Shaughnessy Number: 114501

Date Out of EAB: 6/24/88

TO: Dennis H. Edwards, Jr.
Product Manager 12
Registration Division (TS-767C)

FROM: Patrick Holden, Team Leader PWH
Ground-Water Team
Exposure Assessment Branch/HED (TS-769C)

THRU: Paul F. Schuda, Chief
Exposure Assessment Branch/HED (TS-769C)

Paul F. Schuda

Attached, please find the EAB review of:

Reg./File #: 264-379

Chemical Name: Thiodicarb

Type Product: Insecticide

Company Name: Rhone-Poulenc

Purpose: Review of field leaching study for thiodicarb and its metabolite methomyl.

Date Received: 3/17/88 ACTION CODE: 300

Date Completed: 6/20/88 EAB #(s): 80587

Monitoring study requested: X Total Review Time: 40 hr

Monitoring study voluntarily: ___

Deferrals To: ________ Ecological Effects Branch

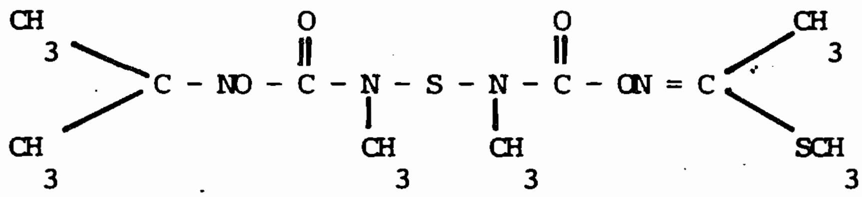
________ Residue Chemistry Branch

________ Toxicology Branch

REVIEW OF FIELD LEACHING STUDY

1. CHEMICAL:

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



2. TEST MATERIAL:

Thiodicarb and methomyl (metabolite of thiodicarb).

3. STUDY/ACTION TYPE:

Review of field leaching study of thiodicarb and its metabolite methomyl.

4. STUDY IDENTIFICATION:

Title: "Thiodicarb Insecticide Field Research Studies on the Movement and Degradation of Thiodicarb and its Metabolite Methomyl" by R.L. Jones, T.W. Hunt, F.A. Norris, and C.F. Hardin, File No. 40242, Rhone-Poulenc Ag Company, Research Triangle Park, NC, 2/33/88 with amendment submitted 5/10/88.

Submitted with letters dated 2/29/88 and 5/10/88 from Lizabeth Huckaba, Associate Registration Manager, Rhone-Poulenc Ag Company to Dennis H. Edwards, Jr., Registration Division, U.S. EPA.

Submitted by: Lizabeth Huckaba, Associate Registration Manager
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Identifying No.: 264-379
Action Code: 300
Accession Number: 405322-01
Record Number: 216,472
Date Sent to HED: 3-17-88

5. REVIEWED BY:

W. Martin Williams
Hydrologist
OPP/HED/EAB/Ground-Water Team

Signature: W. Martin Williams
Date: 6/14/88

6. APPROVED BY:

Patrick Holden
Team Leader
OPP/HED/EAB/Ground-Water Team

Signature: [signature]

Date: 6/24/88

7. CONCLUSIONS:

1) Thiodicarb is presently registered for food crops. All requirements have been satisfied for registration for terrestrial food crops (EAB #80133-80134).

2) Monitoring data obtained to date on methomyl (as Linnate) indicate that methomyl is unlikely to cause adverse toxicological concerns in ground water based on the small ratio of positive samples found per number of samples examined (29/3945) and the low concentrations found (traces up to 9 ppb maximum) in the positives. These concentrations are significantly lower than the EPA Office of Drinking Water proposed lifetime health advisory of 175 ppb.

3) Thiodicarb can be classified as mobile but not persistant under both laboratory and field environments. The field dissipation half-life of thiodicarb is only a few hours in surface soils and less than one week in subsoils. Laboratory data suggests that methomyl is mobile and fairly persistant. However, the field dissipation half-life of methomyl in the present study is several days in surface soils and varies from about two to eight weeks in subsoils. The longer subsoil half-lives occurred in the Clayton, North Carolina test plot in which a soil injection application process was used — which is not the procedure used in agricultural practice. Mobility is offset by rapid soil degradation.

