Shaugh. No. 114501

EAB Log Out Date: MAY 5 1987

To: D. Edwards
Product Manager 12
Registration Division (TS-767)

From: Carolyn K. Offutt
Chief, Environmental Processes and Guidelines Section
Exposure Assessment Branch, HED (TS-769)

Attached, please find the environmental fate review of:

Reg./File No.: 264-379

Chemical: Thiodicarb

Type Product: Insecticide

Product Name: LARVIN

Company Name: Union Carbide

Submission Purposes: Protocols for field leaching studies

Action Code: 352

Date In: 4/17/87

EAB#: 70517

Date Completed: 5/5/87

TAIS (Level II) 301

Days 1.5

Monitoring study requested: x

Monitoring study voluntarily:

Deferrals To:

_____ Ecological Effects Branch

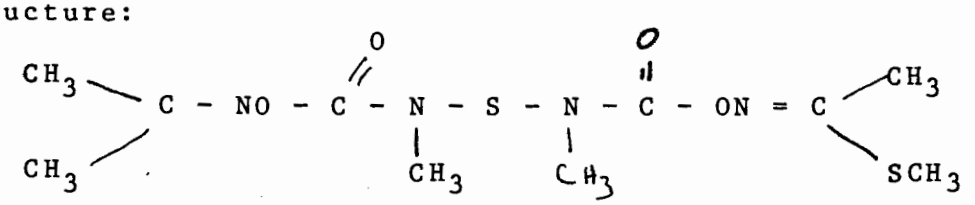
_____ Residue Chemistry Branch

_____ Toxicology Branch

EVALUATION OF THIODICARB PROTOCOLS FOR FIELD LEACHING STUDIES

1. CHEMICAL:

Chemical name: Dimethyl-N,N'[thiobis[(methylimino)carbonyloxyl]) bis [ethanimidothioate]
Common name: Thiodicarb
Trade name: LARVIN
Structure:



2. TEST MATERIAL:

Methomyl (formulation not specified - proposed for unsaturated zone monitoring)
Thiodicarb (formulation not specificed - proposed for saturated zone monitoring)

3. STUDY/ACTION TYPE:

Evaluation of protocols for field research to determine the leaching potential of thiodicarb.

4. STUDY IDENTIFICATION:

Title: letter from J.S. Lovell to E.F. Tinsworth, dated 3/6/87, and attached protocol entitled, "Protocols for Thiodicarb Field Research Studies" (8421y)
Author: Union Carbide Agricultural Products Company, Inc.
P.O. Box 12014
T.W. Alexander Drive
Research Triangle Park, North Carolina 27709
Identifying No: 264-379
Issue Date: 3/6/87
Record No: 193446
Accession No: not given

5. REVIEWED BY:

Matthew N. Lorber, Agricultural Engineer Date 5/5/87
Environmental Processes and Guidelines Section/EAB/HED

6. APPROVED BY:

Carolyn K. Offutt, Chief Date 5/5/87
Environmental Processes and Guidelines Section/EAB/HED

2

7. CONCLUSIONS:

The unsaturated zone field study is unacceptable. An alternative study is suggested in its place. The saturated zone monitoring studies are acceptable. See Discussion section for further details.

8. RECOMMENDATIONS:

Require the registrant to submit a revised protocol based on comments in this review.

9. BACKGROUND

Union Carbide is seeking registration of thiodicarb for ornamental and non-crop uses. However, this registration has been denied due to leaching concerns of primarily the first degradate product, methomyl. Based on field studies submitted by the registrant, it is established that thiodicarb metabolizes to methomyl rapidly (less than a week, as short as two days in some cases). Further, methomyl has been shown to hydrolyze slowly, with data in EAB files indicating no hydrolysis after 30 days at pH 5 and 7, but hydrolysis occurring with a half-life of 30 days at pH 9 (see Reg/File No: 352-366, EAB review dated 1/9/85). Finally, thiodicarb has been shown to have some, although limited, mobility with water. Therefore, the concern was raised that thiodicarb could leach with rainfall near the time of application to the point where the primary degradate, methomyl, would not be subject to the typically more rapid microbial decay of the upper soil zones, but rather to the slower process of chemical hydrolysis which predominates in the lower soil zones and the ground water. For these reasons, a registration for ornamentals and noncrop uses was denied based on ground water concerns.

