Shaughnessy No.: 128834

Date Out of EFGWB: MAR 16 1990

TO: Robert Taylor
Product Manager # 25
Registration Division (H7505C)

FROM: Paul Mastradone, Chief
Environmental Chemistry Review Section #1
Environmental Fate and Groundwater Branch

THRU: Henry Jacoby, Chief
Environmental Fate and Groundwater Branch
Environmental Fate and Effects Division (H7507C)

Attached please find the EFGWB review of:

Reg./File # : 42545-LE and 42545-LG

Chemical Name : Pyridate

Product Type : Herbicide

Product Name : Tough

Company Name : Agrolinz, Inc.

Purpose : Agrolinz Response to Pyridate New Chemical Registration Standard

Date Received : 3/6/90 Action Code: 101

Date Completed : 3/14/90 EFGWB No. : 90-0412-13

Total Reviewing Time (decimal days): 5.5

Deferrals to :
_____ Ecological Effects Branch, EFED
_____ Science integration & Policy Staff, EFED
_____ Non-Dietary Exposure Branch, HED
_____ Dietary Exposure Branch, HED
_____ Toxicology Branch, HED

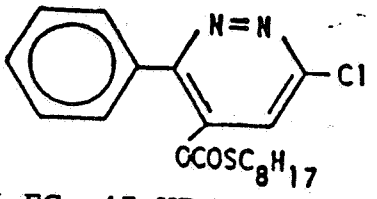
1.0 CHEMICAL:

Common Name: Pyridate

Chemical Name: O-(6-Chloro-3-phenyl-4-pyridazinyl)- S-octyl-carbonothioate.

Trade Names: Tough

Structure:



Formulations: 3.75 EC, 45 WP

Chemical/physical properties:

Molecular formula: $C_{19}H_{23}ClN_2O_2S$
Molecular weight: 378.9
Physical state: crystalline solid
Vapor pressure: 133 nPa
Solubility: ≈1.5 mg/L in water at 20°C; highly soluble in organic solvents.

2.0 TEST MATERIAL: Not applicable since no study was submitted.

3.0 STUDY/ACTION TYPE: Review Agrolinz response to the EFGWB science chapter of the Pyridate new chemical registration standard.

4.0 STUDY IDENTIFICATION: Agrolinz response to the Pyridate new chemical registration standard. Authors: S. Creeger, H. Bodingbauer, and J. R. Fisher. Performed by Environmental Chemistry Institute, Pittsburgh, PA, 15217 and Agrolinz, Inc., Memphis, TN, 38119. Pack No. 50191 EFED, record nos. 260287, 260288 No MRID or Accession numbers.

5.0 REVIEWED BY:

Richard J. Mahler
Hydrologist, Review
Section 1, EFGWB, EFED

Signature: Richard J. Mahler

Date: MAR 15 1990

6.0 APPROVED BY:

Paul J. Mastradone, Chief
Review Section 1, EFGWB, EFED

Signature: Paul J Mastradone

Date: MAR 16 1990

7.0 CONCLUSION:

Agrolinz, Inc., the registrant, presented their responses to the Pyridate EFGWB science chapter new chemical registration standard dated 12/21/89. In general, the responses have only changed the status of one of the studies (Confined Accumulation in Rotational Crops--165-1) as presented in the EFGWB science chapter. After a thorough review of the study, EFGWB has concluded that the Confined Accumulation in Rotational Crops study is scientifically valid and satisfies the data requirements. However, many major validity questions remain unanswered in regards to the other studies that do not satisfy the data requirements.

The following Environmental Fate studies still remain unfulfilled:

161-2--AQUEOUS PHOTODEGRADATION
161-3--SOIL PHOTODEGRADATION
162-2--ANAEROBIC SOIL METABOLISM
163-1--LEACHING AND ADSORPTION/DESORPTION (PARTIALLY SATISFIED)
164-1--FIELD DISSIPATION

EFGWB original comments (as paraphrased by Agrolinz), Agrolinz response to EFGWB original comments and EFGWB rejoinder are listed below under section 10.0, "Discussion of Individual Studies."