4) The reviewer concurs with the author's conclusions that it is unlikely that concentrations of methomyl approaching health guidelines will result in ground water from the normal use of thiodicarb. The ground water studies were designed to be representative of worst case field situations -- sandy soils and shallow water tables. Detections of methomyl occurred essentially in only one sample from both wells in only one well cluster of only one site. The concentrations in the upper and lower well of the positive cluster were 20 and 2 ppb, respectively, which is significantly lower than the proposed ODW health advisory level of 175 ppb. However, thiodicarb has the potential to cause ground water concerns under different application rates and frequencies than those used in Palermo and Olviedo.

8. RECOMMENDATIONS:

On the basis of potential for thiodicarb/methomyl to contaminate ground water, the reviewer sees no objection to additional registration of thiodicarb for ornamental and non-crop uses under the application methods, rates, and schedules used in the Florida and New York field leaching studies reviewed herein. It is suggested that the detections of methomyl in ground water (up to 20 ppb), from this study and elsewhere, be brought to the attention of the Toxicology Branch prior to approving this additional registration. Because of the chemical properties of methomyl, the registrant would be wise to keep an eye on different hydrogeological areas in which thiodicarb is used to verify that adverse environmental conditions do not occur.

9. BACKGROUND:

Thiodicarb is an insecticide used to control worm pests on sweet corn, cotton, and soybeans. Registration for thiodicarb for ornamental and non-crop uses was denied based on leaching concerns for methomyl, the primary degradate of thiodicarb (EAB review 70106 dated 1/6/87). Field studies and soil metabolism studies submitted by the registrant, illustrate that thiodicarb rapidly metabolizes to methomyl (within a week). 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 be soluble and to move with water.

In EAB review #70106, 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 more rapid microbial decay of the upper soil zones. EAB recommended that an actual field leaching study on thiodicarb be required prior to registration on ornamentals and non-food uses (EAB file #70135).

Union Carbide has submitted several iterations on a protocol for a field leaching study (EAB files #70517 and #70780) in order to address EAB's concerns. The completed study is being reviewed herein.

10. DISCUSSION:

The completed field leaching study being reviewed herein is a modification of EAB's small-scale prospective ground-water monitoring study. The study was designed prior to EAB formalizing guidelines for the small-scale prospective study and, therefore, soil-water measurement using suction lysimeters and other present requirements for the small-scale prospective study have been relaxed. Although the leaching study for thiodicarb does not adhere exactly with present guidelines, the study has been well-designed to address concerns regarding the potential of methomyl to reach ground water.

The study was conducted correctly pursuant to the revised protocol dated 6/15/88 (EAB review #70780). The protocol had been found acceptable with the following three provisions: 1) all soil and water samples would be analyzed for (and separately report) methomyl and thiodicarb; 2) the sensitivities of water and soil samples must be a maximum of 1 and 5 ppb, respectively; and 3) the criteria for halting soil sampling would be based on a "sample" defined as a composite of the highest residue level from each depth increment of 16 cores analyzed, and a calculation of the mass from that "sample" results in less than 5% of applied material remaining. While EAB has no record from Rhone-Poulenc that these provisions would be adhered to prior to implementing the study, these provisions have been adopted in the study.

The study was designed as two parts. The objective of the first part was to determine the movement and degradation of thiodicarb and methomyl under actual field application procedures. Two sites (sweet corn) were selected as representative of areas most vulnerable to leaching where the product will be used (permeable soils and shallow ground water). One site is near Palermo in Oswego County, New York. Soils are described as Hinkley gravelly loamy sands which probably enhances macropore flow. Variations in soil composition and pH with depth are given in "Table 1" from the report which has been attached to this review. The water table is approximately 1.5 meters (five feet) from the surface. The second site is near Olviedo in Seminole County, Florida. The soils are described as Immokale fine sands. Soil composition and pH are given in "Table 1", attached. The water table resides approximately 0.1 to 0.9 meters (0.3 to 2.3 feet) from the surface. Thiodicarb was applied to both sites as a folier spray six times a year at the maximum use rate (0.84 kg/ha or 0.76 lb/ac) during a two week period. Both sites were irrigated (weekly) as necessary to achieve 1.5 times the average normal rainfall.