A meeting was held on 10/2/86 between representatives of Union Carbide, and EPA representatives including Sam Creeger (who recommended against the registrations) and Matt Lorber. Union Carbide presented their case that thiodicarb would not be a threat to ground water based on evidence of rapid decay of thiodicarb and methomyl residues. They forwarded this evidence to Dennis Edwards of the Registration Division. Review of that data can be found in EAB files under #70106, dated 1/8/87. Briefly, EAB concluded that leaching events near the time of thiodicarb application potentially could transport methomyl residues, and that actual use field studies would be necessary to evaluate this potential.

Union Carbide has submitted the protocols reviewed here in an attempt to answer EAB's concerns on the leaching potential of thiodicarb.

10. DISCUSSION

Union Carbide contends that determination of a soil half-life for thiodicarb is not possible because thiodicarb is applied to foliage several times in one season. Once applied to the foliage, it would not be possible to precisely determine the amount of residue which washes off the leaves to enter the soil. Determination of this "source term", or amount initially in the soil, is necessary for half-life determination. For this reason, Union Carbide has recommended innovative studies in order to determine half-lives. Each of their study protocols will be reviewed separately.

Unsaturated Zone Field Study:

These studies are unacceptable mainly because the primary degradate, and the degradate of major concern for leaching potential, methomyl, is being applied rather than parent compound thiodicarb. As well, some aspects of the proposed study design, such as irrigation, require refinement. Rather than a point-by-point discussion of Union Carbide's proposal, the following study design is recommended.

- The proposed site is acceptable.

- One study plot would be acceptable if all the other specifications of this review are met - two plots are not necessary although the registrant is encouraged to continue with two plots if they feel that their case would be strengthened.

- Application of 3 lb/ac of thiodicarb directly to the soil surface in the same liquid formulation that normally is applied as a foliar spray. No shanking or mixing into the soil.

- Application 6-8 weeks following planting as proposed.

- Irrigation to insure that 150% of normally occurring rainfall is applied to the plot. Checks on this percent should occur in the following interval: weekly for one month following application, and monthly thereafter. At each checkpoint, the actual rainfall plus irrigation should be compared to historical averages to insure that the cumulative amount of water applied to the plot (at the checkpoints) is 150% of normally occurring rainfall. For example, if the application is made on May 1, then the checkpoints would be May 8, 15, 22, and May 31. At these four dates, the rainfall plus irrigation should equal 1/4 of May's historical rainfall times 1.5 on May 8, 1/2 the historical monthly amount times 1.5 on May 15, 3/4 times 1.5 on May 22, and total times 1.5 on May 31. For the saturated zone studies, Union Carbide proposed weekly irrigations to insure that monthly totals equal 150% of historical totals. These weekly irrigations are acceptable for months following the first month after application,

and the amounts of weekly irrigations needn't be rigorously determined as recommended for each weekly checkpoint of the first month following application.

- Soil sampling should occur pre-treatment, post-treatment, day 3, 7, 14, 21, 28, 56, 84, 112, 140, and continuing at 28-day intervals until all the residues have dissipated. The sampling increments should be 0-6 inches, 6-12 inches, and at one-foot increments to a total depth which insures that residues have been accounted for, or to ten feet, as proposed by Union Carbide. A minimum of four samples per depth per date is required. Union Carbide is encouraged to follow the design of previous aldicarb studies, in which the study field is broken into quadrants, and four samples per quadrant are composited, resulting in analysis of four composited samples. Union Carbide should not begin the study until they are assured that the soil sampling procedure does not result in the cross contamination problems which were partially responsible for invalidating the earlier bare soil thiodicarb dissipation studies.