8.0 RECOMMENDATIONS: Inform the registrants of EFGWB's specific reply to each of their responses to the EFGWB Science Chapter New Chemical Registration Standard for Pyridate dated 12/21/89.

9.0 BACKGROUND: The applicant has responded to the EFGWB Science Chapter for the New Chemical Registration Standard for Pyridate.

10.0 DISCUSSION OF INDIVIDUAL STUDIES:

10.1 **PHOTOLYSIS IN WATER--161-2**

1. EFGWB Original Comment: Material balance incomplete.

Agrolinz Response: The material balance presented in this study is not based on actual measurement but by extrapolation from a separate study showing the radioactivity not in solution is CO_2. Adding in production of CO_2 corrects the material balance.

EFGWB Rejoinder: EFGWB does not accept the rationale as presented by the registrant related to the material balance. Prudent scientific methodology dictates that material balance be determined at each sampling time. The study author failed to do this except for irradiated samples of CL-9673 for day 23 at pH 5 which included predominantly CO_2. This reviewer concedes that CO_2 was the only product of volatilization at day 23 and in a pH 5 solution that had been irradiated. However, extrapolating the amount of CO_2 produced at one time and pH value to other times and pH values is not scientifically supported. The study author, at a minimum, should have measured volatile products at one or two other sampling times and pH values.

2. EFGWB Original Comment: All degradates >10% of initial material not identified (61.87% was origin material).

Agrolinz Response: Origin material was separated by TLC into 6 peaks each not exceeding 10% of the initial material.

Only one instance of unidentified product exceeding 10% at pH 5 and only at Day 23 of the 35 day study (16.6%). This unidentified product did not form at all at pH 7 and pH 9. Natural aquatic systems are not typically at pH 5.

EFGWB Rejoinder: If the registrant can provide the data that shows that the origin material separated by TLC into 6 peaks did not exceed 10% of the initial material, then EFGWB will probably conclude that the comment has been responded to adequately. The registrant should note that Subdivision N Guidelines, Photodegradation Studies in Water, Section 161-2 (d)(3) states in part that "the test report should contain the following specific information: Identification of each photoproduct produced in greater than 10 percent yield at any point during the course of the study..."

3. EFGWB Original Comment: Acetonitrile comprised 5% by volume instead of maximum of 1%.

Agrolinz Response: True. However, no significant differences are anticipated between studies done at 5% and 1% acetonitrile. Use of acetonitrile as a cosolvent at 5% was necessary to effect a starting concentration high enough to allow the study to be conducted.

EFGWB Rejoinder: EFGWB can not accept the rationale that no significant differences are anticipated without submission of data showing no differences between studies done at 1% and 5% acetonitrile concentration. Furthermore,

based on EFGWB experience, the Subdivision N Guidelines, Photodegradation Studies in Water, Section 161-2 (c)(2)(ii) were written to state in part, "For pesticides of low water solubility, an appropriate solubilizing co-solvent may be added to increase water solubility. However, use of such agents should be avoided whenever possible, and, if used, the concentration of co-solvent in the final solution should not exceed 1 percent by volume."

4. EFGWB Original Comment: Volatiles traps were analyzed on Day 23 only.

Agrolinz Response: Production of volatiles was monitored in a separate 23-day experiment which showed CO_2 to be the only volatile produced during 23-days of irradiation. Therefore, it was assumed that no other volatiles would be produced during the rest of the 30-day study.

EFGWB Rejoinder: While this may be true for the solutions at pH 5, EFGWB can not assume that the same conditions would prevail under other pH values and therefore, cannot accept the rationale as presented by the registrant. Refer to the discussion above under number 1.

5. EFGWB Original Comment: Daily meteorological data not provided.

Agrolinz Response: True. However, these data are available, and show typical weather conditions were prevalent.

EFGWB Rejoinder: Before EFGWB can accept this response in resolving the original comment, the registrant should provide the data that supports this.

6. EFGWB Original Comment: Conditions of sterility, buffer composition, dark control incubation conditions, and certain methodology not provided.

Agrolinz Response: Solutions were sterile, typical buffers were used, dark controls were maintained at same temperature as exposed samples, and complete analytical methodology is available.

