestrial field dissipation of EC, Mcap, and G formulations of dithiopyr in several soils treated at a rate of approximately 1 lb ai/A or greater.

4. No additional information concerning terrestrial field dissipation of dithiopyr is required at this time.

METHODOLOGY:

A 3 lb/gal EC, a 4 lb/gal Mcap, and a 0.5% G formulation of dithiopyr were each applied at nominal rates of 0.5, 1, and 2 lb ai/A to turfgrass plots (50 x 25 ft) of various soil types located at 14 sites in 13 states (Table I). A single application at each rate was made in the spring of 1987 or 1988 to the plots. Pesticide histories of the plots varied from no pesticide use to multiple treatments with herbicides and insecticides. Soil cores (10 cores/site, 1-inch diameter) at 12 of the 14 sites were taken at 0- to 6- and 6- to 12-inch depths. At the remaining two sites, both located on sandy loam soil in CA, soil cores were taken at 0- to 3-, 3- to 6-, 6- to 9-, 9- to 12-, 12- to 18-, and 18- to 24-inch depths; additional cores were taken at depths up to 8 feet at 182 or 204 days posttreatment in plots treated at 2 lb ai/A. Soils were sampled at intervals up to 359-369 days posttreatment. The variability in the rates of application was examined by collecting three soil samples from defined sections of the CA plots at 1, 3-4, 7, and 14-18 days posttreatment, and conducting separate analyses of the three samples. All collected samples were frozen immediately and stored frozen at unspecified temperatures prior to analysis.

Samples from plots treated at 0.5 and 1.0 lbs ai/A were analyzed for parent only; soil samples from plots treated at 2.0 lb ai/A were analyzed for parent and degradates. Multiple soil core segments from individual plots were composited prior to analysis for the parent dithiopyr. Subsamples were extracted by shaking with 20% aqueous acetonitrile:isooctane (1:5). The sample was allowed to settle, and the extract was filtered through glass wool prior to analysis for dithiopyr by GC equipped with a ^{63}Ni electron capture detector. Additional soil subsamples were analyzed for dithiopyr degradates. The samples were extracted with acidified acetonitrile and filtered using a buchner funnel under vacuum. The filtrate was concentrated by rotary evaporation, dissolved in 0.02 M sodium hydroxide, adjusted to pH 10, and partitioned with ethyl ether. The sodium hydroxide layer was acidified to pH 2, and again partitioned with ethyl ether.

The ethyl ether layer was concentrated by rotary evaporation, dried over anhydrous sodium sulfate, and further concentrated under a stream of nitrogen. Residues in the ethyl ether concentrate were methylated by adding an ethereal solution of diazomethane; the solution was concentrated to dryness under a stream of nitrogen. The residues were redissolved in octane and eluted through a solid phase extraction column with ethyl acetate/isooctane (1:9). The eluate was analyzed for the methyl derivatives of the diacid, normal acid, and reverse acid dithiopyr degradates using GC with electron capture detection. Quantitation of the dithiopyr degradates was determined using external calibration curves. The lower limit of detection for dithiopyr and the dithiopyr degradates was 0.01 ppm. Data were corrected for recoveries obtained from fortified soil samples. Half-life estimations were made assuming first order kinetics.

Field data: A summary of field data provided for each test site is included below. Unless otherwise specified, no pesticide other than dithiopyr was applied during the test, and no pesticide use was reported for the site in the two previous years.

FLORIDA: SANDY LOAM SOIL
Vegetation: Bermuda grass
Location: Keystone Heights, FL.
Slope: Approximately 0%.
Maximum and minimum air temperatures: 60.7-97 F and 28-68 F, respectively (data from Gainesville Municipal Airport and NOAA station in Jacksonville, FL).
Cumulative precipitation: 66.55 inches (source unspecified).

OHIO: LOAM SOIL
Vegetation: Fescue farm
Location: New Holland, OH.
Slope: 2% to the north.
Maximum and minimum air temperatures: 36-87 F and 16-65 F, respectively (data from unspecified source in New Holland, OH)
Maximum and minimum soil temperatures: 32-94 F and 32-80 F, respectively (data from unspecified source in New Holland, OH)
Cumulative precipitation: 45.6 inches (source unspecified).

NEW YORK: LOAM SOIL
Vegetation: Bluegrass/fescue.
Location: Union Springs, NY.
Slope: 2-6% to the east.
Maximum and minimum air temperatures: 30-82 F and 14-63 F, respectively (data from unspecified source in Geneva, NY)
Maximum and minimum soil temperatures: 33-81 F and 33-72 F, respectively (data from unspecified source in Geneva, NY).
Cumulative precipitation: 24.7 inches (Union Springs, NY).

TEXAS: LOAM SOIL
Vegetation: Bermuda turf
Location: Snook, TX.

Slope: 2% to the west.
Maximum and minimum air temperatures: 58-97 F and 30-70 F, respectively.
Maximum and minimum soil temperatures: 43-98 F and 41-91 F, respectively.
Cumulative precipitation: 38.8 inches (data from Texas A&M Univ. Farm, College Station, TX).

ILLINOIS: CLAY LOAM SOIL
Vegetation: Kentucky bluegrass
Location: Downers Grove, IL.
Slope: 1.5% to the south.
Maximum and minimum air temperatures: 24-88 F and 6-67 F, respectively.
Cumulative precipitation: 49 inches (data from unspecified source in St. Charles, IL).

OREGON: SILT LOAM SOIL
Vegetation: Lawn
Location: Beaverton, OR.
Slope: 0%.
Maximum and minimum air temperatures: 44-82 F and 33-54 F, respectively.
Cumulative precipitation: 71.4 inches (data from unspecified source in Beaverton, OR).
Pesticide use history: Not provided for this site.

NEW JERSEY: LOAM SOIL
Vegetation: Kentucky bluegrass
Location: Frenchtown, NJ.
Slope: 2% to the south.
Maximum and minimum air temperatures: 32-86 F and 11-63 F, respectively.
Cumulative precipitation: 40.6 inches (data from unspecified source in Flemington, NJ).

SOUTH CAROLINA: LOAMY SAND
Vegetation: Turf farm
Location: John's Island, SC.
Slope: 0%.
Maximum and minimum air temperatures: 52-92 F and 35-75 F, respectively.
Maximum and minimum soil temperatures: 40-94 F and 37-85 F, respectively.
Cumulative precipitation: 41.7 inches (data from unspecified source in Elko, SC).
Pesticide use history: The turf was treated during the study with 2,4-D (two applications at 1 lb ai/A) and Dursban (two applications at 1 lb ai/A) and in the previous year with 2,4-D (three applications at 1 lb ai/A), simazine (2 lb ai/A), Dursban (four applications at 1 lb ai/A), and MSMA (three applications at 1.5 lb ai/A). The site was

not cropped or treated with pesticides during the second year prior to treatment with dithiopyr.

PENNSYLVANIA: SILT LOAM SOIL
Vegetation: Bluegrass turf.
Location: Doylestown, PA.
Slope: Very slight slope (undefined) to the north.
Maximum and minimum air temperatures: 38-91 F and 13-65 F, respectively (data from unspecified source in Neshaminy Falls, PA).
Cumulative precipitation: 38.1 inches (data from unspecified source in Doylestown, PA).
Pesticide use history: The site was planted to corn in the two years prior to the turf study. No pesticide usage was reported for the site.

MISSOURI: SILT LOAM SOIL
Vegetation: Red top and timothy turf.
Location: Clarence, MO.
Slope: 2% to the south or southwest.
Maximum and minimum air temperatures: 35-94 F and 15-69 F, respectively.
Cumulative precipitation: 72.3 inches (data from unspecified source in Clarence, MO).