Saturated Zone Monitoring

The proposal by Union Carbide for saturated zone monitoring is essentially acceptable with the following exceptions:

- The irrigation schedule should be similar to the irrigation schedule proposed for the unsaturated zone study, including the rigorous schedule for weekly checkpoints for the first month following application.

- The proposal for two nested wells per site is acceptable. Both sets of wells should be sufficiently distant from each other to insure that they are not sampling from the same location in the saturated zone. However, sampling of these should not be keyed to soil sampling. Soil sampling is unnecessary, and needn't be conducted by the registrant for these saturated zone monitoring.

- The well sampling schedule should be as follows:
  pre-application, immediately post-application (i.e., after the last foliar application)
  minimum of weekly samples for two months post-application, and monthly samples up to a period of one year post-application, and for monthly periods following one year if the last sampling periods showed residues in the wells.
  sampling following rainfall or irrigation events sufficient to cause recharge. Best judgement of the registrant should be used to determine whether a rainfall or irrigation event causes recharge. In general, 1/2 inch or more water should be considered sufficient to cause recharge. Sampling following such events can supercede the weekly or monthly schedule suggested above. For example, the regularly scheduled sampling does not have to occur if a recharge event occurred within 3 days of the regularly scheduled

weekly sampling, or within 14 days of the regularly scheduled monthly sample.

- The registrant is encouraged to sink additional wells as proposed, if there is evidence that thiodicarb or methomyl has reached the saturated zone. For example, if high residues of methomyl have reached the on-site nested wells, followed by readings of lower residues, followed by non-detects, it is quite possible that the residues have moved off-site, rather than degrading prior to moving off-site. For this reason, additional wells placed off-site would be needed to precisely determine the fate of residues which reached the saturated zone on-site as evidenced by positive findings on several dates of sampling.

Soil Sampling Procedure

This sampling would appear to be sufficient. The registrant is encouraged to field test it if there is some reason to believe that samples can become cross-contaminated as occurred in the earlier thiodicarb bare soil studies which were deemed unacceptable.

6

Rick - I was aware of ... problem in para #2. I ... this to Anne Barton ... I suggest McCone/Barton ... this ... we meet to discuss
Jim Akin

UNION CARBIDE

UNION CARBIDE AGRICULTURAL PRODUCTS COMPANY, Inc.
P. O. BOX 12014, T. W. ALEXANDER DRIVE
RESEARCH TRIANGLE PARK, N. C. 27709
(919) 549-2000

March 6, 1987

(1) HED check

(2) HED/... - Gen'l policy - Specific ... - Status of ...

(3) A...

(4) I'll call

Mr. Edwin F. Tinsworth
U.S. Environmental Protection Agency
Crystal Mall Building 2
1921 Jefferson Davis Highway
Arlington, VA 22202

Dear Mr. Tinsworth:

The purpose of this letter is to bring to your attention certain registration difficulties and delays we are experiencing due to uncertainties over the Agency's groundwater policy, and to request a meeting with you to resolve those uncertainties. Although we have experienced groundwater policy problems with registration actions on a number of products, the current situation involves our LARVIN® brand thiodicarb insecticide. Thiodicarb is a carbamate insecticide registered for use on cotton, soybeans and sweet corn. Registrations are pending for its use on vegetable crops, almonds and ornamentals. Thiodicarb initially degrades to methomyl, which as you know is a widely registered pesticide, and further degradation is of course the same as that for methomyl.

Our concern is that the Exposure Assessment Branch (EAB) is implementing a groundwater "policy" that results in denying new use registrations unless there is no chance that a pesticide can reach groundwater at any depth, at any concentration, under any circumstance. We believe that this EAB "policy" -- which has been expressed to us on several occasions orally and in writing--does not represent the views of OPP or OPTS senior management.

