

Shaughnessy #: 027301

Date out of EAB: MAY 08 1985

Signature: *JM*

To: H. Jacoby  
Product Manager # 21  
Registration Division (TS-767)

From: John Jordan, Ph.D., Acting Chief  
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*John Jordan*

Attached please find the EAB review of:

Reg./File No.: 41014-7

Chemical: Chloroneb

Type Product: F

Product Name: \_\_\_\_\_

Company Name: \_\_\_\_\_

Submission Purpose: Data in response to RS

Action Code: 660

Date In: 4/16/85

EAB # 5492

Date Completed: MAY 08 1985

TAIS (level II)            Days           

Deferrals To:

          40                     5          

\_\_\_\_\_ Ecological Effects Branch

\_\_\_\_\_ Residue Chemistry Branch

\_\_\_\_\_ Toxicology Branch

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

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

Conclusions

Metabolism-Aerobic soil metabolism

- 1). This study does not fulfill EPA Guidelines for the Registration of Pesticides because there is no purity reported for the  $^{14}\text{C}$  test substance or the unlabeled substance; there is no ambient temperature or test condition reported; there is no description or quantitation of the residues. There is no materials balance and the analysis method is inadequately described or inadequate methodology was used.

Materials and Methods

Moist Flanagan silt loam and Fallsington sandy loam soil were weighed to widemouth jars (50g dry weight). These were treated with 1 ml of 46 ppm solution of  $^{14}\text{C}$  (UL)-chloroneb in methylene chloride with a specific activity of  $10^4\text{Ci ng}$ . High level samples were treated with an additional 1 ml of 300ppm solution of unlabeled chloroneb. These treatments correspond to rates of .9ppm and 6.9ppm. Soil was kept moist until sampled. Samples were frozen for later analysis.

Biometer flasks were set up containing 50 g (dry weight) of each soil type and was treated with  $5.66 \times 10^5$  dpm of  $^{14}\text{C}$ -celulose or  $2.02 \times 10^6$  dpm of  $^{14}\text{C}$ -chloroneb. A sidarm flask was charged with 10ml of 0.1N NaOH and a few drops of phenolphthalein indicator. NaOH samples were taken at regular intervals. To verify all observed activity was due to  $^{14}\text{CO}_2$  a 0.5 ml aliquot of NaOH solution was treated with 0.5ml of  $\text{BaCl}_2$  and 100  $\mu\text{l}$  of 2m  $\text{K}_2\text{CO}_3$ , centrifuged, and the supernatant counted for residual activity.

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A second biometer study was set up as previously described and charged with  $1.0 \times 10^6$  dpm  $^{14}\text{C}$ -chloroneb applied in 1 ml of methylene chloride. The channel between the sidearm of the flasks was filled with a porous polyurathane plug which was renewed when each NaOH sample was taken. Plug was extracted with 100 ml acetone.

Soil samples were taken at 0, 1, 3, 7, 14, 28, 56, 112 and 365 days post application and extracted with three 75 ml portions of acetone followed by three extractions with 75 ml of methanol. These were combined and concentrated under a dry nitrogen stream. A portion of the concentrate was applied to a 0.25 mm silica G TLC plate and developed in methylene chloride. Radioactive regions detected by a Berthold LB-2760 scanner. Radioactive soil residues were determined by combustion in a Packard 306 oxidizer and quantitated using liquid scintillation counting.

#### Reported Results

Little production of  $^{14}\text{CO}_2$  from  $^{14}\text{C}$ -chloroneb was noted (about 1% through 4 months) indicating the microorganisms present were incapable of converting significant amounts of ring label to  $^{14}\text{CO}_2$ .

For greenhouse soils most of the applied radioactivity was accounted for as acetone and methanol extract or unextracted bound residue. Most residues were found in the acetone extract with less than 10% of extractable residue found in methanol extract. Bound residues reported as maximized at 6-12% at 56-112 days. Intact chloroneb was the major radioactive component; half life reported as 4-5 weeks in the Flanagan soil and 2-3 in Fallsington soil. Higher rates had slightly shorter half-lives.

Biometer flask foam plugs are reported to show an almost constant rate of volatilization. TLC-autoradiograms of the foam plug extract indicated essentially all of the volatilized material is intact  $^{14}\text{C}$ chloroneb.