MICHIGAN: SANDY LOAM SOIL
Vegetation: Kentucky bluegrass and red and tall fescue.
Location: Haslett, MI.
Slope: 3-5% to the west or northwest.
Maximum and minimum air temperatures: 29-86 F and 10-64 F, respectively (data from unspecified source in East Lansing, MI).
Cumulative precipitation: 30.4 inches (data from unspecified source in Meridian, MI).
Pesticide use history: The site was treated with one application of 2,4-D (1 lb ai/A) during the study and in both previous years.

WISCONSIN: SILT LOAM SOIL
Vegetation: Turf.
Location: Verona, WI.
Slope: 2-3.5% to the southeast.
Maximum and minimum air temperatures: 22-85 F and 5-56 F, respectively.
Cumulative precipitation: 33.8 inches (data from unspecified source in Verona, WI).

PALM DESERT, CALIFORNIA: SANDY LOAM
Average maximum and minimum air temperatures: 78-103 F and 60-87 F (data from unspecified source).
Average maximum and minimum soil temperatures: 57-84 F (data from unspecified source).
Cumulative precipitation: 157.4 inches (including irrigation) (data from unspecified source).

SACRAMENTO CALIFORNIA: SANDY LOAM
Average maximum and minimum air temperatures: 66-89 F and 52-71 F (data from unspecified source).
Average maximum and minimum soil temperatures: 52-72 F (data from unspecified source).
Cumulative precipitation: 101 inches (including irrigation) (data from unspecified source).

DATA SUMMARY:

Dithiopyr was applied as emulsifiable concentrate (EC), micro-encapsulated (Mcap), and granular (G) formulations at 0.5, 1.0, and 2.0 lb ai/A to turf plots of soils ranging in texture from sand to clay loam in 13 states in the spring of 1987 or 1988 (Table 1). The concentrations of dithiopyr present in the 0- to 6-inch or 0- to 3-inch depths of the day 0 soil samples did not confirm the stated application rates at the majority of test sites. The 2.0 lb ai/A application was intended to equal 2X the maximum proposed application rate of 1 lb ai/A. Although the 2 lb ai/A application rate was not confirmed in the majority of the day 0 soil samples, at several sites, application rates were determined to be approximately ≥0.88 lbs ai/A (measured dithiopyr concentrations of 0.44 ppm or greater in the 0- to 6-inch soil depth or 0.88 ppm or greater in the 0- to 3-inch soil depth). Data from these sites were reviewed in detail since these data can be used to determine the field dissipation of dithiopyr following the application at the maximum use rate. Due to the volume of data included in the original report, data for sites where dithiopyr was applied at <0.88 lbs ai/A were briefly summarized and were not reviewed in detail.

Emulsifiable Concentrate

Dithiopyr, applied as an emulsifiable concentrate (EC) at approximately 1.22-1.34 lb ai/A (measured concentrations of 0.61-0.67 ppm in the upper 6 inches of soil) to three silt loam soils (OR, PA, and WI), dissipated from the upper six inches of soil with calculated half-lives of 0.6-7.99 days. Dithiopyr degradates isolated at the 0- to 6-inch soil depth were

the normal acid (maximum concentrations 0.037-0.17 ppm immediately posttreatment),

the diacid (maximum concentrations 0.016-0.13 ppm at 60-120 days posttreatment), and

the reverse acid (maximum concentrations 0.012-0.054 ppm at 60-68 days posttreatment)

(Tables 25, 34, and 49). The diacid was isolated at 0.012 ppm at the 6- to 12-inch soil depth at the Pennsylvania site after 180 days posttreatment. In the rest of the soil samples taken from these

plots, parent dithiopyr and its degradates were not detected below the upper 6 inches of soil.

At sites treated with the EC formulation of dithiopyr at ≤0.84 lb ai/A (measured concentrations ≤0.42 ppm in the upper 6 inches of soil), dithiopyr dissipated with calculated half-lives of 2.25-68.04 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, with the exception of the Palm Desert, California site, dithiopyr and its degradates were not isolated below the upper 6 inches of soil. In the sandy loam soil at the Palm Desert, California site treated with dithiopyr at approximately 0.37 lb ai/A (measured concentration 0.37 ppm in the upper 3 inches at 1 day posttreatment), the normal acid, reverse acid, and diacid degradates were each isolated at up to 0.058 ppm at 6- to 9-, 9- to 12-, 12- to 18-, and 18- to 24-inch depths at 45-178 days posttreatment.

Micro-Encapsulated

Dithiopyr, applied as a micro-encapsulated (Mcap) at approximately 0.88-1.16 lb ai/A (measured concentrations of 0.44-0.58 ppm in the upper 6 inches of soil or 0.97 ppm in the upper 3 inches of soil) to a loam, a silt loam, and two sandy loam soils, dissipated from the upper six inches (TX, MI, and WI sites) or three inches (Palm desert, CA site) of soil with calculated half-lives of 14.03-58.85 days. Dithiopyr degradates isolated at the 0-to 6-inch soil depth were the normal acid (maximum concentrations 0.029-0.050 ppm at 1-30 days posttreatment), the diacid (maximum concentrations 0.021-0.093 ppm at 30-180 days posttreatment, not detected at the Texas site), and the reverse acid (maximum concentrations 0.017-0.027 ppm at 30-60 days posttreatment) (Tables 17, 44, and 50). In the upper three inches of soil at the California site, the normal acid, diacid, and reverse acid degradates were isolated at maximum concentrations of 0.51 ppm (1 day posttreatment), 0.28 ppm (45 days) and, 0.072 ppm (30 days), respectively (Table 10). At the 6- to 12-inch soil depth, dithiopyr was not detected with the exception of the day 7 sample from the Michigan site (0.071 ppm) and the day 1 sample from the Texas site (0.021 ppm). Dithiopyr degradates were not detected at the 6- to 12-inch depth with the exception of the day 180 sample from the Michigan site (0.037 ppm of the diacid) and the California site. At the California site, dithiopyr was not detected below the 6-inch soil depth; however, the diacid, normal acid, and reverse acid degradates were each isolated in the 6- to 9-, 9- to 12-, 12-to 18-, and 18- to 24-inch depths at up to 0.90 ppm after 60 days posttreatment.

At sites treated with the Mcap formulation of dithiopyr at ≤0.76 lb ai/A (measured concentrations ≤0.44 ppm in the upper three inches of soil or ≤0.38 ppm in the upper six inches of soil), dithiopyr dissipated with calculated half-lives of 6.21-134.53 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, dithiopyr and its degradates were not isolated below the upper 6 inches of soil.

Granular

Dithiopyr applied as a granular (G) at approximately 0.88-2.14 lb ai/A (measured concentrations of 0.44-1.07 ppm in the upper 6 inches of soil or 0.90 ppm in the upper 3 inches of soil) to one clay loam, one loamy sand, one sandy loam, three silt loam, and four loam soils, dissipated from the upper six inches (TX, NY, PA, SC, IL, OH, NJ, OR, and WI sites) or three inches (Palm Desert, CA site) of soil with calculated half-lives of 3.87-96.70 days. Dithiopyr degradates isolated at the 0-to 6-inch soil depth were the normal acid (maximum concentrations 0.035-0.12 ppm at 1-67 days posttreatment), the diacid (maximum concentrations 0.014-0.057 ppm at 30-120 days posttreatment), and the reverse acid (maximum concentrations 0.017-0.078 ppm at 14-120 days posttreatment) (Tables 21, 24, 27, 30, 33, 36, 42, 45, 48, and 51). In the upper three inches of soil at the California site, the normal acid, diacid, and reverse acid degradates were isolated at maximum concentrations of 0.21 ppm (30 days posttreatment), 0.044 ppm (45 days) and, 0.11 ppm (30 days), respectively (Table 11). In general, dithiopyr and the normal acid, diacid, and reverse acid degradates were not detected below the upper six inches of soil; dithiopyr and its degradates were isolated in a few soil samples taken below the 6-inch depth at several sites.

