

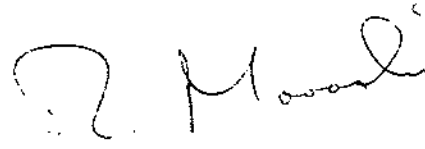
US EPA ARCHIVE DOCUMENT

105001

Date Out EPB: 04 NOV 1983

TO: Wm. Miller
Product Manager 16
TS-767

FROM: Dr. Richard Moraski
Acting Chief
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division



Attached please find the environmental fate review of:

Reg./File No.: 241-238

Chemical: Terbufos

Type Product: Insecticide

Product Name: Counter

Company Name: American Cyanamid

Submission Purpose: Review aerobic and anaerobic soil metabolism study and exposure assessment study.

ZBB Code: ?

ACTION CODE: 400

Date in: 7/8/83

EPB # 3447

Date Completed: 04 NOV 1983

TAIS (level II) Days

Deferrals To:

67

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_____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1.0 INTRODUCTION

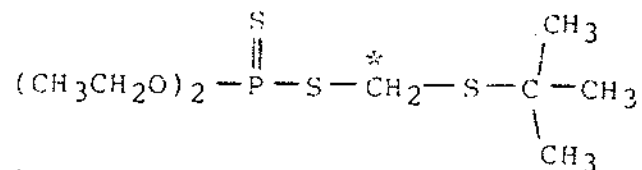
American Cyanamid Company has submitted an aerobic and anaerobic soil metabolism study and exposure analysis to support the registration of Counter 15G, EPA Reg. No. 241-238 (terbufos, as a.i.).

1.1 Chemical

Common name: Terbufos

Chemical name: S-[[[1,1-dimethylethyl)thio]methyl] O,O-diethylphosphorodithioate

Chemical structure:



*-Denotes position of radiolabel used in studies considered in this review.

2.0 DIRECTIONS FOR USE

No use directions were included in the submission (no new uses were proposed).

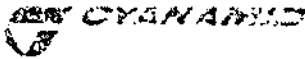
3.0 DISCUSSION OF DATA

COUNTER Terbufos (Cl 92,100): Aerobic and Anaerobic Metabolism of CL 92,100 in a Silt Loam Soil. January 27, 1983. R. P. Peterson. Cyanamid Report No. PD-M Volume 20-4. Acc. No. 250661.

Procedure

Air-dried, sieved (to 2 mm) Wisconsin silt loam soil (characterized in Table 1) was fortified to 5 ppm methylene-¹⁴C-terbufos. Distilled water was added to give 75% field moisture capacity at 1/3 bar. Flasks were covered with aluminum foil and incubated at 19° C ± 2° C. To trap volatiles and CO₂ from soil, humid air was passed over soil and into traps of ethylene glycol (volatiles trap) and then monoethanolamine (CO₂ trap).

For the anaerobic soil, flasks were incubated aerobically for 30 days then flooded with water to initiate anaerobic conditions. Incubation period was 60 days.



Report No. NC-100-1

Table 1. Analysis of Wisconsin Soil*

| | |
|----------------------------------|-----------|
| Soil Texture | Silt (mm) |
| pH (Salt Solution) | 6.7 |
| Field Moisture (at 1/2 inch) (%) | 24.45 |
| Organic Matter (%) | 3.2 |
| Sand (%) | 33.6 |
| Silt (%) | 51.2 |
| Clay (%) | 15.2 |
| C.E.C. (meq/100 g) | 14.17 |
| NO ₃ -N (ppm) | 7.4 |
| Bulk Density on Dry Soil (g/cc) | 1.35 |
| Phosphorus (ppm-P) | 90 |
| Potassium (ppm-K) | 642 |
| Magnesium (ppm-Mg) | 654 |
| Calcium (ppm-Ca) | 2408 |
| pH (Soil) | 5.9 |

*Performed by: United States Testing Company, Incorporated
 Memphis Laboratory
 Cotton Exchange Building
 Memphis, Tennessee 38103

Note: Soil obtained from Lodi, Wisconsin

Aerobic soil was sampled over the 365 day incubation period. Anaerobic soil was sampled at initiation of anaerobic conditions (day 0) and then 30 and 60 days later.

Soil was either extracted immediately or frozen at approximately 0° C until analysis. Serial extraction of soil was carried out with: 10% aqueous methanol; methanol; then acidified (0.5% HCL) methanol. Aliquots were partitioned with methylene chloride. The dried methylene chloride fractions were analyzed by two-dimensional TLC.