While we are aware that OPP/OPTS has not yet firmly established a final agrochemical groundwater policy, we understand that an interim working policy is in place which involves evaluation of the potential for residues to reach groundwater, including estimation of the magnitude of such residues, identification of the conditions under which leaching might occur, and the predicted frequency of occurence. These predictions are then compared to a probable Health Advisory Level for the chemical and a judgement of registerability is made. Based upon Union Carbide's experience, and the experience of other registrants with whom we have compared notes, this OPP/OPTS interim policy has not been adequately or effectively communicated to the management or staff of EAB.

RECEIVED
MAR 12 1987

13-076

7

We believe we have submitted the necessary information to adequately demonstrate acceptability of proposed registrations for LARVIN® under the OPP/OPTS interim working policy. However, we do not believe it is possible to demonstrate that any product will always meet the criteria envisioned by the Exposure Assessment Branch. A summary of our evaluation, along with a summary of the points of agreement and disagreement with the EAB, is appended.

We have been asked to conduct very difficult, costly and time consuming field research to prove that our product meets the criteria set out by EAB. Obviously we are concerned that no guidelines are in place that allow objective determination of when such studies are necessary, how to conduct such studies so they will be acceptable to the Agency, and how to interpret results once they are in hand. We are concerned that under EAB's current interpretation we will still not get the desired registration, regardless of study results.

We request your assistance in resolving this matter. Specifically, we request reconsideration of our groundwater assessment in accordance with OPP/OPTS interim working policy. If the Agency still considers the research requested by EAB to be necessary, we request timely approval of protocols and agreement on how results will be used in the registration decision. We are enclosing protocols which we have developed to address the concerns raised by EAB so that review can be completed and agreement on the protocols reached by May 1. Please do not misinterpret our submission of protocols for these studies. Although we believe these studies are unnecessary, we are including them as a contingency measure to assure timely approval of the protocols if your decision is that the studies are indeed necessary.

We would like to meet with you early next week to resolve this issue, but no later than March 20, 1987 if at all possible. Thank you for your consideration.

Sincerely,

J.S. Lovell
Registration Manager

cc: James Akerman
Dennis Edwards

8

SUMMARY OF THIODICARB GROUNDWATER ASSESSMENT

- Laboratory studies show that thiodicarb is unstable in sterile and non-sterile soils (half-life <1 wk), and that methomyl is similarly unstable in microbially active soils.

- Laboratory soil leaching studies show that thiodicarb is essentially immobile while methomyl is relatively mobile.

- Field studies (6 trials in 3 widespread geographical locations) show both thiodicarb and methomyl to be relatively non-persistent in soil (half-life of 3-8 days) and show no significant movement of either compound below one foot.

- Extrapolations via PRZM simulation to worst case conditions project no significant movement of residues below two feet.

- Long Island monitoring of approximately 7,500 water samples by Suffolk County in 1982 and 1983 showed detectable residues in only 38 samples, none greater than 10 ppb. (Methomyl has been registered for use on Long Island for well over a decade. The probable Health Advisory Level for Methomyl is 200 to 250 ppb).

- Based on the above, the proposed uses of thiodicarb appear to represent a minimal risk to groundwater, and any risks involved are negligible in comparrison to risks related to the existing widespread registered uses of methomyl.

ANALYSIS OF THIODICARB GROUNDWATER REVIEW COMMENTS

MAJOR POINTS OF AGREEMENT

The half-life of thiodicarb and its metabolite methomyl is less than two weeks in surface soils.

If the half-life of thiodicarb and its metabolite methomyl are 3 to 8 days as indicated in Union Carbide's field studies, model simulations indicate little potential for leaching (No significant residues below two (2) feet).

Residues observed below two feet in field dissipation studies were the result of contamination introduced during the sampling process.

MAJOR POINTS OF DISAGREEMENT

The reviewer believes that methomyl will not degrade below the root zone while UCAPCO feels, based on the field dissipation study results and Long Island groundwater monitoring, methomyl continues to degrade.

Because residues were found in deeper soil samples as a result of the soil sampling procedure in the 1982 field dissipation studies, the reviewer feels that the entire studies are not valid. UCAPCO believes that analyses of core samples near the end of the study are conclusive in demonstrating the rapid dissipation of thiodicarb residues in soil (since the sampling procedure could not cause false readings of non-detectable residues).