At sites treated with the G formulation of dithiopyr at ≤0.84 lb ai/A (measured concentrations ≤0.53 ppm in the upper three inches of soil or ≤0.42 ppm in the upper six inches of soil), dithiopyr dissipated with calculated half-lives of 7.40-221.20 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, dithiopyr and its degradates were not isolated below the upper 6 inches of soil.

COMMENTS:

1. Measured concentrations of dithiopyr in the 0- to 6-inch or 0- to 3-inch depths of the day 0 soil samples did not confirm the stated application rates at the majority of test sites. The 2.0 lb ai/A application was intended to equal 2X the maximum proposed application rate of 1 lb ai/A. Although the 2 lb ai/A application rate was not confirmed in the majority of the day 0 soil samples, at several sites, application rates were determined to be approximately ≥0.88 lbs ai/A (measured dithiopyr concentrations of 0.44 ppm or greater in the 0- to 6-inch soil depth or 0.88 ppm or greater in the 0- to 3-inch soil depth). Data from these sites were reviewed in detail since these data can be used to determine the field dissipation of dithiopyr following the application at the maximum use rate. Only data from sites treated with dithiopyr at a rate approximating the proposed maximum application rate of 1 lb ai/A can be used to fulfill data requirements. Due to the volume of data included in the original report, data for sites where dithiopyr was applied at <0.88 lbs ai/A were briefly summarized and were not reviewed in detail; al-

though these data are acceptable, they cannot be used to fulfill data requirements because dithiopyr was applied at less than the maximum use rate.

2. The storage stability of dithiopyr and its degradates in soil were studied; however, storage conditions and the type of soil used in the experiment were not provided (Table 52). Recoveries of the diacid, normal acid, and reverse acid dithiopyr degradates ranged from 76.1 to 114.1% in fortified soil samples stored for up to 123 days. Recoveries of dithiopyr ranged from 88.2 to 102.2% in fortified soil samples stored for up to 364 days. The registrant stated that these data are preliminary and that the storage stability experiments will be conducted for a period of two years. The amount of time that the soils were stored frozen during the actual study was not reported.

3. Results reported for the field data are corrected for average recoveries obtained from fortified samples.

4. The concentrations of dithiopyr and its degradates were reported for values greater than the limit of detection (0.01 ppm), but with the less-than symbol (<). The study author did not describe the calculation of these data, which may reflect averaging of concentrations from three samples including <0.01 ppm concentrations.

5. The study author reported that the 0.5 lb ai/A treatment is a typical use, 1 lb ai/A is the maximum proposed use, and 2 lb ai/A is an exaggerated rate treatment.

6. Data for the Pennsylvania site treated with the microencapsulated formulation of dithiopyr and for the Haslett, Michigan, and Keystone Heights, Florida, sites treated with the granular formulation of dithiopyr at a nominal rate of 2.0 lb ai/A were not reviewed because the data were too variable to accurately assess the decline of dithiopyr in the soil. For the Pennsylvania site at the 0- to 6-inch soil depth, dithiopyr was 0.11 ppm immediately posttreatment, increased to 1.1 ppm at 1 day posttreatment, decreased to 0.11 ppm at 3 days posttreatment, and then increased to 0.30 ppm at 30 days posttreatment (Table 26). For the Haslett, Michigan site at the 0- to 6-inch soil depth, dithiopyr was 0.38 ppm immediately posttreatment, 0.28-0.37 ppm at 1-14 days posttreatment, increased to 0.70-0.75 ppm at 14-30 days posttreatment, decreased to 0.22 ppm at 60 days posttreatment, and then increased to 0.49 ppm at 120 days posttreatment. For the Keystone Heights, Florida, site at the 0- to 6-inch soil depth, dithiopyr was 0.41 ppm immediately posttreatment, decreased to 0.20-0.23 ppm at 1-3 days posttreatment, increased to 0.53 ppm at 7 days posttreatment, decreased to 0.23 ppm at 14 days posttreatment, and then increased to 0.33 ppm at 30 days posttreatment.

7. The calculated half-lives for the Palm Desert, California, and Haslett, Michigan, sites treated with the microencapsulated formulation of dithiopyr at a nominal rate of 0.5 lb ai/A were not included in the summary section of this review because they did not agree with

the actual data. For the Palm Desert site, the observed half-life occurred between 14 and 45 days posttreatment; however, the calculated half-life was 193.56 days (Table 10). For the Haslet, Michigan site, the observed half-life occurred at approximately 180 days posttreatment; however, the calculated half-life was 315.92 days (Table 17).

8. Separate analyses of three soil samples that were each taken at 1 day posttreatment from the 0- to 3-inch depth of defined sections of sandy loam soils at the two California sites treated with the EC, Mcap, and G formulations of dithiopyr indicated that interplot variability was as great as 47.5% and as little as 1.6% (percentages calculated by the Dynamac reviewer, Tables 6-8 and 13-15).

9. For all treatments at the Palm Desert, CA, and Sacramento, CA, sites, additional soil cores below the 24-inch depth were taken in 12-inch incraments to a depth of 96 inches at 182 or 204 days posttreatment. Dithiopyr and the diacid, normal acid, and reverse acid degradates were not detected below the 24-inch soil depth in any of these samples (Tables 5 and 12). Only the plots at the Palm Desert, CA site treated with Mcap and G formulations at a nominal rate of 2 lb ai/A contained concentrations of dithiopyr that confirmed application rates of approximately 1 lb ai/A.

Table I.

SOIL CHARACTERIZATION DATA

Soil Type location	Sand	Silt	Clay	Organic Matter	pH	CEC (meq/100 g)
	---------Percent----------					
LOAM						
NJ	30	48	22	2.1	6.7	5.5
NY	40	40	16	4.4	7	10.8
OH	40	44	16	3.7	6.9	10.7
TX	36	48	16	1.2	7.8	11.7
SILT LOAM						
MO	28	52	20	2.5	6.3	25.6
OR	34	52	14	4.3	5.2	8.9
PA	16	58	26	2.2	6.4	7.4
WI	22	58	20	3	6.7	9.4
SANDY LOAM						
Plm D., CA	66	26	8	1.4	7.7	7.8
Sac., CA	60	30	10	2.2	6.9	7
MI	62	24	14	2.8	6.8	5.8
LOAMY SAND						
SC	84	10	6	2	6.6	4.9
SAND						
FL	94	2	4	1.6	6.7	4.7
CLAY LOAM						
IL	32	40	28	3.2	6.9	12.6

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DATA EVALUATION RECORD

STUDY 4

CHEM 128994 Dithiopyr §165-4

FORMULATION--OO--ACTIVE INGREDIENT

STUDY ID 41001518
Forbis, A.D. and K.A. Chott. 1989. Uptake, depuration and bioconcentration of ^{14}C-MON-7200/15100 to bluegill sunfish (Lepomis macrochirus). Laboratory Project Identification R.D. No. 900 (Part I) and MSL-8347-48 (Part II). Unpublished study performed by Analytical Bio-Chemistry Laboratories, Inc., Columbia, MO, and Monsanto Agricultural Company, St. Louis, MO. Submitted by Monsanto Agricultural Company, St. Louis, MO.