Total ^{14}C in solutions and on TLC separations were analyzed by LSC. ^{14}C on TLC plates was located by autoradiography. Tentative identification of extracted ^{14}C and separated on TLC plates was with co-chromatography of known standards. Unextracted (bound) ^{14}C in soil was determined by combustion of soil and analysis of $^{14}\text{CO}_2$.

Results

The author reports average recovery of $95.7\% \pm 3\%$ for the aerobic soil samples and for the anaerobic soil was reported as 60.7% (volatiles were not collected).

Over the 365 day aerobic incubation period, $^{14}\text{CO}_2$ accounted for 46% of the total applied radioactivity. Other volatiles accounted for $<0.5\%$ of the applied radioactivity. ^{14}C and bound material increased with incubation time. See Table 2.

Terbufos sulfoxide (Cl 94,301) and terbufos sulfone (Cl 94,320) were the two major metabolites of terbufos with maximum concentration occurring after 30 days and 60 days, respectively. Both metabolites then declined over the remainder of the incubation period. See Table 3.

The following half-lives were reported:

| <u>Compound</u> | <u>Half-life</u> |
|--------------------|------------------|
| Terbufos | 5 days |
| Terbufos sulfoxide | 100 days |
| Terbufos sulfone | 100 days |

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Table of Compounds

| <u>CL Number</u> | <u>Chemical Name</u> | <u>Structure</u> |
|------------------|-------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| 97,100 | Phosphorodithioic acid, <u>S</u> -(1-butylthio) methyl <u>O,O</u> -diethyl ester (terbufos) | $\begin{array}{c} \text{S} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |
| 94,301 | Phosphorodithioic acid, <u>S</u> -(1-propylsulfinyl) methyl <u>O,O</u> -diethyl ester (terbufos sulfone) | $\begin{array}{c} \text{S} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |
| 94,320 | Phosphorodithioic acid, <u>S</u> -(1-propylsulfonyl) methyl <u>O,O</u> -diethyl ester (terbufos sulfone) | $\begin{array}{c} \text{S} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |
| 94,211 | Phosphorothioic acid, <u>S</u> -(1-butylthio) methyl <u>O,O</u> -diethyl ester (terbufoxon) | $\begin{array}{c} \text{O} \\ \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |
| 94,302 | Phosphorothioic acid, <u>S</u> -(1-butylsulfonyl) methyl <u>O,O</u> -diethyl ester (terbufoxon sulfone) | $\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |
| 94,365 | Phosphorothioic acid, <u>S</u> -(1-butylsulfonyl) methyl <u>O,O</u> -diethyl ester (terbufoxon sulfone) | $\begin{array}{c} \text{O} \quad \quad \text{O} \\ \parallel \quad \quad \parallel \\ (\text{C}_2\text{H}_5\text{O})_2\text{P}-\text{S}-\text{CH}_2-\text{S}-\text{C}(\text{CH}_3)_3 \end{array}$ |

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Table 2. Radiobalance of Applied Radioactivity in CL 92,100 Aerobic Soil Study

| Fractions | Percent of Applied Dose at Indicated Time Interval ^{a)} | | | | | | | | | |
|---------------------------------|------------------------------------------------------------------|-------|-------|--------|--------|--------|---------|---------|---------|---------|
| | 0-Day | 4-Day | 7-Day | 14-Day | 30-Day | 60-Day | 120-Day | 180-Day | 270-Day | 365-Day |
| Extract 1 (Aqueous/Methanol) | 107.4 | 89.7 | 84.5 | 79.2 | 70.6 | 61.4 | 53.8 | 46.6 | 38.5 | 28.0 |
| Extract 2 (Methanol) | 0.1 | 0.8 | 0.6 | 0.9 | 0.9 | 1.2 | 0.8 | 2.9 | 0.9 | 0.7 |
| Extract 3 (HCl/Methanol) | 0.1 | 1.1 | 1.2 | 1.4 | 5.6 | 6.1 | 7.0 | 7.0 | 10.2 | 6.9 |
| Soil (Air-Dried) | 0.1 | 0.7 | 2.0 | 5.5 | 4.6 | 5.8 | 10.0 | 11.1 | 12.2 | 21.4 |
| Volatiles (Trap) | - | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | <0.1 | <0.1 | 0.1 | 0.1 |
| Carbon Dioxide (Trap) | - | 1.8 | 4.9 | 9.0 | 13.5 | 18.8 | 22.0 | 25.3 | 33.6 | 45.9 |
| TOTAL | 107.7 | 96.4 | 94.0 | 96.1 | 95.3 | 93.4 | 93.6 | 92.9 | 95.5 | 93.0 |

a) Percentages are based upon the applied dose of 5.0 ppm carbon-14 CL 92,100.

