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Monsanto Company

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

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

FEB 1 1991

MEMORANDUM

SUBJECT: Lawn Application Exposure Assessment for Dithiopyr Applied By Hand Held Spray (HED Project #1-0040)

TO: Flora Chow
Reregistration Section
Science Analysis and Coordination Branch
Health Effects Division (H7509C)

FROM: Curt Lunchick, Acting Section Head
Special Review and Registration Section
Occupational and Residential Exposure Branch
Health Effects Division (H7509C)

THRU: Charles L. Trichilo, Ph.D., Chief
Occupational and Residential Exposure Branch
Health Effects Division (H7509C)

The Occupational and Residential Exposure Branch has completed the evaluation of Monsanto's dithiopyr lawn exposure study, "Assessment of Worker Exposure to Diothiopyr From the Lawn Care Application of Dimension Herbicide," J.E. Cowell Study Director, 17 October 1990. The Study consisted of two distinct subparts, a passive dosimetry portion and a concurrent biological monitoring portion.

The study data were reviewed by OREB's contractor, Versar, and the draft study evaluations are attached. OREB accepts the basic conclusions presented by Versar and has requested that the draft reports be finalized. The final reports will specifically itemize supporting chemistry deficiencies in the study that Monsanto must address. In regards to the passive dosimetry portion of the study, OREB is concerned about the insufficient duration of the field recoveries. Because of this concern, OREB will not utilize the passive dosimetry data until Monsanto supplements the field recovery data with 6 to 7 hour field recovery data conducted under environmental conditions similar to those that existed during the study. OREB is not concerned about the fact that two Chem Lawn applicators wore gloves

despite the label not requiring gloves. OREB concludes that this is reflective of actual use practices and is therefore representative of professional lawn care application. Because all mixer/loaders wore protective gloves the data are reflective only of labels requiring protective gloves during mixing and loading. Registration Division must require that the dithiopyr label be amended to require protective gloves during mixing and loading. This is basic hygiene for handling any pesticide concentrate.

The biological monitoring data also will require supplementation as well as will be itemized in the final report from Versar. It is the conclusion of both OREB and Henry Appleton, the reviewer, that the biological monitoring supporting chemistry deficiencies does not preclude use of the dosage data at this time. OREB therefore accepts the conclusion the dosage from the lawn application of dithiopyr is $4.6 \times 10^{-5}$ mg/kg/lb ai.

The label maximum application rate is 0.5 ai/acre. Assuming a professional lawn applicator will treat 15 lawns of 5,000 sq. ft. daily with dithiopyr, the amount of active ingredient handled daily is (15 x 5,000 sq.ft. x 1 acre/43,560 sq.ft. x 0.5 lbs ai/acre)0.86 lbs ai/day. The actual daily dosage for a professional lawn applicator mixing/loading and applying dithiopyr is ($4.6 \times 10^{-5}$ mg/kg/day x 0.86 lbs ai/acre)$4.0 \times 10^{-5}$ mg/kg/day. The applicator would handle dithiopyr up to 30 days annually, resulting in an annual dosage of $1.2 \times 10^{-3}$ mg/kg/year. The annual dosage amortized to an average daily dosage is $3.3 \times 10^{-6}$ mg/kg/day.

Attachments (2)

cc: Joanne Miller, PM23, RD(H7505C)
P. Chin, Toxicology Branch (H7509C)
Dithiopyr File
Correspondence File w/o attachments
Curt Lunchick

**Final Report**

**Review of Dithiopyr Worker Exposure Study**
**EPA Contract No. 68-D9-0166**
**Task No. 2-2**

Prepared for:

U.S. Environmental Protection Agency
Office of Pesticide Programs
Health Effects Division
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U.S. Environmental Protection Agency

February 4, 1991

Table of Contents

## 1. INTRODUCTION

The purpose of this report is to review the mixer/loader and applicator dithiopyr exposure study submitted to the Environmental Protection Agency by the Monsanto Agricultural Company. The study monitored exposure to lawn care specialists (ChemLawn Corporation) during the mixing/loading and application to turfgrass of dithiopyr formulated as Dimension 1EC, an emulsifiable concentrate.