DIRECT REVIEW TIME = 16

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CONCLUSIONS:

Laboratory Accumulation - Fish

1. This study can be used to fulfill data requirements.

2. Dithiopyr accumulated in bluegill sunfish exposed to 0.0024-0.0093 ppm of dithiopyr, with maximum bioconcentration factors of 320x, 1400x, and 930x in edible tissues, nonedible tissues, and whole fish, respectively. Three degradates identified in the fish tissues were the reverse acid [6-(difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-2-(trifluoromethyl)-3-pyridinecarboxylic acid], the normal acid [(2-difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid], and the diacid [2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoro-

methyl)-3,5-pyridinedicarboxylic acid]. Depuration rates in the edible, nonedible, and whole fish tissues were 92-94% of the accumulated [^{14}C]residues by day 14 of the depuration period.

3. This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides by providing information on the accumulation of [^{14}C]dithiopyr in laboratory fish.

4. No additional information on the accumulation of [^{14}C]dithiopyr in laboratory fish is required at this time.

METHODOLOGY:

Laboratory Accumulation - Fish

Bluegill sunfish (Lepomis macrochirus; average length and weight of 64 mm and 8.2 g, respectively) were held in culture tanks on a 16-hour daylight photoperiod for at least 14 days prior to the initiation of the study. Flow-through aquatic exposure systems were prepared using four 70-L aquaria. Aerated well water (Table 1) was provided to each aquarium at a rate of approximately 7.2 turnovers per day. The aquaria were immersed in a water bath and maintained at 22 ± 1 C.

Bluegill sunfish (110) were placed in each aquarium, and two of the aquaria were continuously treated with [^{14}C]dithiopyr (MON 7200, radiochemical purity 99.5%, specific activity 26.21 mCi/mM, Monsanto) at a nominal concentration of 0.01 ppm. Due to suspected compound volatility, the treated aquaria and flow-through proportional diluter system were covered with glass in order to keep as much of the test substance in the system as possible. The two remaining aquaria served as untreated controls. Following a 35-day exposure period, the water in the treated and control aquaria was siphoned to a depth of approximately 8 cm and refilled with pesticide-free water twice. The depuration period lasted 14 days. Water samples were taken prior to the introduction of the fish into each aquarium, and water and five fish samples were taken after 2-6 hours and 1, 3, 7, 14, 21, 28, and 35 days of exposure. During the depuration period, water and five fish from the treated and untreated aquaria were sampled on days 1, 3, 7, 10, and 14.

Triplicate aliquots of the water samples were analyzed for total radioactivity using LSC. The remaining water samples were stored frozen in dry ice during shipment and were then stored frozen at -20°C prior to further analyses. The water samples were thawed, and then analyzed again by LSC. Additional aliquots of water samples taken on days 3, 28, and 35 of the exposure period were thawed prior to analyses for dithiopyr and its degradates. The water samples were extracted as shown in Figure 10. The water samples were centrifuged, particulates were analyzed for total radioactivity by LSC following combustion, and particulate-free water was analyzed by LSC. The

particulate-free water was acidified to pH 1.0 with 6 N hydrochloric acid and then extracted five times with isobutyl alcohol. The isobutyl alcohol extracts from each sample were combined and concentrated to dryness by rotoevaporation and then redissolved in methanol. The methanol concentrates were analyzed for total radioactivity by LSC and for dithiopyr by HPLC/LSC using a mobile phase of either 0.1% trifluoroacetic acid and acetonitrile or 1% acetic acid and acetonitrile. The extracted aqueous phase from the 35-day water sample contained significant radioactivity and was further analyzed. The sample was concentrated to dryness by rotoevaporation, and extracted three times with water. The combined water extracts were analyzed by LSC and HPLC/LSC as described. The remaining residue was analyzed for total radioactivity by LSC following combustion.

At each sampling interval, ten treated fish and ten control fish (five fish per aquarium) were each pooled. Six of the treated and control fish were dissected into edible tissues (body, muscle, skin, skeleton) and nonedible tissues (fins, head, internal organs). The remaining four treated and control fish were reserved for whole fish analyses. The fish samples were stored frozen, then individual samples were homogenized with dry ice and analyzed for total radioactivity by LSC following combustion. Recoveries of [^{14}C]dithiopyr residues from fortified fish samples ranged from 94 to 100% (Table 7). The detection limits for LSC analysis of whole fish, edible tissues, and nonedible tissues were 0.00524, 0.00526, and 0.00519 ppm, respectively. The remaining fish samples were stored frozen in dry ice during shipment and then were stored frozen at -20 C prior to further analyses. Following the storage period, edible, nonedible, and whole fish tissues from days 3, 28, and 35 of exposure and day 3 of depuration were analyzed again by LSC following combustion. Additional fish sampled on days 3, 28, and 35 of the exposure period and on day 3 of the depuration period were analyzed for dithiopyr and its degradates. The fish were thawed, divided into edible, nonedible, and whole fish fractions, and extracted as shown in Figure 11. Samples (2-3 g) of the tissues were weighed into centrifuge tubes and extracted four times with acetone, then two times with water. The four acetone extracts were combined and concentrated by rotoevaporation to a yellow oil; the distillate was analyzed by LSC. The oil was extracted several times with methanol; the extracted oil was analyzed by LSC, and the methanol extracts were analyzed by LSC and by HPLC/LSC as described. The methanol extract of the day 35 nonedible tissue sample was further analyzed for parent compound by GC with chemical ionization mass spectrometry. The water extracts from the whole fish and nonedible tissues were concentrated, and the concentrate was analyzed by LSC and HPLC/LSC as described. The precipitate that was formed during concentration was extracted twice with water. The water extracts were analyzed by LSC, and the solids were analyzed by LSC following combustion. The water extracts from the fillet tissues were not further characterized. The extracted fish tissues were analyzed for unextractable [^{14}C]residues by LSC following combustion.

Storage Stability

In order to assess the stability of the [^{14}C]residues in frozen water and fish samples, storage stability studies were conducted using day 28 water and whole fish samples. The water samples were stored frozen for either 114 days or 240 days. The water sample stored for 240 days was extracted and analyzed as described above. The water sample stored for 114 days was extracted using a slightly different procedure. The sample was filtered and then extracted five times with ethyl acetate. The aqueous solution was adjusted to pH 1.0 using 6 N hydrochloric acid and extracted four times with isobutyl alcohol. Triplicate aliquots of the ethyl acetate and isobutyl alcohol extracts and the extracted aqueous phase were analyzed for total radioactivity by LSC. The extracts which contained radioactivity were combined and concentrated to dryness by rotoevaporation; the distillate was analyzed by LSC. The dried concentrate was dissolved in methanol, analyzed by LSC, and analyzed by HPLC/LSC as described above.

Whole fish samples taken at 28 days were stored frozen for 108 or 206 days. The tissue samples were analyzed as described in the bioconcentration portion of the study, except that the water extracts of fish samples stored for 108 days were acidified to pH 1 and then extracted with isobutyl alcohol. The isobutyl alcohol extract was concentrated and analyzed by HPLC/LSC.

DATA SUMMARY:

Total [^{14}C]dithiopyr residues accumulated in bluegill sunfish with maximum bioconcentration factors of 320, 1400, and 930x in edible tissues (fillet), nonedible tissues (viscera), and whole fish, respectively, during 35 days of exposure to [^{14}C]dithiopyr (radiochemical purity 99.5%) at concentrations ranging from 0.0024 ppm to 0.0093 ppm in a flow-through system (Table 3). Maximum accumulation of [^{14}C]residues was 2 ppm in edible tissues (day 35), 8.7 ppm in nonedible tissues (day 35), and 5.6 ppm in whole fish (day 28). In 3, 28, and 35-day fish samples, dithiopyr was 0.77-1.7 ppm in the edible tissues, 2.8-6.1 ppm in the nonedible tissues, and 1.6-2.6 ppm in the whole fish (Table 11 A). Three degradates identified in the fish tissues were

the reverse acid (Monoacid II; maximum concentrations of 0.014, 0.29, and 0.13 ppm in the edible tissues, nonedible tissues, and whole fish, respectively, at 35 days);

the normal acid (Monoacid III; detected in the nonedible tissues and whole fish only, at maximum concentrations of 0.15 and 0.053 ppm, respectively, at 28 days); and,

the diacid (Diacid IV; detected in the nonedible tissues and whole fish only, at maximum concentrations of 0.057 and 0.031 ppm, respectively, at 35 days).