EFGWB Rejoinder: Before EFGWB can accept this response in resolving the original comment, the registrant should provide the data that supports this.

AGROLINZ CONCLUSIONS: Although the study did not strictly follow the Guidelines protocol, it provides information showing Pyridate to rapidly hydrolyze ($t_{1/2}$ less than one

day to three days) to CL-9673 which in turn photodegrades principally to numerous polar compounds and CO_2.

EFGWB CONCLUSIONS: This study still does not fulfill EPA Data Requirements for Registering Pesticides. Not only has the registrant not adequately responded to the above comments by EFGWB, but they failed to respond to all the comments that were mentioned in the EFGWB Science Chapter for Pyridate. Two studies were submitted (See attached DERs for Studies 2 and 3) related to aqueous photolysis of pyridate and CL-9673; however, the registrant has neglected to respond to all of the comments in the two studies.

10.2 **PHOTOLYSIS ON SOIL--161-3**

1. EFGWB Original Comment: Too few data points. Degradation half-life cannot be estimated from the data. Linear regression not applicable.

Agrolinz Response: There were five data points, whereas the Guidelines only require four. The reported half-life of 1.7 days is correct. The reviewer's calculated half-life of -7.7 is incorrect. The logarithmic conversion of the data are linear with a correlation coefficient of 0.833. The reviewer's graphical representation does not show the data to be linear because the x- and y-axes are out of proportion.

EFGWB Rejoinder: EFGWB can not accept the rationale that the data presented is in fact linear, since in all four soil treatments more than 50% of the applied pyridate degraded prior to the second sampling interval. As has been previously stated (See attached DER for Study Number 4), three of the five data points used for each treatment were for intervals after which little pyridate remained. More frequent sampling intervals should have been used.

2. EFGWB Original Comment: Material balances were incomplete.

Agrolinz Response: At the end of the study, actual material balance measurements were made and each showed material balances greater than 87%. Therefore, material balances during the earlier periods of the study can reasonably be assumed to be greater than 87%. These values indicate good material balances during the study.

EFGWB Rejoinder: EFGWB does not accept the rationale as presented by the registrant related to the material balance. Prudent scientific methodology dictates that material balance be determined at each sampling time.

Furthermore, although the registrant stated that actual material balances were obtained for the 68-day sampling interval, footnotes in Tables 1 and 2 (attached) state that the percentage of carbon dioxide was calculated by subtracting the sum of the measured extractable and nonextractable radioactivity from the value for the material balance. If the percentage of evolved CO_2 was calculated, how was this "actual measurement" material balance determined? Therefore, the material balances presented for the 68-day intervals are questionable.

3. EFGWB Original Comment: Temperatures of the irradiated and dark controls differed by 11°C.

Agrolinz Response: True. However, this study shows no difference in the half-lives and pattern of degradation between the irradiated and control samples. This indicates no soil photodegradation to be occurring. Also, the photostability of pyridate is supported by the UV absorption data which show pyridate not to absorb light above 310 nm and only weakly absorbs light between 290-310 nm.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment. EFGWB notes that given the 11 °C higher temperature of the irradiated samples, one might have predicted that the hydrolysis and aerobic soil metabolism reactions would have occurred more rapidly than in the control samples, thereby increasing the apparent degradation.

AGROLINZ CONCLUSIONS: Although this study was not complete in its presentation and did not strictly follow the Guidelines protocol, it nevertheless provides information showing Pyridate to be stable to photodegradation on soil surfaces.

EFGWB CONCLUSIONS: This study still does not fulfill EPA Data Requirements for Registering Pesticides. Not only has the registrant not adequately responded to the above comments by EFGWB, but they failed to respond to all the comments that were mentioned in the EFGWB Science Chapter for Pyridate. EFGWB concludes that the sampling intervals were insufficient to accurately estimate the degradation half-life of pyridate or its degradates.