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Table 3. Retention and Distribution of CL 92,100 and Its Metabolites in Methylene Chloride Extracts of Aroclor Soil at Various Times

| Compound | 0-Day | | 4-Day | | 7-Day | | 14-Day | | 20-Day | | 28-Day | | 42-Day | | 70-Day | | 120-Day | | 180-Day | | 270-Day | | 365-Day | | |
|-------------|---------|------|-------|------|-------|------|--------|------|--------|------|--------|------|--------|------|--------|------|---------|------|---------|------|---------|------|---------|------|------|
| | Dpm (%) | %C | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | DPM | % | |
| CL 92,100 | 6.31 | 86.2 | 2.93 | 52.1 | 1.93 | 38.9 | 0.77 | 15.4 | 0.21 | 4.1 | 0.06 | 1.2 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.03 | 0.6 | 0.03 | 0.03 | 0.6 | 0.03 | 0.03 | 0.6 |
| CL 94,301 | 0.31 | 6.2 | 1.50 | 29.9 | 2.06 | 41.3 | 2.55 | 50.9 | 2.62 | 52.3 | 1.75 | 34.9 | 1.47 | 29.4 | 1.24 | 24.7 | 0.88 | 17.2 | 0.88 | 17.2 | 0.88 | 17.2 | 0.88 | 17.2 | 0.88 |
| CL 94,320 | - | - | 0.11 | 2.3 | 0.11 | 2.5 | 0.40 | 8.1 | 0.53 | 10.5 | 1.00 | 20.1 | 0.85 | 17.0 | 0.71 | 14.3 | 0.60 | 12.0 | 0.60 | 12.0 | 0.60 | 12.0 | 0.60 | 12.0 | 0.60 |
| CL 94,321 | 0.05 | 0.8 | 0.03 | 0.6 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| CL 94,305 | - | - | 0.03 | 0.6 | 0.03 | 0.6 | 0.02 | 0.4 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| CL 94,302 | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - | - |
| CL Origin | 0.02 | 0.4 | 0.10 | 2.0 | 0.01 | 0.3 | 0.01 | 0.2 | 0.01 | 0.1 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 | 0.2 | 0.01 |
| Unknowns d) | - | - | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 | 0.6 | 0.03 |
| TOTALS | 4.68 | 93.6 | 4.61 | 87.9 | 4.26 | 84.5 | 3.78 | 75.0 | 3.40 | 67.6 | 2.88 | 57.3 | 2.45 | 48.0 | 2.08 | 41.5 | 1.55 | 30.9 | 1.55 | 30.9 | 1.55 | 30.9 | 1.55 | 30.9 | 1.55 |

- a) Soil extracts #1 and #2 (Table II) were combined, diluted with water and extracted with acetylene chloride.
- b) ppm of chemical in soil are calculated from amount found in methylene chloride phase.
- c) Percent of applied dose based on ppm found divided by 5.0 ppm (applied dose).
- d) No individual compound was greater than 0.1% of applied dose.

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NOTE: EAB regression analysis indicated that, considering the data through 60 days incubation, EAB regression analysis calculated the half-life of terbufos to be approximately 10 days ($r^2 = .948853$). See Table 4.

Also, EAB regression analysis of the decline of the metabolites indicated the half-lives for terbufos sulfoxide (CL 94,301) was approximately 122 days ($r^2 = .922303$) considering data over the period of decline from day of maximum concentration (day 30) to end of incubation period. Also, the half-life of terbufos sulfone (CL 94,320) was calculated to be approximately 106 days ($r^2 = .784916$) considering data from the date of maximum concentration (day 60) to end of the incubation period. See Table 5.

Terbufoxon (oxygen analog of terbufos) and terbufoxon sulfoxide were found in minimum amounts during the initial part of the incubation period. Terbufoxon sulfone was not detected at any sampling period.