The objective of the second part of the study was to determine degradation rates and field dissipation half-lives of thiodicarb in surface soils and methomyl in both surface and subsoils. This study was designed separately due to the multiple foliar application of actual use practices which interferes with the ability to determine in-situ half-lives. One site was selected having three test plots. The site is near Clayton in Johnston County, North Carolina. Soils are described as Norfolk sandy loams. Soil composition and pH are summarized in "Table 1", attached. Water table depths exceed nine feet. On one plot, thiodicarb was applied at a rate of 3.36 kg/ha (3 lb/ac) as a spray to the soil surface between cotton rows. Irrigation was applied weekly on this plot as necessary to achieve 1.5 times the average normal rainfall. On the second plot, methomyl was applied at a rate of 3.36 kg/ha (3 lb/ac) as a spray to the soil surface between cotton rows. On the third plot, 3.36 kg/ha (3 lb/ac) of methomyl was injected into the soil at a depth of 0.3 meters (one foot) between cotton rows. Supplemental irrigation was not applied to the last two plots because the objective was to measure degradation at two different soil depths rather than to measure mobility under conditions favorable to leaching.

Clayton, NC Thiodicarb Plot. The study illustrates that thiodicarb rapidly degrades to methomyl. Within four hours of application, soil cores averaged 51 ug/kg of thiodicarb and 70 ug/kg of methomyl. The field half-life of thiodicarb was therefore under four hours. By day 6, thiodicarb degraded entirely with the exception of 1 ug/kg detection in a couple of soil cores. No detections were found below 0.6 meters. Methomyl degraded with a field dissipation half-life of less than six days. Methomyl remained relatively immobile in that detections were not reported below 0.3 meters. By day 13, the average soil core concentration was 2 ug/kg. A summary of soil core concentrations is shown in "Table 3" from the report (attached to this review). The lack of detection below 0.3 meters indicates degradation as opposed to migration.

Clayton, NC Methomyl Foliar Application. Field half-lives in the study remained under two weeks. Only concentrations at day 13 were reported and concentrations ranged from no detection to a high of 18 ug/kg with an average concentration of 1 ug/kg over 16 soil core samples. Although only day 13 was reported, it is unlikely that higher concentrations leached beyond the depths sampled based on the more frequent time snapshots and depths given in the other Clayton test plots. A summary of soil core concentrations is shown in "Table 4" from the report (attached to this review).

Clayton, NC Methomyl Injected. This application process illustrates that methomyl is more persistant in sub-soils than surface soils treated with a foliar application. Field half-lives range from 17 to 60 days. After 190 days, average concentrations in 0.0-0.3, 0.3-0.6, 0.6-1.2 and 1.2-1.8 meter depth ranges were 2, 18, 4, and <1 ug/kg, respectively. Concentrations exceeding 7 ug/kg were not reported in the 1.2 to 1.8 foot range. A summary of soil core concentrations is shown in "Table 5" from the report (attached to this review).

Palermo, NY. Soil cores were only taken twice — pre-treatment and two months after treatment. No detections of thiodicarb were reported in any soil cores. Detections of methomyl two months after treatment averaged 2 ug/kg with a maximum of 11 ug/kg in the 0.0 to 0.3 meter range as shown in "Table 6" from the report (attached to this review). Average concentrations were under 1 ppb for all successive depths with maximum concentrations of 2, 1, and <1 ppb in the 0.3-0.6, 0.6-1.2, and 1.2-1.8 meter ranges. Water samples contained one positive detection 10.08 feet deep at 1 ppb on 10/30/87 as shown in "Table 7" from the report (attached to this review). No further positives were reported at later sampling periods (next sample was 30 days later). The positive occurred after a period in which a combined total of 1.55 inches of rainfall and irrigation was applied over a three day period. At first glance, one may suspect that this detection resulted from this recharge event and that other samples were not positive due to insufficient rainfall around the time of sampling. However, two other samples, one in August and one in September, were taken after several preceding wet days — 1.35 inches and 1.90 inches of combined rainfall and irrigation. Since, these samples were non-detectable, it is less likely that the sampling program "missed" periods of leaching.