The following information identifies the report and the data submitter:

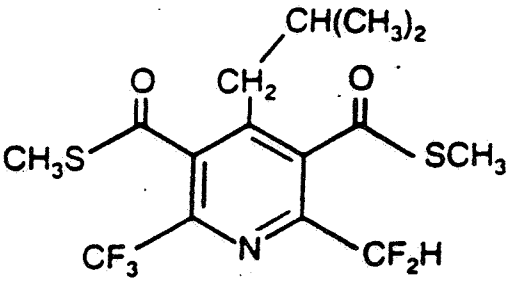
| | |
|---|---|
| TITLE: | Dithiopyr (MON-15100) Applicator Exposure Studies<br>Section A: Assessment of Worker Exposure to<br>Dithiopyr from the Lawn Care Application of<br>Dimension™ Herbicides |
| SUBMITTER: | Monsanto Agricultural Company<br>700 Chesterfield Village Parkway<br>St. Louis, Missouri 63198 |
| AUTHOR: | JE Cowell, MJ Manning, CM Lottman |
| MRID NO.: | 416646-01 |
| DATE: | October 17, 1990 |

The review of the study included evaluating the validity of the quality assurance, application, and sampling procedures as well as calculating the exposure of the test subjects to dithiopyr. Exposure estimates calculated by Versar represent the methodology specified in the Subdivision U guidelines (e.g., use of 1/2 the quantification limit for nondetects and body surface areas).

## 2. BACKGROUND

The chemical characteristics and identity of dithiopyr, 2-(difluoromethyl)-4-(2-methylpropyl) -6-(trifluoromethyl)- 3,5-Pyridinedicarbothioic acid, S, S-dimethylester are listed below:

- Molecular weight: 401.4
- Empirical formula: $C_{15}H_{16}F_5NO_2S_2$
- Chemical structure:




- CAS number: None
- Trade name: Dimension 1EC
- Vapor pressure: 4 x $10^{-6}$ mmHg at 25°C*
- Water solubility: 1.38 ppm at 20°C
- Mode of action: Herbicide
- Formulation: Emulsifiable concentrate, granular

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All background information was obtained from the Monsanto Technical Data Sheet

* Vapor pressure is reported on the Monsanto Technical Data Sheet as 4 x $10^{6}$ mmHg at 25°C. However, given the molecular weight, the reported vapor pressure must be incorrect. It is assumed that the vapor pressure is 4 x $10^{-6}$ mmHg at 25°C.





6

## 3. DITHIOPYR EXPOSURE REVIEW

This section reviews the inhalation, dermal, and hand exposure assessments of mixer/loaders and applicators to dithiopyr. The dithiopyr was applied by professional lawn care operators to turfgrass. Included is a review of the study's quality assurance, mixing/loading and application procedures, exposure monitoring techniques, analytical results, and exposure estimates.

### 3.1 Quality Assurance Review

#### 3.1.1 Method Validation

The analytical methodologies for determining the extraction efficiency of dithiopyr from each type of sampling matrix were validated in the laboratory prior to the field trials. The method validation results were as follows:

| | Silica air sampling tubes | Gauze pads | Hand rinse solution |
|---|---|---|---|
| Fortification (range) | 0.025 - 50µg (n=14) | 0.05 - 5000µg (n=18) | 0.002 - 20µg (n=13) |
| Recovery (range) | 86.0 - 108.9% | 89.0 - 130.0% | 78.7 - 120.8% |
| Mean recovery | 95.5% | 111.8% | 94.7% |
| Standard deviation | 6.8% | 11.5% | 13.2% |
| Coefficient of variation | 7.2 | 10.3 | 13.9 |

#### 3.1.2 Laboratory Recovery Experiments

Laboratory fortified control samples were analyzed concurrently with each set of test samples. The average recovery levels were as follows:

| Matrix | Range of fortification (μg) | Average recovery (%) | Coefficient of variation |
|---|---|---|---|
| Silica gel tubes | 0.025 - 50 (n = 12) | 94.4 ± 7.1 | 7.5 |
| Gauze pads | 0.05 - 5000 (n = 36) | 109.1 ± 10.7 | 9.8 |
| Hand rinse (2% Igepal) | 0.0005 - 5 (n = 16) | 89.3 ± 12.6 | 14.1 |

### 3.1.3 Field Recovery Experiments

Silica gel tubes and gauze pads were fortified in the field. These experiments, however, were not conducted on the same day as the field sampling. Instead, the field recovery experiments were conducted the day prior to the field monitoring at each site. Meteorological conditions were not recorded during the field recovery experiments. Moreover, the sampling matrices were exposed to the environmental conditions at each site for only one hour. The average applicator sampling time was 6.7 hours (mixer/loader < 1 hour sampling). Therefore, the results of the field recovery experiments should not be considered valid for the applicator sampling period.