10.3 **ANAEROBIC SOIL METABOLISM--162-2**

1. EFGWB Original Comment: The data were too variable.
Agrolinz Response: True, but this was probably due to incomplete mixing of the material into the soil. However,

the data still provided a correlation coefficient of 0.77, half-life of 11 months (if one data point is considered an outlier) and a material balance of 95.0-106.8%. Note that the Guidelines protocol for this study includes a total of only 3 data points over 60 days and this study included 7 data points over 477 days.

EFGWB Rejoinder: As was stated in the EFGWB Science Chapter for Pyridate, the data were too variable to establish the half-life of the test substance. Parent CL-9673 declined from 93% of the applied immediately posttreatment to 47.2% after 16 days, then ranged from 44.2 to 70.2% of the applied throughout the remainder of the study.

The registrant calculated a half-life (675 days) using only four of the seven data points (days 43, 130, 290, and 477) stating that anaerobicity did not exist until 43 days posttreatment and that the data point from day 184 was considered an "outlier". Even with these adjustments, the correlation coefficient for the half-life calculations was only 0.71.

2. EFGWB Original comment: The TLC solvent systems did not adequately resolve the broad bands of radioactivity (metabolism products) found during the study.

Agrolinz Response: This is true but is typical of what happens when compounds are greatly metabolized. This indicates the soil metabolism products formed during this study are very many and of very low concentration.

EFGWB Rejoinder: EFGWB can not accept this rationale. Since the TLC solvent systems used did not resolve the broad bands of radioactivity found during the study, the registrants should have used other solvent systems and/or possibly other separation techniques to attempt to resolve the problem as necessary.

3. EFGWB Original Comment: There were other resolvable peaks during the study at levels up to 0.29 ppm.

Agrolinz Response: Not so. The peaks found were broad peaks that could not be resolved to show their individual components.

EFGWB Rejoinder: EFGWB can not accept this rationale. Since the TLC solvent systems used did not resolve the broad bands of radioactivity found during the study, the registrants should have used other solvent systems and/or possibly other separation techniques to attempt to resolve the problem as necessary.

4. EFGWB Original Comment: The position of radiolabeling was not specified.

Agrolinz Response: The starting material was labeled in the 4- and 5-positions of the pyridazine ring.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

5. EFGWB Original Comment: The analytical methodology was not completely described.

Agrolinz Response: Complete details on the analytical methodology are available and are the same as those used in the aerobic soil metabolism study that was acceptable.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

6. EFGWB Original Comment: Pyridate degradation product (CL-9673) was used as the starting material in this study and not Pyridate that had been aerobically aged for one half-life.

Agrolinz Response: True. However, CL-9673 is the only major soil degradation product of Pyridate and would be the principal material that would reach anaerobic depths in soil.

EFGWB Rejoinder: In the aerobic soil metabolism study (judged acceptable, see attached Study 5), the major ^{14}C degradation product of CL-9673 was 3-phenyl-4-methoxy-6-chloropyridazine (CL-9673-OMe) and was approximately 3.9 to 16% of the applied radioactivity. The identity of CL-9673-OMe was confirmed by MS, UV, TLC and electrophoresis in reference to an authentic sample. Because of the manner in which this study was conducted (see comment 6 in attached DER for Study 6), CL-9673-OMe would probably not have a chance to form; therefore, it would not be detected. However, had this study been performed correctly, there is the possibility that CL-9673-OMe would have been detected.

7. EFGWB Original Comment: No attempt was made to identify CL-9673-OMe.

Agrolinz Response: The report stated that no products could be identified other than CL-9673 (starting material) and CO_2. A check of the TLC chromatograms verified the absence of CL-9673-OMe in this study.

EFGWB Rejoinder: See EFGWB response above, number 6.

8. EFGWB Original Comment: Anaerobic incubation conditions were not verified, maintenance of 100% moisture capacity was not verified, and the water used was not characterized.

Agrolinz Response: The soil was brought to 100% of its maximum water holding capacity and, in addition, was purged with oxygen-free nitrogen. The Guidelines state that either one of these methods would be acceptable in bringing about anaerobic conditions. Since both methods were used, it is highly likely that anaerobic conditions were prevalent during incubation.