The reviewer states that both thiodicarb and methomyl are mobile in soil while UCAPCO data indicate that thiodicarb is immobile (In later oral discussions the reviewer agreed with UCAPCO).

The reviewer (in both oral comments and in the written review) believes the <u>possibility</u> of any detectable concentrations in any groundwater is sufficient grounds for denying registration of a pesticide. UCAPCO believes registration decisions should be related to potential health effects.

Protocols for Thiodicarb
Field Research Studies

The field research studies outlined in this protocol are designed to address the questions raised by EPA's Exposure Assessment Branch in a recent review concerning soil half-lives and leaching potential of thiodicarb and its metabolite methyomyl. Because thiodicarb is applied to foliage several times in one season, precise measurement of soil half-life is not possible under typical use conditions. Therefore, the proposed studies consists of two different parts. The first part consists of unsaturated zone studies with single applications of methomyl to address EAB's concern that the relatively mobile metabolite methomyl will not degrade in sub-surface soils. The second part consists of saturated zone monitoring in two locations underneath plots treated under maximum thiodicarb use conditions to determine the extent and persistence of residues that might reach shallow groundwater.

Unsaturated Zone Field Study

Purpose

The purpose of this experiment is to determine the persistence of methomyl (the mobile metabolite of thiodicarb) in both root zone and sub-surface soils.

General Description

Methomyl will be applied to two plots of cotton. In one of the plots methomyl is shanked into the soil to a depth of 12 inches. This will allow the determination of half-life in subsoil. In the other plot methomyl will be sprayed on the soil surface to determine the half-life in the root zone. Soil samples are collected and analyzed to determine the degradation rate of methomyl in each plot.

Methomyl is applied rather than thiodicarb in the study because the relatively immobile thiodicarb will not move significantly downward until transformed into methomyl. Therefore only the half-life of methomyl is relevant below the surface layer of soil. Methomyl is applied to the surface plot to provide a comparison for the subsoil degradation rate and because the depth and magnitude of residue leaching (but not the timing) will be relatively independent of the transformation rate of thiodicarb to methomyl.

Site Description

The two plots, not previously treated with methomyl or thiodicarb, will be located on a Norfolk sandy loam soil at the UCAPC research farm near Clayton, North Carolina. Each plot will be approximately a quarter acre in size and a cotton crop will be grown on each plot using conventional agricultural practices for the area.

Pesticide Application

Approximately six to eight weeks after planting methomyl will be applied to both plots at a rate of 3 lb of active ingredient acre. In one plot, the methomyl will be sprayed directly onto the soil between the cotton rows. In the other plot, the methomyl will be shanked into the soil to a depth of 12 inches. These application procedures are designed to place the methomyl at the soil surface in one plot and directly into the subsoil in the other plot for the purposes of this study only. Such application procedures do not represent commercial practice for either methomyl or thiodicarb.

Soil Samples

Soil samples will be collected prior to treatment with methomyl and at intervals of about 1/2, 1 and 2 months and at two month intervals thereafter. Sample collection will be terminated after the amount of residues remaining drops to below about 10 percent of the applied material. The pretreatment sampling will consist of four cores (two for each plot) down to a depth of 10 feet divided into increments of 0-1, 1-2, 2-4, 4-6, 6-8, and 8 to 10 feet. At each post-treatment sampling interval, 16 cores will be collected from each plot. The actual depth of the post-treatment cores will depend on the amount of rainfall occurring during the experiment and the soil sample analysis from the previous sampling interval. All soil samples will be collected using the appended bucket auger soil sampling procedure.

Saturated Zone Monitoring

Purpose

The purpose of these experiments is to determine the extent and magnitude of thiodicarb or methomyl residues that reach shallow groundwater under actual thiodicarb use conditions.

General Description

Thiodicarb will be applied to corn using maximum use conditions at two plots, one located in New York and the other in Florida. Shallow monitoring wells will be installed in the plots to determine the amount and persistence of thiodicarb or methomyl residues entering the saturated zone.

