EEB BRANCH REVIEW

DATE:	IN ____ OUT ____	IN 1/4/78 OUT 6/28/78	IN ____ OUT ____
	FISH & WILDLIFE	ENVIRONMENTAL CHEMISTRY	EFFICACY

FILE OR REG. NO. 1016-69 and 78

PETITION OR EXP. PERMIT NO. 6F 1829

DATE DIV. RECEIVED

DATE OF SUBMISSION

DATE SUBMISSION ACCEPTED

TYPE PRODUCT(S): (I) D, H, F, N, R, S

PRODUCT MGR. NO. 12 Sanders

PRODUCT NAME(S) Temik

COMPANY NAME Union Carbide Corp.

SUBMISSION PURPOSE Added new use- Oranges

CHEMICAL & FORMULATION Aldicarb (2-methyl-2-(methylthio) propionaldehyde O-(methylcarbamoyl) Oxime) (Temik)

1.0 Introduction

1.1 Aldicarb, Temik

1.2 Resubmission of 1016-69,78 of 9/7/77. This review was originally an expedite request per PM 12 (Frank T. Sanders) of 1/4/78; which was assigned to this reviewer 3/15/78, as such. The review was terminated 3/20/78, to work on Bolstar Cotton Insecticide submission, a higher priority set by Mr. Johnson. Work again restarted 5/9/78, and is being handled as an expedite again (over all other submissions).

1.3 Two formulations 10 and 15% granular with three proposed uses: oranges, tobacco, and dry beans/ soybeans.

1.4 This review is for use on oranges.

1.5 See other reviews:

1016-69,78	9/7/77
PP # 6F 1829	8/23/76
1016 - EUP	11/4/75

1.6 Acc# 096671. Book I, Ref. 1-25. Environmental Chemistry of Temik Aldicarb Pesticide.
Acc# 096670. Book II, Ref. 26-47. Environmental Chemistry of Temik Aldicarb Pesticide.

2.0 Directions for Use.

Crop & Time of Application	Pounds/Acre 10G(A) 15G(B)	Ounces/1000 Feet of Row	Recommended Application
ORANGES..... Just prior to or during spring flush of foliage growth	50-100A... 33-67B	Not applicable	Apply in band along drip-line on both sides of tree row by spreading granules uniformly and immediately working into soil or shanking 2 to 3 inches deep on 12 inch centers. Band width should equal one fourth tree row spacing.
	100 A 67 B		Or, apply in irrigation furrows using 2 shanks per furrow. Promptly and thoroughly irrigate after treatment.

Oranges
- Do not make more than one application per year.

2.1 Disposal

Keep out of any body of water. Do not contaminate water when cleaning of equipment or disposing of wastes.

3.0 Discussion of Data

3.1 Physico-chemical

3.1.1 Hydrolysis - data submitted or referenced.

3.1.2 Photodegradation - data submitted or referenced.

3.2 Metabolism

3.2.1 Aerobic soil - data submitted or referenced.

3.2.2 Effects of Microbes on Pesticides - data submitted or referenced.

3.2.3 Effects of Pesticides on Microbes - data submitted or referenced.

3.3 Mobility

3.3.1 Leaching - data submitted or referenced.

3.3.2 Volatility (Reentry) - data submitted or referenced.

3.4 Field Dissipation

3.4.1 Soil - data submitted or referenced.

3.5 Accumulation.

3.5.1 Fish - data submitted or referenced.

3.5.2 Rotational Crop - data submitted or referenced.

3.6 Environmental Chemistry data submitted Acc#S 096671,096670 Book 1 and 2, Ref. 1-47. Environmental Chemistry of Temik Aldicarb Pesticide.

(Attachment A) UC 21149-111-SBF. Determination of total Toxik, Temik Residues in Sugar Beet Fractions by GLC (Thin juice method).

1. Anderson, J.P.E., "Factors Influencing Insecticide Degradation by a Soil Fungus, Mucor alternans," Diss. Abstr. Int., 32 (6): 3414B-3415B (1971).

2. Andrawes, N.R., W.P. Bagley, and R. A. Herrett, "Fate and Carryover Properties of TEMIK Aldicarb Pesticide [-Methyl-2-(methylthio)propionaldehyde O-(methyl-carbomoyl)oxime] in Soil," J. Agr. Food Chem. 19: 727-730 (1971).