The soil was purged with water-saturated nitrogen and not dry nitrogen. Use of water-saturated nitrogen would prevent removal of moisture from the soil.

Distilled water was used.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

AGROLINZ CONCLUSIONS: Although this study did not strictly follow the Guidelines protocol, it demonstrates that CL-9673 (the major soil degradation product of Pyridate) degrades slowly to numerous polar unidentifiable compounds. The half-life is between 11 and 22 months. Based on field dissipation studies, parent Pyridate will not persist long enough in soil to leach to anaerobic depths.

EFGWB CONCLUSIONS: This study still cannot be used to fulfill data requirements because the data are considered to be too variable to establish the half-life of the test substance and should have been replicated sufficiently to provide interpretable data for analysis.

The analytical methodology (TLC) did not adequately resolve and identify the sample radioactivity. Perhaps other TLC solvent systems and/or possibly other separation techniques should have been used to attempt to resolve the problem as necessary.

Furthermore, sample calculations were not provided relating radio-TLC scans to distribution of radioactivity in soil.

There was no indication of when the soils were analyzed in relation to when samples were collected. If samples were stored before extraction and analysis, it must be shown that no residues degraded under storage conditions.

10.4 **LEACHING AND ADSORPTION/DESORPTION--163-1**

1. EFGWB Original Comment: Only 20 cm and not 50 cm of water were used to irrigate the soil columns.
Agrolinz Response: True. However, only 20 cm were used because it took 7 days for the 20 cm to percolate through the column. Use of 20 cm indicate strong leaching potential of Pyridate, repeating the study with 50 cm of water will also show strong leaching potential of Pyridate.

EFGWB Rejoinder: While EFGWB accepts this response in resolving the original comment, EFGWB notes that the length of time required for leaching of 20 cm of water was excessively long. Based on a review of the particle size analysis of the soils used (see attached DER for Study 10, page 10.4), this reviewer concludes that water should have leached through these soil quite rapidly. The method used to pack the soil columns (i.e., "Then the column was filled up to 30 cm with soil under repeated pushing. The packing of the column was completed when the surface of the column no longer settled down." From Report No. 681, page 68, Accession Number 72352), probably resulted in the soil being compacted (i.e., increased bulk density) to excess , thereby increasing time required for leaching.

2. EFGWB Original Comment: The soil column was not analyzed to track the downward movement of Pyridate residues.

Agrolinz Response: True. However, analysis of the soil columns would not change the conclusion that Pyridate has strong potential to leach.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment; however, analysis of the soil cores might have provided further evidence for the existence of CL-9673-OMe.

AGROLINZ CONCLUSIONS: Leaching data show Pyridate and its major degradation product to have strong potential to leach in soil. Agrolinz will conduct an additional leaching study on parent Pyridate following the Guidelines protocol. Although this data shows pyridate has potential to leach in soil, aerobic soil metabolism data shows pyridate will degrade rapidly in soil. Field dissipation data indeed shows degradation and metabolism of pyridate in soil will occur before pyridate residues will leach. The data showed this to be true even under conditions of above average rainfall.

EFGWB CONCLUSIONS: This study still only partially satisfies the leaching data requirement and an aged leaching study is still needed. Since the aerobic soil

metabolism study has shown that a major ^{14}C degradation product of CL-9673 was 3-phenyl-4-methoxy-6-chloropyridazine (CL-9673-OMe) and was approximately 3.9 to 16% of the applied radioactivity, it would be prudent to conduct an aged leaching study to determine the fate of this product.

10.5 **FIELD DISSIPATION FOR TERRESTRIAL USES--164-1**

1. EFGWB Original Comment: Data are variable.

Agrolinz Response: A variable ("choppy") decline curve for degradation of chemicals in soil is not unexpected for field studies due to the fluctuation in soil temperature, soil moisture, and soil characteristics over the treated plot during the study period. (The impact of these parameters on microbial metabolism and physical degradation of chemicals in the environment have been well studied and documented in the technical literature). However, data decline curves for three of the four field dissipation studies provide correlation coefficients (r) of 0.6723 (the Georgia study), 0.8750 (the North Carolina study), and 0.9634 (the Louisiana study). These values indicate the data are statistically reliable and show Pyridate residues are dissipating in these studies.