Under anaerobic conditions, terbufos sulfoxide and terbufos sulfone were also found. The concentration of both declined during the incubation period. The author reported that terbufos (parent) concentration actually increased during the anaerobic incubation period. This suggested that some terbufos sulfoxide present at the initiation of anaerobic conditions was reduced back to terbufos. See Table 6.

In the anaerobic soil, after 30 and 60 days incubation, 12.8% and 18.0%, respectively, of the applied ^{14}C was unextracted (i.e., bound).

Conclusion

Terbufos degraded rapidly with a half-life of approximately 10 days (EAB regression analysis) in silt loam soil maintained under aerobic soil conditions. Degradation continued through mineralization to CO_2 . The major metabolites found were terbufos sulfoxide (with an EAB calculated half-life of approximately 122 days) and terbufos sulfone (with an EAB calculated half-life of approximately 106 days).

In anaerobic soil, the metabolites formed under aerobic conditions continued to disappear, with partial reduction of terbufos sulfoxide back to terbufos (i.e., terbufos concentration actually increased under anaerobic conditions). However, the larger portion of the disappearance of

TABLE 4

REGRESSION ANALYSIS OF RESIDUE DECLINE DATA

NAME: FLETCHER

DATE: 10/24/83

TITLE: TERBUFOS DECLINE

REMARKS:

| | | |
|------------|-----------------------|-------------------|
| FILE NAME: | RESIDUE LEVELS IN PPM | INTERVALS IN DAYS |
|------------|-----------------------|-------------------|

DATA ENTRIES 1 TO 6

| | | |
|----------------|----------------|----------------|
| 4.31 at 0 DAYS | 1.95 at 7 DAYS | .21 at 30 DAYS |
| 2.61 at 4 DAYS | .77 at 14 DAYS | .06 at 60 DAYS |

N= 6 SUM X= 115 SUM X²= 4761 SUM Y=-1.54731 SUM Y²= 13.9199 SUM X*Y=-210.771
 For the 95% confidence level, the appropriate 't' VALUE=2.1314 (For a one tailed test)

DF=4 R SQUARED=.948853 CHI SQUARED=1.72872 % Probability of a good fit=63.1%
 Y-INTERCEPT= 1.09979 RELATIVE % ERROR OF THE SLOPE= 11.6% % LOSS PER DAY= 6.84%

SLOPE= -.071, its UPPER 95% CL= -.053 and its LOWER 95% CL= -.088
 HALF LIFE= 9.8 DAYS, its UPPER 95% CL= 13 DAYS and its LOWER 95% CL= 7.8 DAYS

DAY ZERO LEVEL=3.004 PPM, its UPPER 95% CL=8.284 PPM and its LOWER 95% CL=1.089 PPM

TABLE 5

REGRESSION ANALYSIS OF RESIDUE DECLINE DATA

NAME: FLETCHER

DATE: 10/25/83

TITLE: CL 94,301 DECLINE

REMARKS:

FILE NAME: RESIDUE LEVELS IN PPM INTERVALS IN DAYS

DATA ENTRIES 1 TO 6

| | | |
|-----------------|------------------|-----------------|
| 2.62 at 0 DAYS | 1.47 at 90 DAYS | .88 at 240 DAYS |
| 1.75 at 30 DAYS | 1.24 at 150 DAYS | .29 at 335 DAYS |

N= 6 SUM X= 845 SUM X²= 201325 SUM Y= .757456 SUM Y²= 2.98425 SUM X*Y=-361.639
 For the 95% confidence level, the appropriate 't' VALUE=2.1314 (For a one tailed test)

DF=4 R SQUARED=.922303 CHI SQUARED=.61171 % Probability of a good fit=89.4%
 Y-INTERCEPT= .927428 RELATIVE % ERROR OF THE SLOPE= 14.5% % LOSS PER DAY= .57%

SLOPE= -.006, its UPPER 95% CL= -.004 and its LOWER 95% CL= -.007
 HALF LIFE= 121.8 DAYS, its UPPER 95% CL= 176.4 DAYS and its LOWER 95% CL= 93.1 DAYS

DAY ZERO LEVEL=2.528 PPM, its UPPER 95% CL=4.602 PPM and its LOWER 95% CL=1.389 PPM

REGRESSION ANALYSIS OF RESIDUE DECLINE DATA

NAME: FLETCHER

DATE: 10/25/83

TITLE: CL 94320 DECLINE

REMARKS:

FILE NAME: RESIDUE LEVELS IN PPM INTERVALS IN DAYS

DATA ENTRIES 1 TO 5

| | | |
|----------------|-----------------|-----------------|
| 1 at 0 DAYS | .71 at 120 DAYS | .11 at 305 DAYS |
| .85 at 60 DAYS | .6 at 210 DAYS | |

N= 5 SUM X= 695 SUM X²= 155125 SUM Y=-3.22311 SUM Y²= 5.27672 SUM X*Y=-831.342
 For the 95% confidence level, the appropriate 't' VALUE=2.3465 (For a one tailed test)

DF=3 R SQUARED=.784916 CHI SQUARED=.790041 % Probability of a good fit=67.4%
 Y-INTERCEPT= .265885 RELATIVE % ERROR OF THE SLOPE= 30.2% % LOSS PER DAY= .65%

SLOPE= -.007, its UPPER 95% CL= -.002 and its LOWER 95% CL= -.011
 HALF LIFE= 105.8 DAYS, its UPPER 95% CL= 363.8 DAYS and its LOWER 95% CL= 61.9 DAYS

DAY ZERO LEVEL=1.305 PPM, its UPPER 95% CL=5.238 PPM and its LOWER 95% CL=.325 PPM

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Table 6. Nature and Distribution of CL 92,100 and Its Metabolites in Methylene Chloride Extracts ^(a) of Anerobic Soil at 30 and 60 Days

| Compound | 0-Day ^(b) | | 30-Days | | 60-Days | |
|-------------------------|----------------------|------------------|---------|------|---------|------|
| | ppm ^(c) | % ^(d) | ppm | % | ppm | % |
| CL 92,100 | 0.21 | 4.1 | 0.57 | 11.4 | 0.55 | 11.0 |
| CL 94,301 | 2.62 | 52.3 | 0.66 | 13.2 | 0.27 | 5.4 |
| CL 94,320 | 0.53 | 10.5 | 0.08 | 1.6 | 0.05 | 1.0 |
| CL 94,221 | - | - | - | - | 0.02 | 0.4 |
| CL 94,365 | - | - | 0.01 | 0.2 | - | - |
| CL 94,302 | - | - | - | - | - | - |
| TLC Origin | 0.01 | 0.1 | 0.01 | 0.2 | 0.01 | 0.2 |
| Unknowns ^(e) | 0.03 | 0.6 | 0.02 | 0.4 | 0.07 | 1.4 |
| Total | 3.40 | 67.0 | 1.35 | 27.0 | 0.97 | 19.4 |

(a) Soil extracts #1 and #2 were combined, diluted with water and extracted with methylene chloride.

(b) Data from 30-day aerobic sample which was "zero" day for anaerobic study.

(c) ppm of chemical in soil as calculated from amount found in methylene chloride phase.

(d) % of applied dose based on ppm found divided by 5 ppm applied.

(e) No individual compound was greater than 0.1% of applied dose.

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metabolites from the anaerobic soil was unexplained. After 60 days anaerobic incubation, only 44.1% (19.4% extracted, characterized + 18.0% soil bound, unextracted + 6.7% HCl-methanol extracted, uncharacterized) of the applied radioactivity was accounted for in the material balance. Only 47.5% of the applied radioactivity was accounted for after 30 days anaerobic incubation.

The registrant should provide a half-life estimate for terbufos and a more complete material balance of the anaerobic soil metabolism study.

4.0 EXECUTIVE SUMMARY

- 4.1 The aerobic soil metabolism study satisfies this data requirement.
- 4.2 The registrant should be requested to provide a half-life estimate and a more complete material balance of residues for terbufos in soil maintained under anaerobic soil conditions. This information is necessary before this study can satisfy this data requirement.
- 4.3 The exposure analysis is appended to this environmental fate data review.

Clinton Fletcher
Review Section No. 1
Exposure Assessment Branch
Hazard Evaluation Division

1.0 INTRODUCTION

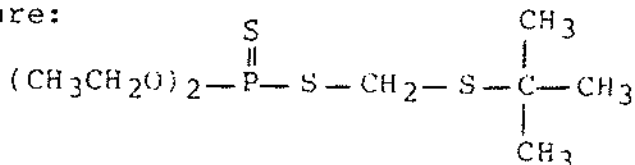
American Cyanamid has submitted an exposure analysis for the soil incorporated insecticide Counter 15G (terbufos, as a. i.)