3. Andrawes, N. R., "Hydrolysis of TEMIK Aldicarb Pesticide in Aqueous Buffer Solutions," UCC Project Report No. 22263, July 7, 1976.

4. Andrawes, N. R., "Hydrolysis of Aldicarb Sulfoxide in Aqueous Buffer Solutions," UCC Project Report No. 22326, July 22, 1976.

5. Andrawes, N. R., "Photochemical Transformation of Aldicarb," UCC Project Report No. 22335, July 26, 1976.

6. Andrawes, N. R., "Photostability of Aldicarb Sulfoxide," UCC Project Report No. 22325, July 22, 1976.

7. Borash, A. J., and J. A. Kramer, Jr., "Experiments Designed to Trace Movements of Aldicarb in Soil," UCC Project Report 17959, July 9, 1973.

8. Bromilow, R. H., "Breakdown and Fate of Oximecarbamate Nematicides in Crops and Soils," Annals. Appld. Biol. 75 (3): 473-479 (1973).

9. Bull, D. L., "Metabolism of UC 21149 (2-methy-2-(methylthio)propionaldehyde O-(methylcarbamoyl) oxime) in Cotton Plants and Soil in the Field," J. Econ. Entomol. 61: 1598-1602 (1968).

10. Bull, D. L., R. A. Stokes, J. R. Coppedge and R. L. Ridgway, "Further Studies on the Fate of Aldicarb in Soil, " J. Econ. Entomol. 63: 1283-1289 (1970).

11. Mellon Institute Special Report 31-173, "TEMIK 10G and TEMIK 10G-V Response of Rats to Saturated Vapors Generated under Simulated Greenhouse Conditions", December 20, 1968.

12. Mellon Institute Special Report 38-141, "TEMIK 10G BC (coal); 10G and 15 (gypsum); 15G (corn cob) - Comparative Toxicity Studies via Peroral, Dermal, and Inhalation Routes", November 19, 1975. (NOT Environmental Chemistry Data).

13. Clarkson, V. A., B. K. Rowe, and R. R. Romne, "TEMIK Insecticide. Field Evaluation of the Persistence and Movement of TEMIK and its Carbamate Metabolites in Soil," UCC Project Report No. 10485, October 28, 1968.

14. Clarkson, V. A., B. K. Rowe and R. R. Romne, "TEMIK Insecticide. Field Evaluation of the Persistence of TEMIK and Its Carbamate Metabolites in Pond Water and Tehir Effect on Pond Fauna," UCC Project Report No. 10491, November 11, 1968.

15. Coppedge, J. R., D. L. Bull and R. L. Ridgway, "Movement and Persistence of Aldicarb in Certain Soils," Arch. Environ. Cont. Toxicol. 5: 129-141 (1977).

16. Coppedge, J. R., D. A. Lindquist, D. L. Bull and H. W. Dorough, "Fate of 2-Methyl-2-(methylthio) propionaldehyde 0-(methylcarbamoyl) oxime (TEMIK) in Cotton Plants and Soil," J. Agr. Food Chem. 15: 902-910 (1967).

17. Gawaad, A. A. A., E. S. N. M. Ali and A. Y. Shazli, "Leaching of Some Soil Insecticides in Three Egyptian Soils," Bull. Entomol. Soc., Egypt Econ. Ser. 5:23-26 (1971). (Cited in Reference 46 of this bibliography).

18. Heywood, D. L., J. W. Bartley, "Metabolism Studies, Hydrolytic Stability of UC 21149," UCC Status Report 855-31101-7073, January 21, 1965.

19. Hirsh, D. H. and K. P. Sheets, "Aldicarb Subsequent Crop Studies," UCC Project Report No. 23520, April 21, 1977.

20. Hough, A., I. J. Thomason and W. J. Farmer, "Behavior of Aldicarb in Soil Relative to Control of Heterodera schachtii," J. Nematol. 7: 214-221 (1975).

21. Iwata, Y. W. E. Westlake, J. H. Barkley, G. E. Carmen and F. A. Gunther, "Aldicarb Residues in Oranges, Citrus By-Products, Orange Leaves, and Soil After an Aldicarb Soil Application in an Orange Grove," J. Agr. Food Chem. 25: 933-937 (1977).

22. Jones, A. S., "Metabolism of Aldicarb by Five Soil Fungi," J. Agr. Food Chem. 24: 115-117(1976).

23. Kaufman, D. C., "Pesticide Metabolism," in Pesticides in the Soil: Ecology, Degradation and Movement. International Symposium on Pesticides in the Soil February 25-27, 1970, Michigan State University, East Lansing.