Olviedo, FL. As with Palermo, soil cores were only taken pre-treatment and two months after treatment. No detections of thiodicarb were reported in any soil cores. Detections of methomyl two months after treatment averaged less than 1 ug/kg with a maximum of 4 ug/kg in the 0.0-0.3 meter range. A methomyl concentration of 1 ug/kg occurred in one soil sample in the 0.3-0.6 meter range. Water samples showed one positve cluster. The cluster showed positive samples in both wells positive on 10/12/87 - 20 ppb in the shallow well and 2 ppb in the deeper well. This sampling event followed a four day period of rainfall in which combined rainfall and irrigation equaled 1.4 inches. As with Palermo, other water samples following periods of recharge produced no detections (2.0 inches prior to the 9/11 sample and 1.5 inches prior to the 10/26 sample). One detection of 1 ppb occurred in the deeper well of this same cluster on 12/10/87. This detection did not follow any recharge event and the concentration is low enough to be insignificant.

Comparison to Previously Submitted Data. Table 1 presents an assessment of the leaching potential of thiodicarb and methomyl based on data from several sources (references given in the table). The table illustrates that thiodicarb is mobile but not persistant. Methomyl appears to be mobile and fairly persistant. The aerobic soil dissipation rates are moderate — generally having half-lives on the order of a few weeks. This could be a concern for some chemicals depending on the frequency and rate of application. Anaerobic soil dissipation is quite rapid. This is a very significant point in that the majority of pesticides are stable under anaerobic conditions but some acutually degrade more rapidly. Methomyl appears to be in this category which reduces the likelihood of significant residues impeding ground water before they are degradd. It is important to note, however, that EAB files do not contain many anearobic soil metabolism studies on methomyl. Methomyl is very soluble and both compounds are stable to hydrolysis at pHs common to ground water (5-8). However, laboratory studies with sterilized reagent water are not necessarily representative of field environments in the soil or subsoil.

Processes other than hydrolysis appear to govern degradation in the field. The field studies support previously reported conclusions that thiodicarb rapidly degrades to methomyl. Field dissipation half-lives on the order of four hours are less than the aerobic and anaerobic soil half-lives in Table 1 and 3-8 day field dissipation half-lives reviewed in EFB #622,623 (5/1/88). Field dissipation half-lives for methomyl (<2 weeks) in surface soils compare favorably to two field dissipation studies (<1 month and <7 days) submitted under the registration for Linnate (Simko, 1987). However, it should be noted that the Linnate studies were found inadequate due to insufficient supporting information. Longer subsoil half-lives in Clayton (up to 6 weeks) support the conclusion in EAB review #70106 (1/8/88) that degradation of methomyl is significantly enhanced by microbial activity.

Other Data Sources. For general information, the Exposure Assessment Branch has no records on monitoring for thiodicarb in ground water to date. However, methomyl (reported as Linnate) has been detected in 29 out of 3945 samples in Suffolk County, New York at concentration levels of "traces up to 9 ppb" (Holden, 1986). These findings indicate a low occurrence in ground water (sample positives to total sample ratio of .0075) at concentrations significantly lower than the proposed lifetime health advisory of 175 ppb (ODW, 1988).

Addressing Concerns of EAB #70106. Registration for ornamental and non-foocrops was denied for four reasons. These reasons, and their current standing, are discussed below.

1) The "integrity and usefulness" of previous field leaching studies were questioned because they "did not mimic actual field conditions". Also,

TABLE 1
LEACHING ASSESSMENT FOR THIODICARB/METHOMYL

Property	Thiodicarb[1]	Methomyl[2]	Guidelines[3]
Adsorption Partition Coefficient	1.34 clay loam 0.58 loamy sand 1.22 sandy loam	0.2-0.7 sandy loam 2.6-2.8 silt loam	<5.0, <1.0 or 2.0
Solubility	35 ppm @ 25° C[4]	58,000 ppm[5]	>30 ppm
Hydrolysis half-life	6 days @ pH 3 stable @ pH 6 0.9 days @ pH 9	stable pH 3 stable pH 6 30 days pH 9	>25 weeks
Photolysis half-life	21 days sandy loam 8 days loamy sand >28 days clay loam 81 days aqueous	34 days silty clay loam 1 day aqueous	>1 week
Aerobic Soil half-life	<1 week	30-45 days silt loam. <1 week sandy loams[1]; stable sterile sandy soils	>2-3 weeks
Anaerobic Soil half-life	1 week	<8 days	>2-3 weeks

[1]EFB Review #622,623 dated 5/1/81
[2]Simko (1987)
[3]Cohen, et.al (1984)
[4]EAB Review #60794 dated 12/5/86
[5]<u>Farm Chemicals Handbook</u> (1984)

assumptions by the registrant to more rapid degradation under actual use conditions had not been scientifically concluded. The present study was performed under worst-case actual use conditions.