1.1 Chemical

Common name: Terbufos (CL 92,100)

Chemical name: S-[[[(1,1-dimethylethyl)thio]methyl] O,O-diethylphosphorodithioate

Chemical structure:



2.0 DIRECTIONS FOR USE

Application was made according to the use directions appended to this review.

Counter 15G is a 15% terbufos granular formulation which is applied with a ground applicator properly calibrated to deliver:

| <u>Field Corn</u> | <u>Sugar Beets</u> |
|---------------------------------------------------------------------------------------------|----------------------------------------------------------------------------------------------|
| 75 gm/100m (0.17 lb/328 ft) row with minimum 75 cm (30 inch) row spacing (1.4 lb. a. i./A). | 45 gm/100m (0.10 lb/328 ft) row with minimum 50 cm (20 inch) row spacing (1.14 lb. a. i./A). |

Only one application is made. The label directions prohibit applying later than at planting time.

The label bears the restriction to wear protective clothing and gloves while handling product.

3.0 Exposure Assessment

3.1 COUNTER Terbufos (CL 92,100/15G): Farmer Exposure Study with Counter 15G (BAND; 3.1 ONT, 1982). American Cyanamid Report No. C-2085. November 1, 1982. R. Peterson and G. Picard.

The protocol by which this study was conducted is attached to this review. The field procedures actually followed are summarized below.

Procedure

Eleven farmers participated in the study as workers (coded A-K). Another five farmers served as controls (coded 1-5). Standard protective clothing, including coveralls and cotton gloves were worn while mixing/loading. Gloves were not worn during application. The same individual did both tasks—mixing/loading and application.

For measurement of potential dermal exposure, a total of six gauze patches were placed on the outside of the protective clothing and located in the chest area, upper back area, front lower leg below the right knee, above the knee on the right thigh, on the back of the right forearm and on the front of the right upper arm. An equal number of patches were located inside the protective clothing similarly placed but not directly under the outside patches.

Respiratory exposure was monitored by taking air samples in the breathing zone. Stainless steel tubes, filled with XAD-2 resin were attached to the worker's collar and to a MSA personal monitoring pump calibrated at 1.5 l/min.

Urine and blood samples were collected as well. Urine samples were subsampled and analyzed (1) for creatinine determination (to determine completeness of 24 hour urine samples) and (2) for CL 92,100-related phosphorus esters (to determine degree of adsorption of CL 92,100).

Immediately after all planting activities, patches were removed and stored in polyethylene bags. Collected patches were stored at -25° C until analysis.

Analysis of gauze patches and air-collection tubes for total CL 92,100 and related compounds was by patch and resin extraction with acetone then quantitation by gas chromatography using a flame photometric detector. [NOTE: For patches, the method sensitivity was 5.0 ng/cm² (recovery ranged from 73 to 100% at fortification levels of 5 to 496 ng/cm² for CL 92,100, terbufos sulfone and a 4:1 mixture of same). For air samples, the method sensitivity is 0.35 ng/L, assuming 720 liters of air and 0.25 ug of compound are drawn into the AXD-2 resin tube (recovery ranged from 77 to 129% at fortification levels of 0.35 to 44 ng/l for CL 92,100 and terbufos sulfone)].

Gauze patch storage stability data were presented showing 78 to 91% recovery for 2 and 8 weeks frozen storage of gauze patches fortified at 124 ng/cm² of the 4:1 mixture.

[Note: Analytical methods for blood and urine samples will be briefly mentioned. EAB defers to Toxicology Branch for review and validation of the submitted data].

Cholinesterase levels were measured in both plasma and red blood cells by using a modified potentiometric method of Michel [J. Lab. Clin. Med. 34, 1564-1568 (1949)].

Urine creatinine analyses were performed using the alkaline picrate Jaffe reaction. Urinary alkyl phosphate metabolite analysis was determined using a gas chromatography.

Results

Workers had a average exposure time of 7.4 hours (range: 4.7 to 11.9 hours), applying an average of 166 kg Counter 15G (range: 92 to 380 kg) on an average of 16.9 hectares (range: 8.1 to 38.9 hectares). See Table I. (Note: averages calculated by EAB.)

Air concentration for CL 92,100-related compounds averaged 6.5 ng/l (range: 1.6 to 16.0 ng/l) for the 11 exposed workers. Average hourly estimated respiratory exposure is calculated to be 11.3 ug/hr (range 2.8 to 27.4 ug/hr). See Table II.