Groups of 6 silica gel tubes were fortified with 0.1 μg, 10 μg, and 20 μg of dithiopyr. After fortification, air was drawn through each sampling tube at a rate of 2 liters/minute for one hour. This was done to measure breakthrough and/or volatilization losses of dithiopyr from the silica tubes. The gauze pads, 6 samples each, were fortified with 0.5 μg, 5.0 μg, and 50 μg of dithiopyr. The results of the 1-hour field recoveries for both the silica gel tubes and gauze pads are as follows:

| Matrix | Storage (days) | Average recovery (%) |
|---|---|---|
| Silica gel tubes | | |
| Atlanta | 123 | 77.8 ± 8.2 |
| Cincinnati | 101 | 86.1 ± 7.9 |
| Cleveland | 91 | 81.2 ± 6.6 |
| Gauze pads | | |
| Atlanta | 227 | 71.9 ± 13.2 |
| Cincinnati | 226 | 60.0 ± 6.8 |
| Cleveland | 268 | 71.9 ± 10.1 |

All field recovery experiment procedures were performed at each of the three field monitoring sites and represent losses due to 1-hour exposure time, transport, and storage.

### 3.1.4 Storage Stability Experiments

Storage stability experiments were performed using the silica gel tubes and the 2 percent Igepal hand rinse solutions. Triplicate silica gel tubes were fortified with 0.1$\mu$g, 10$\mu$g, and 20 $\mu$g in the laboratory. Air was then drawn through the fortified tubes at a flow rate of 2 liters/minute for 10 hours, after which the tubes were frozen for 217 days until analysis. The average storage stability recovery was 81.6 ± 12.7 percent.

The hand rinse solutions were fortified in the field, frozen, transported to the lab, and stored. Six replicate hand rinse solution samples were fortified with 2.0$\mu$g, 20$\mu$g, or 200 $\mu$g. Dithiopyr recovery from the hand rinse solution samples is shown below:

| Site | Storage (days) | Average recovery (%) | Number of samples |
|---|---|---|---|
| Atlanta | 155 | 101.6 ± 8.8 | 18 |
| Cincinnati | 136 | 106.5 ± 13.2 | 18 |
| Cleveland | 129 | 105.7 ± 9.1 | 18 |

No storage stability study using the gauze pads was conducted at the laboratory. The registrant utilized the results from the field fortified gauze pads (Section 3.1.3) to measure dithiopyr stability on the gauze pads.

### 3.1.5 Sample Analysis

Silica gel tubes. The analytical method consisted of extracting the contents of the air sampling tubes (including spacers and glass wool) with acetonitrile by shaking for 5 minutes. The mixtures were then partitioned (25 ml acetonitrile aliquots) with 25 ml of iso-octane by mechanically shaking in a separatory funnel for 5 minutes. After the phases were allowed to separate, the acetonitrile layers were discarded. The iso-octane layers (10 ml aliquots) were then collected for direct quantitation using a gas chromatograph equipped with a Ni63 electron capture detector.

Gauze pads. Gauze pads were extracted in 8 oz. french square bottles with 100 ml of a ethyl acetate/iso-octane solution. Bottles were capped with foil lined caps and shaken on mechanical shakers for 15 minutes. After shaking, aliquots were removed and added to 10 ml tubes containing sodium sulfate as a drying agent. Each sample was then quantitated using a gas chromatograph equipped with a Ni63 electron capture detector.

Hand rinse. The 2 percent Igepal hand rinse solution collected from each field worker (200 ml/hand) was partitioned with one 50 mL aliquot of iso-octane by mechanically shaking it in a separatory funnel for 5 minutes. After the phases were allowed to separate, the aqueous layers were discarded and the iso-octane collected in a beaker to which sodium sulfate was then added as a drying agent. The iso-octane layers were then quantitated by direct injection into a gas chromatograph equipped with a Ni63 electron capture detector.