24. Kearby, W. H., C. D. Ercegovich and M. Bliss, Jr., "Residue Studies on Aldicarb in Soil and Scotch Pine," J. Econ. Entomol. 63 (4): 1317-1318 (1970).

25. Leistra, M., J. H. Smelt, and T. M. Lexmond, "Conversion and Leaching of Aldicarb in Soil Columns," Pest. Sci. 7: 471-482 (1976).

26. Lin, S., B. R. Funke and J. T. Schulz, "Effects of Some Organophosphate and Carbamate Insecticides on Nitrification and Legume Growth," Plant Soil 37 (3): 489-496 (1972).

27. Lykins, H. F., "TEMIK Insecticide. The Effect of Temperature and pH on the Stability of TEMIK, TEMIK Sulfoxide, and TEMIK Sulfone in Water," UCC Informal Report, June 27, 1969.

28. Lynkins, H. F., "Aldicarb Pesticide. Stability of Aldicarb in Water," UCC Project Report No. 16060, August 9, 1971.

29. Payne, L. K., Jr., A. H. Stansbury, Jr., and M. H. J. Weinden, "The Synthesis and Insecticidal Properties of Some Cholinergic trisubstituted acetaldehyde O-(methylcarbamoyl)oximes," J. Agr. Food Chem. 14: 365-365 (1966).

30. Quraishi, M. S., "Edaphic and Water Relationships of Aldicarb and Its Metabolites," Can. Entomol. 104 (3): 1191-1196 (1972).

31. Richey, F. A., Jr., "TEMIK Aldicarb Pesticide. Water Leaching of Aldicarb, Aldicarb Sulfoxide, Aldicarb Sulfone and Internal Standard Chloride Ion in Columns of Four Soil Types," UCC Project Report File No. 16669, January 7, 1972.

32. Richey, F. A., Jr., "TEMIK Aldicarb Pesticide. Upward Movement of Aldicarb through Soil During Water Evaporation," UCC Project Report File No. 17526, August 18, 1972.

33. Richey, F. A., Jr. and H. H. Moorefield, "TEMIK Aldicarb Pesticide. Metabolism by Soils, Laboratory Studies" UCC Project Report, File No. 17507, August 16, 1972.

34. Richey, F. A., W. J. Bartley and K. P. Sheets, "Laboratory Studies on the Degradation of the (pesticide) Aldicarb in Soils," J. Agr. Food Chem. 25: 47-51 (1977).

35. Romine, R. R., "TEMIK Aldicarb Pesticide Leaching of Aldicarb into Sandy Soil with Irrigation of a "TEMIK" Treated Sugar Beet Field," UCC Project Report, File No. 17979, April 11, 1972.

36. Romine, R. R., "Accumulation of Aldicarb Residues in Fish Tissues from Chronic Exposure ot Aldicarb, Sulfoxide, and Aldicarb Sulfone in Aquaria Water," UCC Project Report, File No. 19009, December 10, 1973.

37. Romine, R. R., C. B. Halstead and C. E. Gibson, "TEMIK Insecticide. Leaching Characteristics of TEMIK 10G in Soils," UCC Project Report File No. 10902, November 11, 1968.

38. Sheets, K. P. and D. H. Hirsh, "TEMIK Aldicarb. Metabolism of Aldicarb in Muskingum Silt Loam Soil," UCC Project Report, File No. 22196, June 23, 1976.

39. Skrentry, R. F. and J. A. Ellis, "Control of Aphis fabae on Broad Beans (Vicia faba) by the Systemic Action of Gamma-BHC, Thionazin and Aldicarb," Pest. Sci. 1: 45-48 (1970).

40. Sprengler, H. T., J. E. Griffith and W. S. Tamplin, "TEMIK and TEMIK Metabolites Vapor Pressure Data," UCC Project Report File No. 10819, October 24, 1968.

41. Spurr, H. W., Jr., and A. A. Sousa, "Potential Interactions of Aldicarb and Its Metabolites on Nontarget Organisms in the Environment," J. Environ. Quality, 3(2): 130-133 (1974).

42. Stephen, J. F., "A Study of the Decomposition of TEMIK, TEMIK Sulfoxide and TEMIK Sulfone in Water at 100°C," UCC Project Report No. 11815, April 22, 1969.