After 14-days of depuration, [^{14}C]residues in edible tissues, nonedible tissues, and whole fish were 0.15, 0.62, and 0.29 ppm, respectively, representing depuration rates of 92-94% (Table 1A and Figure 12).

Throughout the study in treated and control aquaria, the water temperatures ranged from 21 to 22°C, the pH ranged from 8.0 to 8.3, and the dissolved oxygen content ranged from 6.5 to 8.5 ppm. In particulate-free water at days 3, 28, and 35 of the exposure period, dithiopyr comprised 64.5-83.6% of the recovered radioactivity, the reverse acid comprised 4.6-6.9%, the normal acid comprised 0.5-1.2%, and, the diacid comprised 0.4-8.2% (Table 6A). Radioactivity in the particulates at 3, 28, and 35 days comprised 8.8-22.7% of that recovered from the water samples (Table 5A).

Freezer storage stability studies were also conducted using water and whole fish samples taken on day 28 of the exposure period. The results of these analyses indicate that [^{14}C]dithiopyr does not degrade in water stored frozen for up to 126 days (Table 6A) and in whole fish samples stored frozen for up to 98 days (Table 7A).

COMMENTS:

1. The nominal concentration of dithiopyr in the water was 0.01 ppm; however, the concentration of dithiopyr was not maintained at this level. Actual measured concentrations of dithiopyr residues in the water were 0.0093 ppm immediately prior to exposure, decreased to 0.0024 ppm at 0.17 days, and ranged from 0.0040 to 0.0080 ppm at 1-35 days.

2. Although freezer storage stability data were provided for storage periods of 126 days in water and 98 days in fish, the amount of time that samples were stored frozen for the actual study were not reported. In addition, the storage stability of degradates in fish was not adequately addressed. Data for freezer storage stability of degradates in fish samples were obtained from 28-day samples stored frozen for 108 or 206 days. Since concentrations of the reverse acid and the normal acid were low ($\leq$2.5% of the recovered) in the sample stored for 206 days and were not detected in the sample stored for 108 days, the stability of these degradates during storage could not be assessed. Data for storage stability of the diacid were not provided.

3. No mortality or abnormal behavior of the fish in the treated or untreated aquaria was observed during the study.

4. A preliminary 7-day toxicity study was conducted to determine the acute toxicity of dithiopyr to bluegill sunfish. The 7-day LC_{50} was calculated to be 2.3 ppm and the no-effect level was 0.50 ppm. However, due to precipitation of the test substance, the actual 7-day LC_{50} was considered to be approximately 0.6 ppm. In view of these results, a nominal concentration of 0.01 ppm (1/60 of the 7-day estimated LC_{50}) was chosen for the bioconcentration study.

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EXECUTIVE SUMMARY

The following findings are derived from those reviewed studies which have met the requirements of 40 CFR Part 158.130 and the guidance of Subdivision N, and were also deemed acceptable.

Hydrolysis

(Pantano, L.K., 40638627)

The hydrolysis of isotopically labelled dithiopyr was studied in sterile deionized water, sterile paddy water collected from a rice paddy during the rice growing season (pH 7.8), and sterile pH 5, pH 7, and pH 9 buffers. The experiment was conducted at a concentration of 1 ppm with 0.4% acetonitrile cosolvent to solubilize the test material. The samples were maintained at 25°C in the dark for a duration of 30 days. After 30 days the rice paddy water solutions showed that greater than 99% of the radioactivity was unchanged parent. Normal monoacid II accounted for 0.3% at 30 days posttreatment. There was no degradation detected in the sterile water, pH 5, and pH 7 solutions. Less than 2% of applied parent material degraded to the normal monoacid II in sterile pH 9 buffer after 30 days posttreatment. Assuming that the rate of degradation of dithiopyr followed first order kinetics, the half-life was determined to be 1053 days. These results suggest that hydrolysis will not be a major route of degradation for dithiopyr in the environment.

Photodegradation in Water

(Klemm, Nadeau, and Solsten, 40638628)

Ring-labelled [$^{13}C/^{14}C$]dithiopyr, at 0.7 ppm, degraded with a half-life of 61.8 hours in a sterile, nonsensitized pH 7 buffered aqueous solution and 72.4 hours in a similar solution amended with humic acid (a photosensitizer) during continuous irradiation under artificial light at 25°C. The intensity of the light source (one 500 watt xenon arc lamp) was 198 mW/cm^2 compared to the registrant-computed sunlight intensity of 58 mW/cm^2. Half-lives in sunlight days, using 58 mW/cm^2 as a reference, were 17.6 and 20.6 for the nonsensitizer and humic acid solutions, respectively. At the termination of the photodegradation experiment (approximately 128 hours artificial light of 36.4 sunlight days) with nonsensitized solution, dithiopyr comprised 24.5% of the applied radioactivity and two degradate monoacids,

...

2-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)-3-pyridinecarboxylic acid (normal acid; II) and

6-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-2-(trifluoromethyl)-3-pyridinecarboxylic acid (reverse acid; III) ...

comprised 27.3 and 14.2%, respectively, of the applied radioactivity. Two minor degradates, each of which comprised approximately 4 to 5% of the applied radioactivity, were ...

2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridine dicarboxylic acid (diacid; IV) and

3,5-bis(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine (V).

Two additional minor degradates together comprised 7.3% of the applied radioactivity ...

3-(methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine (VI) and

3-(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine (VII).

Similar degradates and percentage recoveries were obtained with the humic acid - sensitized solutions. Dithiopyr was stable in all control solutions maintained in the dark. These results indicate that photodegradation in water could contribute significantly to the degradation of dithiopyr in the environment.

Photodegradation on Soil

(Klemm, Nadeau, and Solsten; 40638628)

Ring-labelled [$^{13}C/^{14}C$]dithiopyr, at 1 lb/A on silt loam soil, was slightly degraded to 2-(difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl]-6-(trifluoromethyl)-3-pyridinecarboxylic acid (normal acid; II), which comprised approximately 5% of the applied radioactivity after continuous exposure to 118 hours of artificial light (one 500 watt xenon arc lamp). Dithiopyr was stable in the dark control soil. Photodegradation of dithiopyr on soil was insignificant. Therefore, photodegradation on soil will not contribute significantly to the degradation of dithiopyr in the environment.

Aerobic soil metabolism

(Pantano and Sing, 41001517 & 40638629)

Pyridine ring-labeled [$^{13}C/^{14}C$]dithiopyr (radiochemical purity >99%), at approximately 1 ppm, degraded with registrant-calculated half-lives of 523 days in silt loam soil, 625 days in sandy loam soil, 639 days in clay soil, and 1,125 and 2,300 days in two Japanese loam soils incubated in the dark at 25°C and 75% of 0.33 bar moisture for 12-18 months. At 1 year post-treatment, dithiopyr comprised 51.0-73.1% of the applied radioactivity in the five soils. The degradates

normal acid [(2-difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-6-(trifluoromethyl)-3-pyridinecarboxylic acid],

reverse acid [6-(difluoromethyl)-4-(2-methylpropyl)-5-((methylthio)carbonyl)-2-(trifluoromethyl)-3-pyridinecarboxylic acid], and

diacid [2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-3,5-pyridinedicarboxylic acid]

were isolated at maximum concentrations of 6.3%, 5.0%, and 7.3% of the applied, respectively. The highest concentrations of all three degradates were isolated from the silt loam soil; and, in general, maximum concentrations of the degradates in all five soils were reached at 6-12 months posttreatment. Throughout the study, an unidentified degradate comprised up to 2.0% of the applied radioactivity. At 1 year posttreatment, unextractable radioactivity comprised 3.48-19.08% of the applied, $^{14}CO_2$ comprised 0.11-1.33%, and other volatiles (identified as dithiopyr in selected samples) comprised 7.29-25.86%. Material balances ranged from 85.63 to 102.6% of the applied, with the exception of the immediate posttreatment silt loam soil sample, which had a material balance of 51.63%. Results of this study indicates that microbial degradation will not be a major route of degradation for dithiopyr.