Discussion

- 1). Purity of test substances both  $^{14}\text{C}$  and unlabeled chloroneb not indicated.
- 2). No reported ambient temperatures or soil conditions reported.
- 3). No reported soil preparation methodology such as screening or seiving prior to amendment.
- 4). Soils not reported as mixed after amendment with test material.
- 5). If soils were not mixed, the addition of test was made in an insufficient quantity of liquid to allow for an even distribution in soil.
- 6). Reported TLC auto-radiogram of  $^{14}\text{C}$ -chloroneb and 2,5-dichloro 4 methoxyphenol is unreadable or shows only one peak.
- 7). Results of TLC-autoradiogram of the foam plug extracts are questionable as plug extracts show more  $^{14}\text{C}$ -chloroneb does extract +  $^{14}\text{C}$ -chloroneb addition.
- 8). No materials balance reported.

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Conclusions

Dissipation studies: Terrestrial

- 1). Study is not scientifically valid as there are conflicting results reported.
- 2). Study does not fulfill EPA Guidelines for Registration of Pesticides 1983 because only one field site and soil series is used, there is no designation as to purity or form of unlabelled chloroneb and no control or preapplication sample is reported.

Materials and Methods

Fifteen Stainless Steel cyclinders 3 7/8 in i.d. x 15 in long were driven into a plot of bluegrass over Keyport silt loam to a depth of about 13.5 in. Foliage was trimmed to about 1 in. and 1.0 ml of standard chloroneb solution containing 63  $\mu$ g  $^{14}$ C-chloroneb (99% radiopurity; specific activity= 10.0  $\mu$  ci/mg) and 13.5 mg unlabeled chloroneb was applied by a gastight syringe to the foliage isolated within each cylinder. Rate corresponds to 15.9lb a.i./acre or maximum recommended use rate. Subsequent application were made 96, 259, 288 and 320 after initial treatment.

For analysis the cylinders were dug 0, 7, 119, 267, 295 and 365 days after initial application and stored frozen. The cylinders were divided into foliage thatch and soil segments (0-5cm, 5-10cm, 10-20cm and 20 to end). Foliage was washed with acetone. Foliage and thatch were seperately extracted 3 times with acetone in a Tekman Tissumizer. Aliquots of the wash and extracts were analyzed by liquid scintillation counting. Extacts were concentated under a stream of nitrogen.

Soils samples were air dried in a hood before assaying for total radiolabel. A  $^{14}\text{C}$ -chloroneb spiked sample was air dried in the hood and was combusted and counted with a freshly spiked sample. Radiolabel recovery reported from the air dried sample was only 2% less than fresh spike "indicating that volatilization from soil surface during drying was minimal".

Radiolabel recovery from cylinder segments was determined by homogenizing each segment and combusting and counting a portion of it. Those segments containing a significant fraction of applied radiolabel were extracted with acetone. A portion was counted and the remainder concentrated under a nitrogen stream. The concentrated extracts and the grass and foliage extracts were separated on silica TLC plates developed in methylene chloride that is reported as capable of resolving chloroneb from 2, 5 dichloro-4-methoxyphenol. Areas of radioactivity were detected on TLC plates using Berthold Model LB-2760 or LD-282 scanners.

#### Reported Results

Methods section reports that air drying in a hood only reduced  $^{14}\text{C}$  recovery 2% from freshly spiked sample indicating minimal volatilization from soil surface during drying.

The 0 day sample (taken post application) showed 92% recovery with most  $^{14}\text{C}$  found in the foliage and thatch fraction. The high volatility of chloroneb was reported as reason for only 92% recovery. After 7 days only 45% of the activity remained. The majority of recovery from the soil was reported as intact chloroneb.

Similar results were reported for the sample taken 23 days after the second application. The 267, 295 and 365 day cylinders were analyzed shortly (7, 7 and 45) days after summer applications. These samples show only 15, 11, and 12% of the cumulative applied activity recovered respectively these low recoveries are reported to be due to the apparently higher rates of chloroneb volatilization during this warm period. Figure one summarizes the cumulative applied and recovered amounts of radiolabel during the course of this study as well as monthly precipitation and temperatures. This figure is reported to demonstrate the inverse relationship between temperature and recovery of radiolabel.

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Leaching is reported as minimal since no more than 10% of the cumulative applied label is found in the sum of the bottom three segments of the cylinder.

The results are reported consistent with other studies which showed that most of the  $^{14}\text{C}$ -chloroneb applied to soil was volatilized as intact parent compound.