43. Supak, J. R., "The Volatilization, Degradation, Adsorption and Desorption Characteristics of Aldicarb [2-Methyl-2-(methylthio)propionaldehyde O-(methyl-carbamoyl)oxime] in Soils and Clays. Diss. Abstr. Int. 33 (3): 982B (1972).

44. Verstraete, W. and J. P. Voets, "Impact in Sugar-beet Crops of Some Important Pesticide Treatment Systems on the Microbial and Enzymatic Constitution of the Soil."

45. Tobler, E., "TEMIK Aldicarb Pesticide. Thermal Decomposition and Base and Acid-Hydrolysis of TEMIK," UCC Project Report, File No. 14185, July 28, 1970.

46. U. S. Environmental Protection Agency, "Substitute Chemical Program. Initial Scientific and Minieconomic Review of Aldicarb," EPA-540/1-75-013 (1975).

47. Woodham, D. C., R. R. Edwards, R. G. Reeves and R. L. Schutzmann, "Total Toxic Aldicarb Residues in Soil, Cottonseed, and Cottonlint Following a Soil Treatment with the Insecticide on the Texas High Plains, " J. Agr. Food Chem. 21 (2):303-307 (1973).

We have this data to review.

Physico-Chemical

4.0 Hydrolysis

Acc#096671. Book Ref. #3.

Andraws, N. R., "Hydrolysis of TEMIK Aldicarb Pesticide in Aqueous Buffer Solutions," UCC Project Report No. 22263, July 7, 1976.

4.01 Materials and Methods

S-methy-^{14}C-labeled Aldicarb was introduced into sterile buffered (Clark & Lub's) distilled water, adjusted to pH 5, 7, and 9. The solutions's final concentration was 10 ppm, incubated at 25°C in the dark for 28 days. Samples were taken at 4 hrs., 1, 3, 7, 14, 21 and 28 days. Organosoluable products were extracted by partitioning with (1:1) CH_3 Cl-CH_3 CN solution, dried over sodium sulfate, filtered, and subjected to LCS and two dimensional TLC. Water counted by LCS.

4.02 Results

Aldicarb was stable to hydrolysis under acidic and neutral conditions for a period of 28 days. At basic conditions, two pH units above neutral, aldicarb hydrolyzed with hydrolysis products formed.

4.03 Conclusions.

(at (pH 5) and pH 7) aldicarb is stable to hydrolysis with <1 to 1.2% degradation at the 28-day period. At (pH 9) approximately 23% of the parent compound hydrolized over a 28-day interval. Hydrolysis products identified were: aldicarb sulfoxide (<1%) of recovered activity (100%), aldicarb sulfoxide oxime (<1%), aldicarb oxime (20%), aldicarb nitrile (1.8%) of recovered activity respectively. Water soluable and products at the origin were (<1%). Recovery was greater than 90%.

Extrapolated t-1/2 at pH 9 is ∿ 8.0 days.

From other data we know that at elevated temperatures (80-100°C) at both acidic (6), neutral (7) and basic (8) conditions the compound will hydrolize with t-1/2's of just minutes or hours, thus showing a temperature dependency. No other concentrations were evaluated so that concentration dependency cannot be evaluated, however since at more ambient natural temperatures the compound is stable, we can forego this deficiency.

This study is an acceptable study to fulfill the hydrolysis data requirement and can be used to support any proposed use of aldicarb at the rates evaluated, where this data is required.

Sections 4.04, 4.0.9, 4.1.3 support this study also.

4.03.3 Hydrolysis of S-methyl-^{14}C Aldicarb in pH 9 Aqueous Buffer Solution

Components	% of the Recovered Radioactivity at Indicated Days	
	21	28
Aldicarb	75.1	76.2
Aldicarb Oxime	22.5	19.7
Aldicarb Nitrile	1.2	1.8
Aldicarb Sulfoxide	0.5	0.8
Aldicarb Sulfoxide Oxime	0.5	0.8
Impurity	T	0.5
Origin of TLC	T	0.2
Water-Solubles	T	0.1

Data from 0, 3, 7, 14 days has been submitted

1 T=Detectable amounts of less than 0.1%

2 Impurities present in the radiolabeled aldicarb preparation

3 Radioactivity remaining at the point of application of the organic extracts to the thin-layer chromatograms

4.04 Acc# 096671 Book 1, Ref. 4.

Andrawes, N. R., "Hydrolysis of Aldicarb Sulfoxide in Aqueous Buffer Solutions," UCC Project Report No. 22326, July 22, 1976.