Leaching and adsorption/desorption

(Sing and George, 40638630 & 41135601)

Using batch equilibrium techniques, ring-labelled [^{14}C]dithiopyr, at 0.01 to 0.3 ug/mL, was determined to be slightly mobile to mobile in soil:0.01M $CaSO_4$ solution slurries. Freundlich K values were 6.59 in a Sarpy sandy loam soil, 7.91 in a Dupo silt loam soil, 10.93 in a Drummer silt loam soil, 26.92 in a Sharkey clay soil, 34.74 in a "volcanic ash upland" loam soil, and 64.77 in a "volcanic ash paddy" loam soil; 1/n values were 0.80 to 0.93. The three highest Freundlich K values (approximately 27 to 65) correlated with the soils having the highest CEC values (approximately 27 to 40) and organic matter content (approximately 2 to 5%). Similarly, the sandy loam soil which had the lowest K value (6.59) had the lowest CEC value and percentage organic matter content (approximately 10 to <1, respectively). The K_{oc} values varied from 1141 to 3748. The percentage of dithiopyr desorbed from the soils following adsorption ranged from a low of 5.5% in the "volcanic ach paddy" loam soil to a high of approximately 62% in the Sarpy sandy loam soil.

Based on batch equilibrium experiments, the pyrimidine ring-labeled [^{14}C]dithiopyr degradates normal acid (Monoacid II), reverse acid (Monoacid I), and diacid (radiochemical purities >98%), at 0.01-0.3 ug/mL, were very mobile in sandy loam, clay, and two silt loam soils equilibrated at 22-23 C in soil:0.01 M calcium sulfate solution slurries. Freundlich K_{ads} values were 0.064-0.196 for the normal acid, 0-0.197 for the reverse acid, and 0 for the diacid. In the desorption phase of the study, 65-90% of the dithiopyr degradates adsorbed by soil from soil:solution slurries initially treated at 0.3 ug/mL were desorbed. At the typical use rate 0.5 lb/A, or the maximum labelled rate, 1.0 lb/A of dithiopyr, metabolites would be observed at only barely or nondetectable levels. Dithiopyr residues, when Dithiopyr is used at typical and maximum labelled application rates, should not persist beyond the growing season and should not to any significant extent move vertically in the soil.

Terrestrial field dissipation

(Adams, 41001519)

Dithiopyr was applied as emulsifiable concentrate (EC), micro-encapsulated (Mcap), and granular (G) formulations at 0.5, 1.0, and 2.0 lb ai/A to turf plots of soils ranging in texture from sand to clay loam in 13 states in the spring of 1987 or 1988. The concentrations of dithiopyr present in the 0- to 6-inch or 0- to 3- inch depths of the day 0 soil samples did not confirm the stated application rates at the majority of test sites. The 2.0 lb ai/A application was intended to equal 2X the maximum proposed application rate of 1 lb ai/A. Although the 2 lb ai/A application rate was not confirmed in the majority of the day 0 soil samples, at several sites, application rates were determined to be approximately ≥0.88 lbs ai/A (measured dithiopyr concentrations of 0.44 ppm or greater in the 0- to 6-inch soil depth or 0.88 ppm or greater in the 0- to 3- inch soil depth). Data from these sites were reviewed in detail since these data can be used to determine the field dissipation of dithiopyr following the application at the maximum use rate. Due to the volume of data included in the original report, data for sites where dithiopyr was applied at <0.88 lbs ai/A were briefly summarized and were not reviewed in detail.

Emulsifiable Concentrate

Dithiopyr, applied as an emulsifiable concentrate (EC) at approximately 1.22-1.34 lb ai/A (measured concentrations of 0.61-0.67 ppm in the upper 6 inches of soil) to three silt loam soils (OR, PA, and WI), dissipated from the upper six inches of soil with calculated half-lives of 0.6-7.99 days. Dithiopyr degradates isolated at the 0-to 6-inch soil depth were

the normal acid (maximum concentrations 0.037-0.17 ppm immediately posttreatment),

the diacid (maximum concentrations 0.016-0.13 ppm at 60-120 days posttreatment), and

the reverse acid (maximum concentrations 0.012-0.054 ppm at 60-68 days posttreatment).

The diacid was isolated at 0.012 ppm at the 6- to 12-inch soil depth at the Pennsylvania site after 180 days posttreatment. In the rest of the soil samples taken from these plots, parent dithiopyr and its degradates were not detected below the upper 6 inches of soil.

At sites treated with the EC formulation of dithiopyr at ≤0.84 lb ai/A (measured concentrations ≤0.42 ppm in the upper 6 inches of soil), dithiopyr dissipated with calculated half-lives of 2.25-68.04 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, with the exception of the Palm Desert, California site, dithiopyr and its degradates were not isolated below the upper 6 inches of soil. In the sandy loam soil at the Palm Desert, California site

treated with dithiopyr at approximately 0.37 lb ai/A (measured concentration 0.37 ppm in the upper 3 inches at 1 day posttreatment), the normal acid, reverse acid, and diacid degradates were each isolated at up to 0.058 ppm at 6- to 9-, 9- to 12-, 12- to 18-, and 18- to 24-inch depths at 45-178 days posttreatment.

Micro-Encapsulated

Dithiopyr, applied as a micro-encapsulated (Mcap) at approximately 0.88-1.16 lb ai/A (measured concentrations of 0.44-0.58 ppm in the upper 6 inches of soil or 0.97 ppm in the upper 3 inches of soil) to a loam, a silt loam, and two sandy loam soils, dissipated from the upper six inches (TX, MI, and WI sites) or three inches (Palm desert, CA site) of soil with calculated half-lives of 14.03-58.85 days. Dithiopyr degradates isolated at the 0-to 6-inch soil depth were the normal acid (maximum concentrations 0.029-0.050 ppm at 1-30 days posttreatment), the diacid (maximum concentrations 0.021-0.093 ppm at 30-180 days posttreatment, not detected at the Texas site), and the reverse acid (maximum concentrations 0.017-0.027 ppm at 30-60 days posttreatment). In the upper three inches of soil at the California site, the normal acid, diacid, and reverse acid degradates were isolated at maximum concentrations of 0.51 ppm (1 day posttreatment), 0.28 ppm (45 days) and, 0.072 ppm (30 days), respectively. At the 6- to 12-inch soil depth, dithiopyr was not detected with the exception of the day 7 sample from the Michigan site (0.071 ppm) and the day 1 sample from the Texas site (0.021 ppm). Dithiopyr degradates were not detected at the 6- to 12-inch depth with the exception of the day 180 sample from the Michigan site (0.037 ppm of the diacid) and the California site. At the California site, dithiopyr was not detected below the 6-inch soil depth; however, the diacid, normal acid, and reverse acid degradates were each isolated in the 6- to 9-, 9- to 12-, 12-to 18-, and 18- to 24-inch depths at up to 0.90 ppm after 60 days posttreatment.