## 3.2 Mixer/Loader and Applicator Procedures

Three application sites were selected by the registrant to reflect climates in which Dimension 1EC will potentially be used. Six mixer/loaders and six applicators were monitored at each of the Atlanta, Georgia, Cincinnati, Ohio, and Cleveland, Ohio, study sites. All mixer/loader and applicator procedures were monitored separately. Each participant in the study was a ChemLawn employee and therefore a lawn care professional. The study participants' experience ranged from 35 days to 12 years.

According to the study protocol, characterization of the spray solution was to be performed. However, the study report did not include a spray solution characterization. Characterization of the test substance showed the Dimension 1EC contained 99.2 percent of the theoretical dithiopyr concentration of 1 lb/ai gallon.

Mixer/Loader. Eighteen mixer/loaders were monitored at various ChemLawn dealers (3 sites, 6 participants each). The mixing procedure consisted of open-pouring (1.87 lb ai) of Dimension 1EC from 1-gallon containers into graduated beakers. The measured amount of Dimension was then poured into a closed transfer system. Mechanical agitation was used in each truck tank to mix the spray solution. In addition, fertilizer was added to each truck tank mix.

The prospective Dimension 1EC label (Appendix A) does not specify the use of any personal protective equipment. However, in keeping with ChemLawn policy, each worker wore rubber gloves, a face shield or goggles, and a rubber or plastic apron during the mixing/loading procedure. After the mixing/loading procedures were complete, each worker removed the protective equipment and performed a spray gun calibration as part of the mixer/loader monitoring operation.

Mixer/loader sampling times are listed in Table 1. Average sampling times were 7 minutes (Atlanta), 62 minutes (Cincinnati), and 43 minutes (Cleveland). No explanation was given for the relatively short monitoring time in Atlanta.

Application. Six applicators were monitored at each of the three study sites for a total of 18 replicates. Each applicator treated approximately 15 locations within the simulated lawns (approximately 5,000 $ft^2$ of turf each). The simulated lawns were at the following locations: Al Bishop Sports Complex and Kennesaw State College Campus, Atlanta, Georgia; Spring Grove Cemetery, Cincinnati, Ohio; and Bratenahl Place, Cleveland, Ohio.

Applicator activities included unreeling the hose from the truck, spraying the turfgrass ($\approx$325 gallons per replicate), and reeling in the hose. A ChemLawn spray gun, held approximately waist high, was used for all applications. Each spray gun was calibrated to a flow rate of 4 gallons per minute. The approximate dithiopyr application rate was 1 lb ai/acre (1 gallon Dimension 1EC/acre). The sampling times are reported in Table 1.

The prospective label does not require personal protective clothing; however, two of the applicators chose to wear rubber gloves.

## 3.3 Exposure Monitoring

### 3.3.1 Inhalation Monitoring

Inhalation exposure was monitored using two personal air monitoring pumps worn during both the mixing/loading and application procedures. The monitoring matrices, a silica gel air sampling tube connected to each pump, were placed in the worker's breathing zone. Each pump was calibrated to draw air through the tubes at a flow rate of 2 liters/minute.

Table 1. Mixer/Loader and Applicator Sampling Times

| Site | Replicate | Sampling time (minutes) Mixer/loaders | Applicators |
|---|---|---|---|
| Atlanta (3/13/89) | 1 | 7 | 308 |
| | 2 | 7 | 370 |
| | 3 | 7 | 339 |
| | 4 | 7 | 345 |
| | 5 | 7 | 305 |
| | 6 | 7 | 332 |
| Cincinnati (4/3/89) | 1 | 75 | 418 |
| | 2 | 90 | 420 |
| | 3 | 45 | 452 |
| | 4 | 40 | 433 |
| | 5 | 65 | 461 |
| | 6 | 57 | 477 |
| Cleveland (4/25/89) | 1 | 28 | 409 |
| | 2 | 24 | 457 |
| | 3 | 49 | 406 |
| | 4 | 38 | 431 |
| | 5 | 51 | 448 |
| | 6 | 70 | 416 |

### 3.3.2 Dermal Monitoring

Dermal monitoring was performed using 12 ply (4x4 inch) cotton gauze patches. The study report did not state what type of backing was used for patch construction. The registrant stated that ten pads were fixed to each worker's clothing for dermal monitoring in accordance with Subdivision U Guidelines.