4.05 Materials and Methods

S-methyl-^{14}C-labeled sulfoxide was introduced into sterile buffered (Clark& Lub's) distilled water, adjusted to pH 5, 7, and 9. The solutions having

final concentrations of 10 ppm were incubated in the dark at 25°C for 28 days and sampled at 1, 7, 14, 21 and 28 days (except pH9 which had a 4-hr. interval). Analysis was the same as in the previous hydrolysis study (4.0.1).

4.0.6 Results

Aldicarb sulfoxide is stable to hydrolysis at acidic and neutral conditions for 28 days. At basic conditions rapid hydrolysis occurred and degradates were formed.

4.0.7 Conclusions

At pH's of 5 and 7, only 1 and 7%, hydrolysis occurred at 28 days. At a pH of 9, rapid hydrolysis occurred and an estimated t-1/2 of ∿2 days can be extrapolated. Degradates identified were: aldicarb sulfoxide oxime (49% of recovered activity (99%) at 14 days, aldicarb sulfoxide nitrile (30%), water soluables (10%), and remained at origin (<1%) respectively.

Water soluable accumulation was stated to be from carry over during partitioning and/or degradation during work-up. This is a possibility and we have no discrepancy about the author's statement.

At neutral to basic conditions aldicarb sulfoxide will hydrolyze to the oxime moiety, while under acid conditions the compounds favors the nitrile moiety.

This study by itself is not an acceptable study because we require the use of parent compound for hydrolysis studies. This study does support the previous study (4.0.1) and does give us more information on the fate of this compounds degradative product aldicarb sulfoxide.

The deficiencies mentioned need not be addressed because we have an acceptable study (Section 4.0).

4.07.1 Hydrolysis of S-methyl-^{14}C Aldicarb Sulfoxide In pH 9 Aqueous Buffer Solution

Components	% of the Recovered Radioactivity at Indicated Times	
	7 Days	14 Days
Aldicarb Sulfoxide	11.8	10.6
Aldicarb Sulfoxide Oxime	59.2	49.0
Aldicarb Sulfoxide Nitrile	23.6	29.8
Origin of TLC[2]	1.2	0.6
Water-Solubles	4.2	10.0

Data at 0, 4 hrs., 1, 2, days has been submitted

4.07.2 Hydrolysis of S-methyl-^{14}C Aldicarb Sulfoxide In pH 7 Aqueous Buffer Solution

Components	% of the Recovered Radioactivity at Indicated Days	
	14 Days	28 Days
Aldicarb Sulfoxide	93.7	92.0
Aldicarb Sulfoxide Oxime	4.5	3.6
Aldicarb Sulfoxide Nitrile	1.4	3.1
Origin of TLC[1]	T	0.1
Water-Solubles	0.4	1.3

Data at 0, 1, 7, and 21 days has been submitted

T=Detectable amounts of less than 0.1%

4.07.3 Hydrolysis of S-methyl-^{14}C Aldicarb Sulfoxide In pH 5 Aqueous Buffer Solution

Components	% of the Recovered Radioactivity at Indicated Days
	28 Days
Aldicarb Sulfoxide	97.7
Aldicarb Sulfoxide Nitrile	1.7
Origin of TLC[1]	0.1
Water-Solubles	0.5

Data at 0, 1, 7, 14, 21 days has been submitted

4.0.8 Acc# 096671. Book 1, Ref. #14.

Clarkson, V. A., B. K. Rowe and R. R. Romine, "TEMIK Insecticide. Field Evaluation of the Persistence of TEMIK and Its Carbamate Metabolites in Pond Water and Their Effect on Pond Fauna," UCC Project Report No. 10491, November 11, 1968.

4.0.8.1 This study has been reviewed in the previous submission and was found not to be hydrolysis data, but rather fish accumulation/runoff data. We will not review it again per Dr. Rogoff memo to Mr. Campt of 8/12/77.

For further details see page #37 of 1016-69, 78/9-7-77 (Oranges).

4.0.9 Acc# 096671. Book 1, Ref. #18.

Heywood, D. L., J. W. Bartley, "Metabolism Studies, Hydrolytic Stability of UC 21149," UCC Status Report 855-31101-7073, January 21, 1965.