Summary of dermal patch concentrations were reported as:

| Area | Total CL 92,100-Related Compounds ^a (ng/cm ²) | | | |
|-----------|-------------------------------------------------------------------------|---------|----------------|---------------------|
| | Outside Patches | | Inside Patches | |
| | Average | Range | Average | Range |
| Chest | 109 | 26-529 | 20 | ND ^b -89 |
| Back | 104 | 5-573 | 2 | ND-9 |
| Upper arm | 191 | 14-819 | 8 | ND-43 |
| Lower arm | 96 | 8-350 | 11 | ND-57 |
| Upper leg | 463 | 43-2073 | 36 | ND-255 |
| Lower leg | 42 | ND-175 | 6 | ND-21 |

^aTaken from Tables III and IV.

^bND = <5 ng/cm², the sensitivity of analytical method.

From the data in the above table, the estimated dermal exposure can be calculated:

Estimated Dermal Exposure^a
(ug/hr)

| 1. Area | Unexposed Areas (Inside Patches) | |
|--------------------|----------------------------------|-----------|
| | Average | Range |
| Chest | 9.3 | ND-38.9 |
| Back | 1.4 | ND--6.0 |
| Upper arm | 1.6 | ND 11.4 |
| Lower arm | 2.0 | ND-10.5 |
| Upper leg | 17.1 | ND-97.9 |
| Lower leg | 2.5 | ND--9.9 |
| TOTAL ^b | 34.1 | 4.1-119.2 |

^aSummary of data in Table V.

^bAverage total from Table V--the average of the 11 individual farmer's total, not sum of averages given here.

| 2. Area | Exposed Areas (Outside Patches) | |
|------------------------|---------------------------------|-----------|
| | Average | Range |
| Hands ^a | 14.4 | 1.1-45.3 |
| Head/Neck ^a | 23.9 | 2.1-101.3 |
| Lower arm ^b | 16.8 | 1.4-54.2 |

^aData from Table V.

^bCalculated by EAB. See Table X.

Summary

For exposed areas (outside patches), average estimated dermal exposure for a worker wearing coveralls but no gloves is reported as 14.4 ug/hr for hands and 23.9 ug/hr for head and neck. The average dermal exposure from unexposed areas is reported as 34.1 ug/hr.

Thus, the average total dermal exposure is estimated to be 72.4 ug/hr (14.4 + 23.9 + 34.1 ug/hr) for a worker wearing coveralls but no gloves. The registrant reports that this value over-estimates the actual since the label call for wearing gloves while handling product.

Conclusion

EAB concludes that the data presented for respiratory and dermal exposure adequately reflects the expected exposure potential of the mixer/loader and applicator of terbufos when used according to the attached label directions.

EAB notes that the registrant uses data of the lower arm outside patch to extrapolate to hand exposure. EAB notes that analysis of the cotton gloves themselves would have been preferable for determining hand exposure. However, lacking actual hand exposure measurement, EAB will accept this extrapolation. Moreover, this value may under-estimate the actual value for dermal exposure to unprotected hands.

Also, some minor calculation/tabulation errors were found in the data tables. They did not affect the final estimations.

Data from analyses of the dermal or respiratory exposure were not presented for the workers serving as controls. No were data presented for blank samples of gauze or XAD-2 resin.

EAB defers to the Toxicology Branch for review and validation of the data for blood and urine analyses (Tables VII - IX) and for the % Toxic dose/hr calculation (Table VI).

3.2 RESPIRATORY EXPOSURE

Hourly respiratory exposure for CL 92,100-related compounds averaged 11.3 ug/hr (range: 2.8 to 27.4 ug/hr) for the 11 exposed workers.

3.3 DERMAL EXPOSURE - WITHOUT PROTECTIVE CLOTHING

For this estimation, EAB assumes the worker wears a short sleeved shirt and long-legged pants. No gloves are worn.

The average dermal exposure through exposed hands, lower arms and head/neck is estimated to be 87.0 ug/hr [14.4 ug/hr (hands) + 16.8 ug/hr (lower arms) + 23.9 ug/hr (head and neck) + 31.9 ug/hr (unexposed chest, back, upper arms, legs)].

3.4 DERMAL EXPOSURE - WITH PROTECTIVE CLOTHING

For this estimation, EAB assumes clothing includes coveralls and cotton gloves will be worn during mixing/loading.

[NOTE: EAB generally does not consider cotton gloves as protective clothing. However, they are acceptable in this case for a granular pesticide formulation and used once.]