2) Soil metabolism studies indicate that residues are "stable in sterile and stored soils, which have nonexistant or low microbial populations". The present study was performed in three geographical locations which varied in sand, clay, and organic matter content. Field half-lives under foliar application averaged two weeks for methomyl. Sub-soil half-lives ranged from 2 weeks to 2 months. In actual use, significant degradation appears to occur in surface soils prior to migrating to more microbial free sub-soils.

3) "EAB files indicate methomyl stability to hydrolysis". These files illustrate stability under acidic and neutral sterilized water. However, laboratory studies with sterilized reagent water are not necessarily representative of field environments in the soil or subsoil. Furthermore, pHs in the field studies varied from 4.3 to 6.6 and yet concentrations did not persist. Both the Palermo and Olviedo test sites contained actual application methods and shallow ground water. Processes other than hydrolysis appear to govern the rate of degradation in actual field environments.

4) "Both thiodicarb and methomyl have low adsorption partition coefficients, which translates to rapid downward mobility if transported by water prior to degradation". This is particularly a concern given the high solubility of methomyl. However, the field studies, conducted under environments conducive to leaching, did not show significant transport to ground water. It is possible, but not probable, that methomyl migrated through the soil and was missed by the sampling program due to too infrequent sampling intervals. The schedule approved for the protocol was adhered to in the study, although day six post-treatment soil samples were not reported for either of the methomyl application plots for Clayton. However, the day 13 conditions for both the methomyl and thiodicarb foliar application plots are similar -- this is to be expected given the rapid (several hour) degradation rate of thiodicarb. Since the thiodicarb treated field does not indicate that the sampling program missed movement of methomyl because no detections occurred at the lowest depth interval of each sample interval, one can conclude the same conditions occurred in the methomyl foliar application test plot. This conclusion is substantiated in that irrigation was not applied to the methomyl application plots. Concentrations of methomyl in soil on day six of the methomyl plot with subsoil application would probably not provide additional useful information given the pattern of changes in the successive sample intervals. The dissipation half-life exceeds two weeks and the deepest soil cores do not indicate substantive losses to lower depths.

Soil sampling in Palermo and Olviedo is not frequent enough to track movement through successive soil depths, however, water samples were taken immediately after the last application (roughly one week beyond the first application) and at 0.5, 1, 1.5, 2, 3, and 4 months after the final application. Given the laboratory half-lives for methomyl and the field soil dissipation rates in Clayton, this sampling frequency should catch movement into the ground water. Palermo had 1.0 inches of irrigation during the first few days of thiodicarb application and no recharge for the four following applications leading to the first sample several days later. Olviedo had significant precipitation during the week of application (total combined rainfall and irrigation equalling 8.3 inches). In other words, both sites had very different recharge conditions during application and no detections in ground water occurred in the first sampling immediately after the last application.

<u>REFERENCES</u>

1. Holden, Patrick W., <u>Pesticides in Ground Water Quality: Issues and Problems in Four States</u>, prepared for the Board on Agriculture National Research Council, National Academy Press, Washington, D.C., 1986.

2. Orme, Jennifer, U.S. Environmental Protection Agency, Office of Drinking Water, personal communication, April 1988.

3. Cohen, S.Z., S.M. Creeger, R.F. Carsel, and C.G. Enfiel, "Potential Pesticide Contamination of Groundwater from Agricultural Uses, in Treatment and Disposal of Pesticide Wastes", ACS Symposium Series #259, R.F. Krueger and J.N. Seiber, ed., American Chemical Society, Washington, D.C., 1984.

4. <u>Farm Chemicals Handbook</u>, Meister Publishing Co., Willoughby, Ohio, 1984.

5. "Methomyl Registration Standard (FRSTR)", memorandum to D. Edwards, U.S. EPA/RD, and A. Rispin, U.S.EPA/HED, from S. Simko, U.S.EPA/HED, 11/9/87.