4.1 Materials and Methods

Three different solutions of aldicarb (#1-.27 g aldicarb, 10cc diethyl ether, 2cc water, 10 drops triethylamine; #2-.27 g aldicarb, 2cc dimethyl formamide, 1cc water, 10 drops triethylamine; #3-.26 g aldicarb, 10cc diethyl ether, 1cc 1 M KOH Solution) were allowed to stand at room temperature for four days. Samples (10µℓ) of the organic phase were subjected to TLC anlaysis. Controls with ether, water, dimethyl formamide and aldicarb were also evaluated.

4.1.1 Results

All three solutions evaluated gave reaction products different from the controls.

4.1.2 Conclusions

The use of triethylamine and KOH was used to form varying degrees of basicity. The main hydrolytic pathway was to the oxime moiety-independent of degree of basicity. Intensity (measured as weak, moderate, or intense) of formation increased with increases in basicity.

A large amount of unknown (1) was present.

A material balance was not given, the pH of the solutions was not stated, and the method may not detect all metabolites formed.

The study could not be used to fulfill the hydrolysis data requirement or support any use of aldicarb, but can be used to supplement the acceptable hydrolysis study in Section 4.0. The above deficiencies will not have to be addressed since we have an acceptable hydrolysis study.

4.1.3 Acc# 096670. Book II. Ref. #27.

Lykins, H. F., "TEMIK Insecticide. The effect of Temperature and pH on the Stqbility of TEMIK, TEMIK Sulfoxide, and TEMIK Sulfone in Water," UCC Informal Report, June 27, 1969.

4.1.4 This data has been reviewed in context in the previous 1016-69, 78/9-7-77 (Oranges), review and will not be reviewed again per Dr. Rogoff's memo to Mr. Campt of 8/12/77. See page 6 of previous review for further details.

We note that the company did send us information concerning lighting conditions of hydrolysis data in that all were conducted in the dark. Explanation of the thin juice method, UC 21149-111-SBF, was also provided.

The above two deficiencies from the previous review have been corrected and are not germane. All other comments still are germane to the study but will not have to be addressed since we have an acceptable hydrolysis study (4.0).

4.1.5 Acc# 096670. Book II. Ref. #28.

Lykins, H. F., "Aldicarb Pesticide. Stability of Aldicarb in Water," UCC Project Report No. 16060, August 9, 1971.

4.1.6 Materials and Methods

Samples of distilled water were adjusted to pH values of 6.0, 7.0 and 8.0 and fortified with aldicarb to the concentration of 0.5 ppm. The samples were

covered with aluminum foil and allowed to stand at 25°C for 30 days.

Samples were taken at 5-day intervals and analyzed for total aldicarb.

Pond water from Clayton, N.C. (pH 7.1) and Summersville Lake, W. Va. (pH 7.0) with and without sediment were evaluated along with exposure to pond water to a U.V. light. (8 out of 24 hrs.).

4.1.7 Results

Aldicarb dissipated rapidly in the water and sediment samples and was stable (0-10% reduction) for all water samples and U.V. light exposures.

4.1.8 Conclusions

Distilled water at pH 6.0 exhibited a 5% reduction in 30 days; at pH 7.0 a 8% reduction ; and at ph 8.0 a 7 reduction.

Pond water alone from Clayton, N.C. exhibited a 9% reduction in 30 days. Lake water from Summersville, N. C. exhibited a nil reduction in 30 days.

Pond water + sediment from N. C. exhibited a 98% reduction in 20 days (t.1/2 extrapolated as 5-10 days). Lake water + sediment from W. Va. exhibited a 97% reduction in 20 days (t.1/2 extrapolated as 5-10 days).

Pond water from N. C. exposed to U. V. exhibited a 10% reduction in 30 days.

Author states sediment samples contained <0.011 ppm. It can be extrapolated from this and previous data aldicarb is relatively stable to hydrolysis from a pH range of 5-8; and degradation occurs at pH9 and above. Rapid decline with sediment added indicates degradation in water will be biologically oriented - since sterile pond waters alone did not significantly degrade the compound, Aldicarb in surface waters will be stable. Compound may be stable to U.V. light, although the wavelength is not stipulated.

No mention of analysis procedure was given, no mention of formation and identification of metabolites

was given, material balance not provided.

For the above reasons this study cannot be used alone to support any use of aldicarb where this data is required nor be used to fulfill the hydrolysis data requirement. Since we have an acceptable hydrolysis study (Section 4.0) these deficiencies will not have to be addressed. The study can be used to support the acceptable study in Section 4.0.