The average dermal exposure to a worker wearing coveralls and cotton gloves but exposed head and neck is estimated to be 59.6 ug/hr (1.6 ug/hr* (hands) + 23.9 ug/hr (exposed head and neck) + 34.1 ug/hr (unexposed chest, back, arms, and legs)).

*EAB calculated value. See Table X.

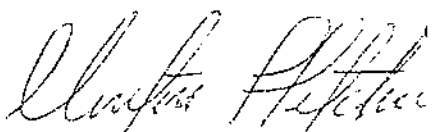
3.5

ESTIMATED TOTAL EXPOSURE

| Condition | Exposure | | Total Exposure |
|------------------------------------------|--------------------|---------------|----------------|
| | <u>Respiratory</u> | <u>Dermal</u> | |
| Without protective clothing ^a | 11.3 ug/hr. | 87.0 ug/hr. | 98.3 ug/hr. |
| With coveralls, no gloves | 11.3 ug/hr. | 72.4 ug/hr. | 83.7 ug/hr. |
| With protective clothing ^b | 11.3 ug/hr. | 59.6 ug/hr. | 70.9 ug/hr. |

^aworker wearing short-sleeved shirt, long-legged pants and no gloves.

^bworker wearing coveralls and cotton gloves.



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SAMPLE CALCULATIONS USED IN THIS REVIEW.

1. Estimated hourly respiratory exposure (ug/hr)

$$\frac{\text{Total ug/hr found}}{\text{Application time (hr)}} \times \text{Human inhalation rate factor}$$

e.g. Farmer A $\frac{2.0 \text{ ug}}{8.2 \text{ hr.}} \times 19.3 = 4.7 \text{ ug/hr}$

2. Estimated hourly dermal exposure (ug/hr)

$$\frac{\text{Dermal patch conc. (ug/cm}^2\text{)} \times \text{regional surface area}}{\text{Application time (hr)}}$$

e.g. Farmer A Chest (inside dermal patch)

$$\frac{0.011 \text{ ug/cm}^2 \times 3063 \text{ cm}^2}{8.2 \text{ hr}} = 4.1 \text{ ug/hr}$$

Farmer A Hands (outsider dermal patch, lower arm)

$$\frac{0.107 \text{ ug/cm}^2 \times 1075 \text{ cm}^2}{8.2 \text{ hr}} = 14.0 \text{ ug/hr}$$

Farmer A Head and neck (average outside dermal patch chest and back)

$$\frac{\frac{185 \text{ ug/cm}^2}{2} \times 1305 \text{ cm}^2}{8.2 \text{ hr}} = 14.7 \text{ ug/hr}$$

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Pages 20 through 28 are not included. The pages contain detailed test results submitted by American Cyanamid.

Table X. Estimated Dermal Exposure
(ug/hr)

| <u>Farmer</u> | <u>Exposure time (hrs)</u> | <u>Exposed Lower Arm (1286 cm²)</u> | <u>Unexposed Hands* (1075 cm²)</u> |
|---------------|--------------------------------|----------------------------------------------------|---------------------------------------------------|
| A | 8.2 | 16.7 | --- |
| B | 8.3 | 54.2 | 1.3 |
| C | 4.6 | 24.0 | 2.3 |
| D | 3.8 | 6.8 | --- |
| E | 11.9 | 9.4 | 1.3 |
| F | 4.7 | 20.3 | 2.1 |
| G | 7.3 | 1.4 | --- |
| H | 7.0 | 10.8 | 8.8 |
| I | 9.6 | 1.3 | --- |
| J | 6.9 | 11.7 | 0.8 |
| K | 9.0 | 27.8 | 2.0 |
| AVERAGE | | 16.8 | 1.6 |

* Used inside value for lower arm.

Sample calculations:

Farmer A Exposed lower arm

$$\frac{107 \text{ ng/cm}^2 \times 1286 \text{ cm}^2}{8.2 \text{ hr.} \times 1,000 \text{ ng/ug}} = 16.7 \text{ ug/hr.}$$

Farmer C Unexposed hands

$$\frac{10 \text{ ng/cm}^2 \times 1075 \text{ cm}^2}{4.6 \text{ hr.} \times 1,000 \text{ ng/ug}} = 2.3 \text{ ug/hr.}$$

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Pages 30 through 38 are not included. The pages contain a detailed test protocol submitted by American Cyanamid.