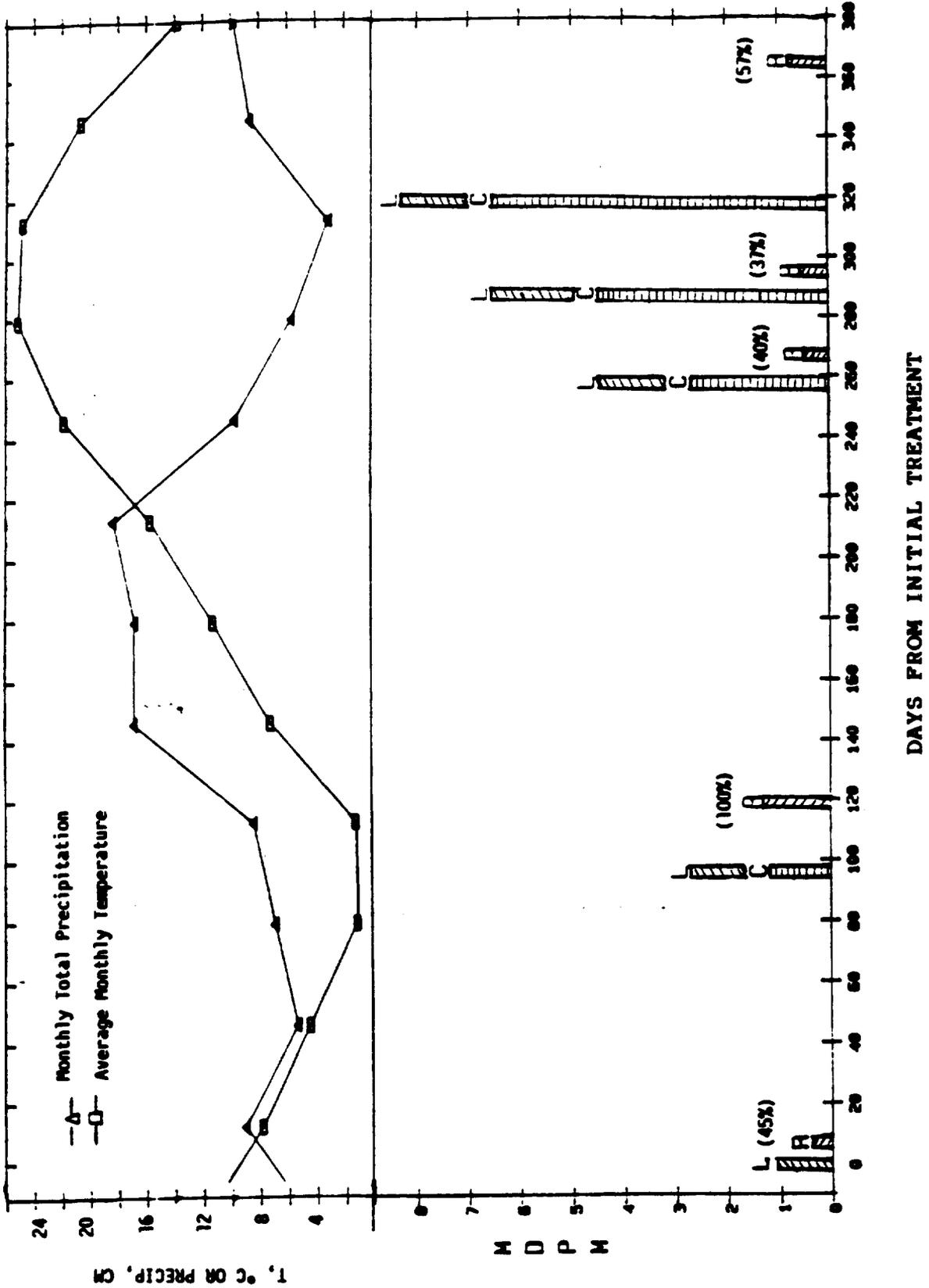
### Discussion

- 1). Results in the methods section reported that only 2 % of  $^{14}\text{C}$  labeled chloroneb was volatilized after drying a soil plug in a hood are in direct conflict with the stated results of the paper which indicate that most of the applied  $^{14}\text{C}$  chloroneb volatilizes as intact parent compound.
- 2). The drying technique used may lead to erroneous determination of the amount of chloroneb leaching through a soil profile.
- 3). There is no designation of purity or form of the unlabeled chloroneb.
- 4). No control plot or preapplication sample is reported.
- 5). No recoveries reported or literature cited for analytical techniques used.
- 6). Only on site and one soil type used. Several more sites and soil types are required.
- 7). Use of small cylinders does not represent a large enough "population" segment to be a valid test for a field study.

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**FIGURE 1**

**RELATIVE AMOUNTS OF APPLIED AND RECOVERED RADIOLABEL, AND TEMPERATURE AND PRECIPITATION FOR THE PERIOD OF THIS STUDY**



DAYS FROM INITIAL TREATMENT

C - CUMULATIVE AMOUNT APPLIED PRIOR TO LATEST APPLICATION  
 L - AMOUNT OF LATEST APPLICATION  
 R - RECOVERED AT LATEST SAMPLING DATE (PERCENT OF LATEST APPLICATION)