The registrant did not specifically specify or provide photos of the location (inside or outside clothing) of the patches. However, the registrant calculated the body dose using a dermal penetration factor. Therefore, it is assumed that all dermal pads were attached to the outside clothing. The protocol stated that the pads would be removed by contaminant-free laboratory personnel (no mention was made in the report of whether this protocol procedure was used).

### 3.3.3 Hand Exposure

Rubber gloves were worn by all mixer/loaders; two of the 18 applicators wore rubber gloves. After the rubber gloves were removed, dermal hand exposure was monitored using a 2 percent Igepal in water hand rinse solution. Each hand was washed separately. The protocol instructions called for the hand rinse solution to be prepared by adding a surfactant to 200 mL of distilled water. The hands were to be shaken for 1 minute in a 1-gallon bag. The registrant did not report whether these exact procedures were actually used in the field.

Hand rinses were collected from each applicator at their request throughout each monitoring period. These requests were for breaks, lunch, and lavatory visits.

## 3.4 Exposure Calculation

Inhalation Exposure. Inhalation exposures were calculated by Versar as mg/lb ai handled/sprayed using one-half the quantification limit for nondetected values. Dithiopyr levels collected in the silica gel sampling tubes ranged from $<0.05$ $\mu$g to 0.11 $\mu$g for the mixer/loaders and from 0.79 $\mu$g to 1.77 $\mu$g for the applicators. A respiratory rate of 25 liters/minute was used to calculate all inhalation exposure values. All dithiopyr residue levels greater than the detection limit were corrected for field recoveries. The field recovery values used to correct the dithiopyr residue levels measured at the Atlanta, Cincinnati, and Cleveland sites were 77.8, 86.1, and 81.2 percent, respectively. The arithmetic and geometric mean inhalation exposures are as follows:

| | Exposure (mg/lb ai handled/sprayed) | |
|---|---|---|
| | Arithmetic mean | Geometric mean |
| Mixer/loader | 0.00014 | 0.00012 |
| Applicator | 0.0038 | 0.0037 |

Dermal Exposure. Dermal exposure to mixer/loaders represents exposure to workers wearing protective rubber aprons. Applicator exposure was monitored using outside patches (no clothing scenario). The range of dithiopyr collected ($\mu g/cm^2$) on each body part is listed in Table 2. All dithiopyr residue levels greater than the detection limit were corrected for field recoveries. The field recoveries used to correct dermal exposure levels were 71.9, 60.0, and 71.9 percent at the Atlanta, Cincinnati, and Cleveland sites, respectively. Dermal exposures were calculated by Versar as mg/lb ai handled/sprayed using one-half the detection limit for nondetects and using the body surface areas from the Subdivision U Guidelines. The geometric mean (the majority of exposure distributions of body parts are lognormal), median, and arithmetic means, normalized by lb ai handled, are as follows:

Table 2. Dithiopyr Residue Levels ($\mu g/cm^2$) Measured on Individual Body Part Locations of Mixer/Loaders and Applicators

| | Mixer/loader | | Applicator | |
|---|---|---|---|---|
| Patch location | Range ($\mu g/cm^2$) | Median ($\mu g/cm^2$) | Range ($\mu g/cm^2$) | Median ($\mu g/cm^2$) |
| Shoulder (right) | ND-1508 | 0.15 | 1.8-30.1 | 5.57 |
| Shoulder (left) | ND-160 | 0.26 | 1.7-29.9 | 5.94 |
| Chest (middle) | ND-13.9 | 0.14 | 1.6-39.1 | 4.71 |
| Back (middle) | ND-17.6 | 0.21 | 1.3-21.4 | 3.73 |
| Forearm (right) | ND-41.4 | 0.54 | 4.0-42.8 | 11.53 |
| Forearm (left) | ND-76.3 | 0.73 | 4.5-38.0 | 12.9 |
| Thigh (right) | ND-39.6 | 0.37 | 149-4830 | 701 |
| Thigh (left) | ND-1151 | 0.31 | 171-3183 | 757 |
| Shin (right) | ND-16.5 | 0.18 | 749-6100 | 2701 |
| Shin (left) | ND-24.5 | 0.12 | 267-8242 | 2232 |