An additional (and valid) concern of the reviewer regarding these field dissipation studies was the occurrence of contamination at the deep soil layers in the treated plots. By reviewing rainfall records for the test locations, it is concluded that these findings are due to inadvertent contamination while taking and processing the soil cores and not due to leaching of pyridate residues. The rainfall records show that there was absolutely no or inadequate rainfall to explain leaching of pyridate to depths of 9-12 inches. This issue is discussed in detail in the Technical Summary (attached) of each field study.

EFGWB Rejoinder: EFGWB can not accept the rationale that the variable data decline curves is due to fluctuations in soil temperatures, soil moisture, and soil characteristics over the treated plots. While this rationalization explains the variation between plots (i.e., replicates) at each sampling date, it is not adequate in explaining the reason why, in some cases, residues were less at posttreatment, declined after several days, increased after several more days and the declined again.

EFGWB can conclude that inadvertent contamination, while taking and processing soil cores, may have occurred in a few cases. It could also be concluded that contamination

explains the "choppy" nature of the residue decline curves and renders the data too variable to accurately assess the dissipation of pyridate residues.

2. EFGWB Original Comment: Examples of unexplained contamination in control plots.

Agrolinz Response: In the LA study, contamination occurred only at the limit of detection (0.01 ppm) and only on one day (Day 14). In the GA study, contamination occurred at 0.01-0.09 ppm but-only on 2 days (Days 3 and 14). In the NC and KS, studies, contamination was found on 3 and 6 days, respectively, during the first month post-application.

In these 4 studies, contamination was not found after the first month. The finding of contamination early in the studies (shortly after application), indicates the contamination may be due to transport of surface material from the treated plots to the control plots (150 feet away) by animals or wind. Another explanation is the samples were contaminated when being extruded from the probes and processed for analysis. This issue is discussed in detail in the Technical Summary (see attached) section of each field study.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment, but concludes that the study personnel probably used careless techniques in sampling and processing soil cores, and this, in and of itself, is sufficient to place the validity of the studies in jeopardy.

3. EFGWB Original Comment: The method did not distinguish between Pyridate and its degradation product.

Agrolinz Response: True, but it is known from the laboratory aerobic soil metabolism data that Pyridate rapidly degrades to only CL-9673 with minor amounts of CL-9673-OMe. In any case, these data show Pyridate or CL-9673 do not leach below 6-9 inches even under conditions of higher than average rainfall. All of the field soil samples were also analyzed for CL-9673-OMe. CL-9673-OMe was not detected (<0.01 ppm) in any sample from the field dissipation studies.

EFGWB Rejoinder: EFGWB accepts this response as resolving the original comment.

4. EFGWB Original Comment: Samples were stored frozen without supporting freezer storage stability data.

Agrolinz Response: Freezer storage stability data show Pyridate to be stable for over one year under conditions of frozen storage.

EFGWB Rejoinder: Before EFGWB can accept this response in resolving the original comment, the registrant should provide the data that supports this.

5. EFGWB Original Comment: Soil and air temperatures and precipitation data were incomplete.

Agrolinz Response: Complete data are available and show typical temperatures and slightly above average rainfall.

EFGWB Rejoinder: Before EFGWB can accept this response in resolving the original comment, the registrant should provide the data that supports this.

AGROLINZ CONCLUSIONS: One study (LA) had no reviewer concerns or questions on data variability or control plot contamination. The other studies had instances of contamination in the treated plots but these have been scientifically shown via rainfall records (in the TECHNICAL SUMMARY section and Tables 1-4 attached) to be due to inadvertent contamination and not leaching.

Although some of these studies had some contaminated samples in both the control plots and the treated plots and the data were variable, this is not unusual for studies conducted under field conditions. The fact that no leaching of residues below 6-9 inches occurred, and the correlation coefficient for the decline curves being greater than 0.67, indicate the data show no leaching of Pyridate residues under field conditions, and even under conditions of higher than average rainfall. As discussed in the Technical Summary section of each field dissipation study, findings of residues at the 9-12 inch soil depth of the treated plots and in certain samples from the control plots are due to inadvertent contamination and not leaching.