At sites treated with the Mcap formulation of dithiopyr at $\leq$0.76 lb ai/A (measured concentrations $\leq$0.44 ppm in the upper three inches of soil or $\leq$0.38 ppm in the upper six inches of soil), dithiopyr dissipated with calculated half-lives of 6.21-134.53 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, dithiopyr and its degradates were not isolated below the upper 6 inches of soil.

Granular

Dithiopyr applied as a granular (G) at approximately 0.88-2.14 lb ai/A (measured concentrations of 0.44-1.07 ppm in the upper 6 inches of soil or 0.90 ppm in the upper 3 inches of soil) to one clay loam, one loamy sand, - one sandy loam, three silt loam, and four loam soils, dissipated from the upper six inches (TX, NY, PA, SC, IL, OH, NJ, OR, and WI sites) or three inches (Palm Desert, CA site) of soil with calculated half-lives of 3.87-96.70 days. Dithiopyr degradates isolated at the 0-to 6-inch soil depth were the normal acid (maximum concentrations 0.035-0.12 ppm at 1-67 days posttreatment), the diacid (maximum concentrations 0.014-0.057 ppm at 30-120 days posttreatment), and the reverse acid (maximum concentrations

0.017-0.078 ppm at 14-120 days posttreatment). In the upper three inches of soil at the California site, the normal acid, diacid, and reverse acid degradates were isolated at maximum concentrations of 0.21 ppm (30 days posttreatment), 0.044 ppm (45 days) and, 0.11 ppm (30 days), respectively. In general, dithiopyr and the normal acid, diacid, and reverse acid degradates were not detected below the upper six inches of soil; dithiopyr and its degradates were isolated in a few soil samples taken below the 6-inch depth at several sites.

At sites treated with the G formulation of dithiopyr at ≤0.84 lb ai/A (measured concentrations ≤0.53 ppm in the upper three inches of soil or ≤0.42 ppm in the upper six inches of soil), dithiopyr dissipated with calculated half-lives of 7.40-221.20 days. At the 0- to 6-inch depth, the normal acid, reverse acid, and diacid degradates were isolated. In general, dithiopyr and its degradates were not isolated below the upper 6 inches of soil.

Accumulation by laboratory fish

(Forbis and Chott, 41001518)

Total [^{14}C]dithiopyr residues accumulated in bluegill sunfish with maximum bioconcentration factors of 320x, 1400x, and 930x in edible tissues (fillet), nonedible tissues (viscera), and whole fish, respectively, during 35 days of exposure to [^{14}C]dithiopyr (radiochemical purity 99.5%) at concentrations ranging from 0.0024 ppm to 0.0093 ppm in a flow-through system. Maximum accumulation of [^{14}C]residues was 2 ppm in edible tissues (day 35), 8.7 ppm in nonedible tissues (day 35), and 5.6 ppm in whole fish (day 28). In 3, 28, and 35-day fish samples, dithiopyr was 0.77-1.7 ppm in the edible tissues, 2.8-6.1 ppm in the nonedible tissues, and 1.6-2.6 ppm in the whole fish. Three degradates identified in the fish tissues were

the reverse acid (Monoacid II; maximum concentrations of 0.014, 0.29, and 0.13 ppm in the edible tissues, nonedible tissues, and whole fish, respectively, at 35 days);

the normal acid (Monoacid III; detected in the nonedible tissues and whole fish only, at maximum concentrations of 0.15 and 0.053 ppm, respectively, at 28 days); and,

the diacid (Diacid IV; detected in the nonedible tissues and whole fish only, at maximum concentrations of 0.057 and 0.031 ppm, respectively, at 35 days).

After 14 days of depuration, [^{14}C]residues in edible tissues, nonedible tissues, and whole fish were 0.15, 0.62, and 0.29 ppm, respectively, representing depuration rates of 92-94%.

Throughout the study in treated and control aquaria, the water temperatures ranged from 21 to 22°C, the pH ranged from 8.0 to 8.3, and the dissolved oxygen content ranged from 6.5 to 8.5 ppm. In particulate-free water at days 3, 28, and 35 of the exposure period, dithiopyr comprised 64.5-83.6%

of the recovered radioactivity, the reverse acid comprised 4.6-6.9%, the normal acid comprised 0.5-1.2%, and, the diacid comprised 0.4-8.2%. Radioactivity in the particulates at 3, 28, and 35 days comprised 8.8-22.7% of that recovered from the water samples.

Freezer storage stability studies were also conducted using water and whole fish samples taken on day 28 of the exposure period. The results of these analyses indicate that [^{14}C]dithiopyr does not degrade in water stored frozen for up to 126 days and in whole fish samples stored frozen for up to 98 days.

In summary, dithiopyr is resistant to hydrolysis and to photodegradation on soil. Dithiopyr photodegraded in a sterile pH 7 buffered aqueous solution with a half-life of 17.6 days. It is slowly degraded (half-lives 523-639 days) in soil. Based on batch equilibrium studies, it was determined that dithiopyr was slightly mobile to relatively immobile in soil, and that the normal acid, reverse acid, and diacid degradates were very mobile in soil. On turf plots treated at $\geq$0.88 lb ai/A, dithiopyr dissipated from the upper 6 or 3 inches of soil with half-lives of 0.6-7.99 days (EC, 3 sites), 14.03-58.85 days (Mcap, 4 sites), and 3.87-96.70 days (G, 10 sites). In general, dithiopyr and the normal acid, reverse acid, and diacid degradates were not detected below the 0- to 6-inch soil depth; however, dithiopyr and its degradates were isolated in a few soil samples taken below the 6-inch depth at several sites. Dithiopyr accumulated in bluegill sunfish exposed to 0.0024-0.0093 ppm of dithiopyr with maximum bioconcentration factors of 320x, 1400x, and 930x in edible tissues, nonedible tissues, and whole fish, respectively. The normal acid, the reverse acid, and the diacid degradates were isolated; in addition, in aqueous photolysis solutions, the degradates 3,5-bis(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine (V), 3-(methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethylpyridine (VI), and 3-(methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethylpyridine (VII) were isolated.

RECOMMENDATIONS

The submission of data required for full registration of dithiopyr for use on terrestrial nonfood and domestic outdoor use sites (turf) is summarized below:

The following data requirements are fulfilled:

Hydrolysis studies: Based on data previously reviewed for the EUP (EAB review dated 09-07-88), no additional data are required.

Photodegradation studies in water: Based on data previously reviewed for the EUP (EAB review dated 09-07-88), no additional data are required.

Aerobic soil metabolism studies: One study (Pantano and Sing, 41001517) was reviewed. This study is acceptable and fulfills data requirements by providing information on the aerobic metabolism of dithiopyr in sandy loam, silt loam, and clay soils.

Leaching and adsorption/desorption: One study (Sing and George, 41135601) was reviewed. This study is acceptable and partially fulfills data requirements by providing information on the mobility (batch equilibrium) of the normal acid, reverse acid, and diacid degradates of dithiopyr in a sandy loam, two silt loams, and a clay soil. A second study previously reviewed for the EUP (EAB review dated 09-07-88) concerning the mobility of parent dithiopyr is acceptable and partially fulfills data requirements by providing information on the mobility (batch equilibrium) of unaged dithiopyr in six soils ranging from a sandy loam to a clay. Together, these studies fulfill the leaching and adsorption/desorption data requirement; no additional data are required.

Terrestrial field dissipation studies: One study (Adams, 41001519) was reviewed. This study is acceptable and fulfills data requirements by providing information on the terrestrial field dissipation of EC, Mcap, and G formulations of dithiopyr in several soils treated at a rate of approximately 1 lb ai/A or greater.