Site Description

The Florida plot will be located on a Pompano loamy sand and the New York plot will be located on a Hinckley sandy loam. Although water tables of five feet or less will be sought for both sites, it may be necessary to select a field with a water table depth up to 10 feet in New York. Each plot will consist of an irrigated one acre corn field. If necessary the plots will be irrigated weekly in order to insure that the amount of rainfall plus irrigation equals 1.5 times the normal monthly rainfall. In all other respects normal agricultural practices for the region will be followed. Both plots should not have received applications of methomyl or thiodicarb in 1986 or 1987 prior to the start of these experiments.

12

Pesticide Applications

At each site six applications of thiodicarb each at a rate of 0.09 lb of active ingredient acre will be made over approximately a two week period beginning in September. Each application of thiodicarb will be made in the form of a foliage spray. This application schedule represents the maximum use of thiodicarb likely to result from any existing or future registration.

Monitoring Wells

In the middle of each field two clusters of wells will be installed prior to application of the thiodicarb. Each well cluster will consist of two wells, one screened just below the water table and the other screened 5 feet below the water table. Each well will consist of 1 1/2 in PVC schedule 80 pipe attached to a one-foot long well screen with 0.006 in slots. Wells will be installed manually by augering to the water table and then driving the casing to the desired depths. If methomyl is detected in water samples, additional wells may be required to determine movement and persistence of any residue plume.

Water Samples

Water samples will be collected from monitoring wells prior to the first thiodicarb treatment, after all of the applications have been completed, and at one and two months following the last application. If soil samples indicate greater than 5% of the applied material remain two months following application, additional water samples will be collected at one month intervals (weather permitting at the New York site). Water samples will be collected using a peristaltic pump. Five times the amount of the water standing in the well will be discarded prior to each sample collection.

Soil Samples

Soil samples will be collected prior to application of thiodicarb and two months following the last application. If greater than 5 percent of the applied material remain after two months, additional soil cores will be collected at approximately two month intervals (weather permitting at the New York site). Pretreatment samples will consist of four cores per plot and post-treatment samples will consist of sixteen cores per plot. Each core will be divided into one-foot increments down to two feet and thereafter in two-foot increments to the water table.

Study Termination

If significant residues are not found in water samples and residues in soil are below 5 percent of the applied material, the study will be terminated with the conclusion that signicant residues did not reach groundwater.

SOIL SAMPLING PROCEDURE

1. Remove loose surface soil and vegetation from the area surrounding the sampling site.

2. Using a 3.25 inch (8.2 cm) bucket auger, turn the handle until the bucket is full (approximately 2-3 cm above the edge of the bucket).

3. Place the entire contents of the auger in a clean 4-8 liter polyethylene bag by shaking the auger (at no time should hands come in contact with the auger bucket or the soil sample).

4. Place the bucket auger back into the hole and obtain another full bucket of soil.

5. Before placing the contents of the auger into the plastic bag, remove the upper 2-4 cm of soil by shaking and rotating the auger.

6. Repeat steps 4 and 5 until the desired depth is reached. Approximately 2 bucketfuls will be required for a 1-foot (30 cm) increment and 4-5 bucketfuls for a 2-foot (61 cm) increment.

7. After all the soil from the desired soil depth has been obtained, mix the soil in the polyethylene bag by sealing the bag and then agitating and kneading the contents.

8. After the soil has been thoroughly mixed, place about a half-liter aliquot of soil into a smaller polyethylene bag taking care to get a representative sample of soil.

9. Place small polyethylene bag containing the soil sample into a properly labeled cloth bag.

10. Immediately store the soil sample in a cool place, such as an ice chest.

11. Carefully clean the bucket auger using water and a scrub brush to remove any soil particles present in or on the auger.

12. Repeat steps 4-11 to obtain soil samples at each of the desired depths.

13. At the end of each day, freeze all of the soil samples and keep them frozen until they are analyzed.