EFGWB CONCLUSIONS: EFGWB can accept the registrants conclusion that findings of residues at certain soil depths of the treated plots and certain control plots are due to inadvertent contamination. However, because there is still the possibility that more of the samples were contaminated, this reviewer does not believe that any conclusion as to the leachability of pyridate can be made at the present time. Therefore, EFGWB still can not accept these studies as satisfying the data requirements for terrestrial field dissipation. The data is still too variable, even after considering the registrants contamination theory, to assess

the dissipation of pyridate residues under terrestrial field conditions.

Furthermore, the registrant failed to respond to all of the EFGWB comments in the 4 studies submitted. For example, in all the studies, recoveries from fortified samples were low and the study author did not attempt to explain the reason for the low percent recoveries that occurred in some cases.

Also, the author did not specify why sampling protocol was changed during the study (see each DER for details, Studies 13-16, attached).

10.6 CONFINED ACCUMULATION IN ROTATIONAL CROPS--165-1

1. EFGWB Original Comment: The inert ingredients used to formulate the test substance must be shown to be inert.

Agrolinz Response: The inert ingredients used to formulate the test substance are inert in that they do not interact with or cause degradation of Pyridate. Therefore, this study provides results substantially similar to those expected to occur had pure Pyridate been used.

Even had pure pyridate been used, it would have been mixed with a solvent to allow it to be sprayed in this study. This is standard procedure for all solid active ingredients that must be sprayed on test plots or soil.

EFGWB Rejoinder: EFGWB does not agree that because certain chemicals are classed as inert ingredients they do not react with the active ingredient (in this case pyridate). However, the environmental fate data as presented for pyridate indicates that it acts as a contact herbicide. Uptake of parent compound by plants would result in plant injury or death due to metabolism of parent pyridate to CL-9673 and resultant reaction with appropriate plant enzyme systems.

Data presented for the rotational crop study indicate that no parent pyridate, CL-9673 or CL-9673-OMe were present. Therefore, it appears that, in this case, the inert ingredients added to this formulation had little effect on the action of pyridate.

AGROLINZ CONCLUSIONS: The data show no uptake of residues by rotational crops. Agrolinz respectively requests this study be found acceptable based on the above response.

EFGWB CONCLUSIONS: EFGWB concludes, after thoroughly reviewing the studies related to Confined Accumulation in

Rotational Crops, that the study is scientifically valid and can be used to fulfill the data requirements.

EFGWB concludes that no residues were detected in lettuce or carrots above the detection limit of 0.01 ppm equivalent CL-9673. While residues were detected in barley straw and grain, the authors attributed the residues (actually ^{14}C) as being incorporated into the cell tissue (i.e., carbon pool of the plant). The data as presented supports this conclusion.

In the future, EFGWB strongly suggests that the registrant follows the suggestions in the Environmental Fate Subdivision N Guidelines related to Confined Accumulation in Crops studies and utilize the radio-labeled analytical grade of the active ingredient and the proper soil type.

11.0 COMPLETION OF ONE-LINER: Not applicable.

12.0 CBI APPENDIX: The registrants makes no claim of confidentiality for any information contained in this study on the basis of its falling within the scope of FIFRA Section 10 (d) (1) (A), (B), or (C).

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

OFFICE OF PREVENTION,
PESTICIDES AND TOXIC
SUBSTANCES

2 JUN 1993

EFGWB #: 93-0381, 93-0382 & 93-0383
Chemical Barcode #: 128834
DP Barcode #: D187552, D187553 & D187554
Case #: 010515, 010516 & 016276

MEMORANDUM

SUBJECT: Review of Agrolinz's Response to EFGWB's Review of Anaerobic Soil Metabolism Study.