Laboratory studies of pesticide accumulation in fish: One study (Forbis and Chott, 41001518) was reviewed. This study is acceptable and fulfills data requirements by providing information on the accumulation of [^{14}C]dithiopyr in laboratory fish.

The following data requirements are deferred or are not required for presently registered uses:

Photodegradation studies on soil: No data were reviewed for this application for full registration; however, no data are required because dithiopyr has no proposed orchard crop, field and vegetable crop, or forestry uses.

Photodegradation studies in air: No data were reviewed. A study of the photodegradation of dithiopyr in air will be required if it is determined that dithiopyr may involve potentially significant exposure to workers.

Anaerobic soil metabolism studies: No data were reviewed; however, no data are required because dithiopyr has no proposed field or vegetable crop uses.

Anaerobic aquatic metabolism studies: No data were reviewed; however, no data are required because dithiopyr has no proposed aquatic or forestry uses, or any aquatic impact uses involving direct discharges of treated water into outdoor aquatic sites.

Aerobic aquatic metabolism studies: No data were reviewed; however, no data are required because dithiopyr has no proposed aquatic uses or uses involving direct discharges of treated water into outdoor aquatic sites.

Laboratory volatility studies: No data were reviewed; however, no data are required because dithiopyr has no proposed greenhouse, orchard, or field and vegetable crop use sites.

Field volatility studies: No data were reviewed; however, no data are required because dithiopyr has no proposed greenhouse, orchard, or field and vegetable crop use sites.

Aquatic field dissipation studies: No data were reviewed; however, no data are required because dithiopyr has no proposed aquatic food crop, aquatic nonfood (including antifouling paints, ditchbanks, and shorelines) or aquatic impact uses involving direct discharge of treated water into outdoor aquatic sites.

Forestry dissipation studies: No data were reviewed; however, no data are required because dithiopyr has no proposed forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed; however, no data are required because dithiopyr has no proposed field and vegetable crop or aquatic crop uses.

Confined accumulation studies on rotational crops: No data were reviewed; however, no data are required because dithiopyr is not proposed for use on areas which may be rotated to a food crop after pesticide use.

Field accumulation studies on rotational crops: No data were reviewed; however, no data are required because dithiopyr is not proposed for use on areas which may be rotated to a food crop after pesticide use.

Accumulation studies on irrigated crops: No data were reviewed; however, no data are required because dithiopyr has no proposed aquatic food crop or aquatic nonfood uses, uses in and around holding ponds used for irrigation purposes, or uses involving effluents or discharges to water used for crop irrigation.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed; however, no data are required because dithiopyr has no proposed forestry, aquatic nonfood, or aquatic impact uses.

Section 158.440, Spray Drift

201-1 Droplet size spectrum
202-1 Drift field evaluation

Pls. correct

These studies are not being required at this time. There is no aerial application (rotary and fixed winged) and mist blowers or other methods of ground application used where the detrimental effect level of nontarget organisms expected to be present would be exceeded. However, the potential of spray drift from applications close to water bodies is of concern, due to the high toxicity of dithiopyr to fish and lack of long term effects on growth and reproduction of fish and other marine life.

Section 158.75, Other Studies

Ground- and/or surface monitoring studies are not required at this time. Dithiopyr is not expected to leach to groundwater or to move to surface water due to its nature. However, the environmental fate data indicates there may be exposure to aquatic organisms through erosion of soil particles to which dithiopyr has absorbed.

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Pantano, L.K. and Y.L. Sing. 1989. The aerobic soil metabolism of dithiopyr, 3,5-pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-S,S-dimethyl ester (MON 7200/15100). Report No. MSL-8551; R.D. No. 900. Unpublished study performed and submitted by Monsanto Agricultural Company, St. Louis, MO. (41001517)

Sing, Y.L. 1988. Adsorption/desorption of MON-7200/15100. Laboratory Project Identification MSL-7778; R.D. No. 866. Unpublished study prepared and submitted by Monsanto Agricultural Company, St. Louis, MO. (MRID 40638630)

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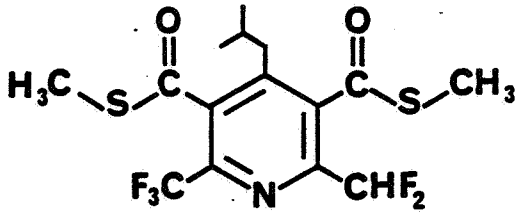
APPENDIX

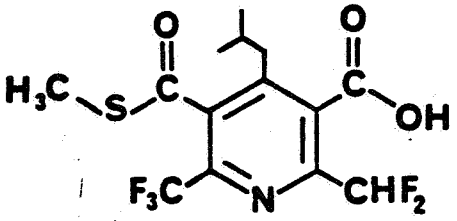
DITHIOPYR AND ITS DEGRADATES



3,5-Pyridinedicarbothioic acid, 2-(difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl)-,S,S-dimethyl ester

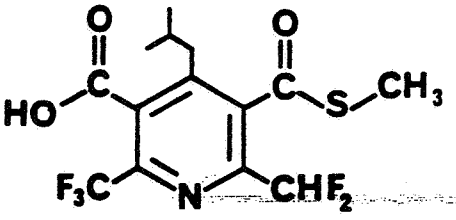
3,5-bis(Methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine

Dithiopyr (MON 15151, MON 7200, MON 15100)



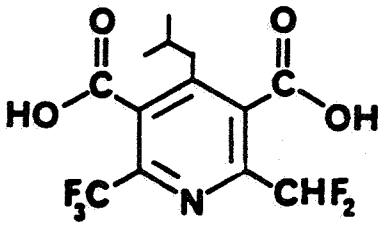
2-(Difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl)]-6-(trifluoromethyl)3-pyridinecarboxylic acid

(Normal acid; II)



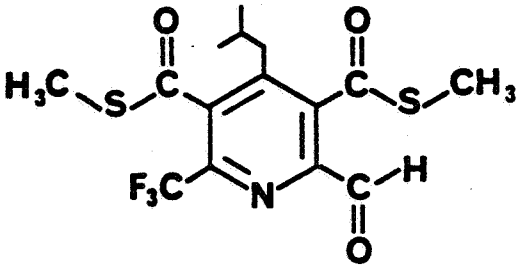
6-(Difluoromethyl)-4-(2-methylpropyl)-5-[(methylthio)carbonyl)]-2-(trifluoromethyl)-3-pyridinecarboxylic acid

(Reverse acid; III)



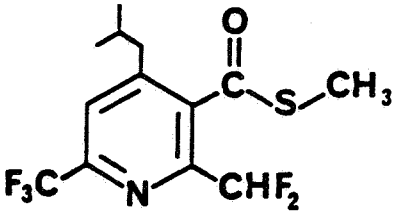
2-(Difluoromethyl)-4-(2-methylpropyl)-6-(trifluoromethyl]-3,5-pyridinedicarboxylic acid

(Diacid; IV)



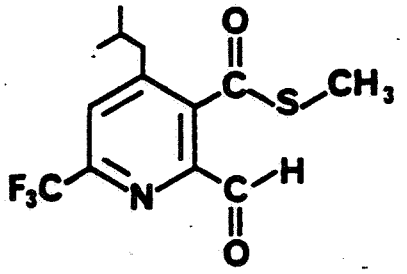
3,5-bis(Methylthiocarbonyl)-2-formyl-4-(2-methylpropyl)-6-trifluoromethyl pyridine

(V)



3-(Methylthiocarbonyl)-2-difluoromethyl-4-(2-methylpropyl)-6-trifluoromethylpyridine

(VI)



3-(Methylthiocarbonyl)-2-formyl-4-(2-methyl-propyl)-6-trifluoromethylpyridine

(VII)