ND - nondetected ($<0.0005\ \mu g/cm^2$)

| | Exposure (mg/lb ai handled/sprayed) | | |
|---|---|---|---|
| | Geometric mean | Median | Arithmetic mean |
| Mixer/loader | 4.7 | 4.6 | 167.9 |
| Applicator (n=18) | 4,492 | 4,783 | 5,791 |

Hand Exposure. Hand exposures for the mixer/loaders represent exposure while wearing protective gloves. Applicator hand exposures represent exposure to 16 workers wearing no gloves and 2 workers wearing rubber gloves. The use of the protective gloves is inconsistent with the label requirements. Hand exposures were corrected for storage stability at 101.6, 106.5, and 105.7 percent for Atlanta, Cincinnati, and Cleveland, respectively.

Hand exposures for mixer/loaders ranged from 0.55 $\mu$g to 1016.1 $\mu$g. Applicator hand exposures ranged from 65.7 $\mu$g to 738.6 $\mu$g. The geometric mean (log normal distribution) and arithmetic mean hand exposures for mixers/loaders and applicators are as follows:

| | Exposure (mg/lb ai handled/sprayed) | |
|---|---|---|
| | Geometric mean | Arithmetic mean |
| Mixer/loader | 0.06 | 0.20 |
| Applicator | | |
| No gloves (n=16) | 0.16 | 0.22 |
| Gloves (n=2) | 0.011 | 0.035 |

Total Exposure. Total exposure levels include the inhalation, dermal, and hand exposures for each mixers/loader or applicator. All exposures are corrected for the appropriate recovery values as mentioned above. The total exposure values are as follows:





17

| | Exposure (mg/lb ai handled/sprayed) | | |
|---|---|---|---|
| | Geometric mean | Median | Arithmetic mean |
| Mixer/loader | 4.8 | 4.7 | 168 |
| Applicator | | | |
| No gloves (n=16) | 4,492 | 4,783 | 5,791 |

## 3.5 Discussion

There are two significant data gaps in the design of the study. The deviations from Subdivision U Guidelines are the following:

- Field recovery experiments were exposed to the environmental conditions at the study sites for an insufficient length of time for the applicator monitoring periods. Field recovery experiments conducted for the inhalation and dermal sampling media were exposed to the environmental elements for only 1 hour. However, the average length of time for the application procedures was 6.7 hours. It is evident from the 1-hour field recovery experiments that dithiopyr is unstable (see Section 3.1.3 field recoveries). Thus, the field recoveries do not adequately assess the loss of dithiopyr from the inhalation and dermal sampling media. Moreover, the field recovery experiments were conducted the day prior to sampling.

- The Dimension label does not specify the use of protective clothing. However, in keeping with ChemLawn policy, the mixer/loaders wore rubber aprons and rubber gloves. In addition, two of the applicators wore rubber gloves. The use of this protective equipment minimizes exposure and does not represent a label requirement.

Minor discrepancies were noted between the sampling times reported on the Exposure Survey Forms and the study text. However, these discrepancies are insignificant and do not affect the outcome or validity of the study.

## 3.6 Summary

The two major deficiencies that were noted in the execution of this study are that (1) field recovery experiements were inadequate, and (2) the mixer/loaders wore protective gloves. Thus, this study, as is, is not acceptable by the Agency as a registration package. It is also important to note that the registrant calculated the body dose assuming a 100 percent protection factor to covered areas of the body. No data are provided by the registrant to support or refute this protection factor.

If the Agency is to accept the reported exposure data, the registrant is required to rerun the field recovery experiments. The field recovery experiments must be exposed to similar environmental conditions as the actual study, for 6 to 7 hours. In addition, the registrant is required to correct the exposure data using the newly generated field recoveries.

Finally, because the mixer/loaders wore protective gloves during the monitoring of the mixing/loading procedures, the Dimension label must be amended to require the use of protective gloves.

# Appendix A
# Proposed Label