FROM: Richard J. Mahler, Hydrologist Richard J. Mahler
Environmental Chemistry Review Section #1
EFGWB/EFED

THRU: Henry Jacoby, Chief Henry Jacoby 6/7/93
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division

Paul J. Mastradone, Chief Paul J Mastradone
Environmental Chemistry Review Section #1
EFGWB/EFED

TO: Cynthia Giles-Parker, Product Management Team #22
Registration Division (H7505C)

CONCLUSIONS:

1. EFGWB has reviewed the original anaerobic soil metabolism study (MRID 42242802) and examined Agrolinz's response (see attached) to the June 29, 1992 review of their submitted anaerobic soil metabolism study. EFGWB concludes that their explanation as to why they were unable to identify certain degradates of pyridate, although not convincing, is acceptable at this time. The anaerobic soil metabolism study is now valid and satisfies the data requirements.

2. Although the registrant did not make a serious attempt to identify the degradates in concentrations >0.01 ppm, they did try to partially characterize them by means of TLC and HPLC techniques. The registrant claims that the degradates

could not be identified either due to their transient nature or because attempts to purify them resulted in further degradation of the samples. However, the latter claim could not be substantiated since the registrant did not try GC/MS analysis or any other confirmation techniques to affirm the identity of the metabolite or its degradation products.

BACKGROUND:

1. The registrant has submitted a response to EFGWB's (6/29/92) review of their anaerobic soil metabolism study.

2. The registrants indicated that, except for the parent pyridate and CL-9673, the identification of the other metabolites >0.01 ppm was unsuccessful, after several attempts, for the following reasons:

    1. Instability of the degradates during analysis and/or storage.

    2. Transient nature of some of the degradates since they appeared at only one sampling interval.

    3. High polarity of some of the compounds which prevented GC-MS analysis.

    4. Non-uniformity of peak which, according to the registrant, makes identification by mass spectrometry impossible (EFGWB strongly disagrees with this line of reasoning).

COMMENTS:

EFGWB notes that while TLC and HPLC provide information related to the number, polarity and relative amounts of the compounds present in the mixture, the final identification, in the absence of standards, can only be made by the use of GC/MS and other confirmatory techniques. Apparently the registrant did not attempt to use these techniques for the confirmation of the identity of these compounds.

The registrant should be informed that on future studies submitted to the Agency for review, GC/MS analysis or other confirmation techniques should be attempted on any compounds that do not have standards available for comparison of Rf values or retention times for TLC and HPLC, respectively. In the absence of standards, these techniques can not provide confirmatory data for the identification of the unknowns.

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

OFFICE OF
PESTICIDES AND TOXIC
SUBSTANCES

July 6, 1992

MEMORANDUM

SUBJECT: Pyridate
Re: Small-Scale Prospective Ground-Water Monitoring Study

FROM: Henry Jacoby, Chief
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division (H7507C)

TO: Frank Sanders, Chief
Fungicide-Herbicide Branch
Registration Division (H7505C)

In my staff's evaluation of the fate and transport of pyridate, there is the finding that due to its rapid degradation pyridate, per se, should not contaminate ground water. Our evaluation also indicates that only in extraordinary circumstances is it likely that the major degradate would leach into ground water. However, the major degradate has the properties and characteristics associated with known ground-water contaminants and has demonstrated its potential to leach into ground water (unconfirmed detection in ground water in Europe). These conditions would lead EFGWB to request the small-scale prospective ground-water monitoring study.

The small-scale prospective monitoring study would develop the information that are needed to address issues of concern. These issues include:

- is the degradation of CL-9673 temperature dependent (i.e., is this why no detections were seen in NC and CA despite the permeable soils and low organic matter), and

- is it possible that in Illinois, where the rainfall was extreme, detections were minimal because the excessive precipitation flushed the chemical either to ground water or into surface runoff?

The small-scale study should give more empirical data on the CL-9673's movement through

the soil profile. If CL-9673 does leach, the study would also obtain field information that would allow the Branch to better utilize modeling in estimating whether the compound could leach in other vulnerable soils. Although a small-scale monitoring study in the vulnerable site is the normal progression of data, the Branch recognizes that there may be little or no concern about the toxicity hazards of CL-9673. Therefore, the Branch recommends that FHB review the hazards associated with CL-9673 to determine if it is worthwhile, from a regulatory standpoint, to pursue additional information on the degradate.