4.1.9 STABILITY OF ALDICARB IN WATER

Sample No.	Description	Total Days Exposed: 0 Days Aldicarb Carbamates, ppm	Total Days Exposed: 30 Days Aldicarb Carbamates, ppm
I	Deionized water adjusted to pH 6.0	0.50	0.45
II	Deionized water adjusted to pH 7.0	0.52	0.44
III	Deionized water adjusted to pH 8.0	0.51	0.44
IV	Pond water Clayton, North Carolina	0.51	0.42
V	Pond water and mud Clayton, North Carolina	0.44	—
VI	Pond water and UV light Clayton, North Carolina	0.43	0.33
VII	Summersville lake water (West Virginia)	0.50	0.50
VIII	Summersville lake water and mud (West Virginia)	0.47	0.03

Data from 5, 10, 15, 20, and 25 Days has been submitted.

4.2 Acc# 096670. Book II. Ref #29.

Payne, L. K., Jr., A. H. Stansbury, Jr., and M. H. J. Weiden, "The Symthesis and Insecticidal Properties of Some Cholinergic trisubstituted acetaldehyde O-(methylcarbamoyl) oximes," J. Agr. Food Chem. 14:365-365 (1966).

4.3 Methods and Materials

2-methyl-2(methylthio) propionaldehyde 0-(methyl carbamoyl) oxime (95g; 0.5 m) was added to a 0.5N NaOH. This solution was stirred at 25-20°C for 36 hrs., the mixture neutralized to pH 7, extracted with isoprophy ether, organic layer evaporated, aqueous phase extracted 3 times with isopropyl ether. Combined organic extracts concentrated and filtered to remove starting material. Filtrate was striped to a residue, stirred with pentane and filtered. Pentane evaporated, and the residue distilled and analyzed by vapor-phase chromatography and spinning band column.

4.3.1 Results

2-methyl-2(methylthio) propion aldehyde 0-(methyl carbamoyl) oxime did hydrolyze.

4.3.2 Conclusions

Approximately 92% of the starting parent aldicarb was hydrolyzed after 36 hours. Two products were formed: 1) 2-methyl-2-(methylthio) propionitrile (28.7%) of original material, 2) 2-methy-2-(methyl thiol propionaldoxime (28.4% original material).

The parent aldicarb was stated not to be attached by a 2% sodium bicarbamate solution at room temperature for 14 days.

Under strong basic conditions aldicarb will hydrolyze to mainly the oxime moiety and to a lessor extent the nitrile moiety.

No data at acid or neutral conditions provided, raw data not provided, lighting conditions not reported, and radiolabeled study preferred.

This study does not fulfill the hydrolysis data requirement and cannot be used to support any use of aldicarb where this data is required, because of the aforementioned reasons. These deficiencies do not have to be addressed because we have an acceptable hydrolysis study in Section 4.0. This study can be used to support the hydrolysis study in Section 4.0 and is in agreement with Section 4.04.

4.3.3 Acc# 096670. Book II. Ref. #42.

Stephen, J. F., "A Study of the Decomposition of TEMIK, TEMIK Sulfoxide and TEMIK Sulfone in Water at 100°C," UCC Project Report No. 11815, April 22, 1969.

4.3.4 Materials and Methods

Solutions of 9.1% concentrations for temik aulfoxide and temik sulfone with a 2.9% solution of temik in distilled water were refluxed for seven hours at 100°C. Samples at 15-minute time intervals were taken, extracted with chloroform/acetonitrile, the organo-soluable portion evaporated, redissolved in chloroform and intensity measured by infrared spectroscopy. TLC analysis of both organo and water soluable fractions was also employed.

4.3.5 Results

Temik, temik sulfoxide, and temik sulfone were found to hydrolyze when refluxed in distilled water at 100°C.

4.3.6 Conclusions

Author states that the t-1/2 of parent temik at 78 minutes with temik oxime (major) and 1,3 dimethylurea and an unknown (minor) as metabolites (organo phase). Water soluable portion contained the minor metabolites.

Temik sulfoxide was stated to have a t-1/2 of 20 minutes with 2-methyl-2-methyl sulfiny proplonitrile (major and 2-methyl-2-methyl salfinyl propionaldehyde oxime; 1,3 -dimethylurea, and an unknown (minors) as metabolites (organo phase). Water phase contained all minor metabolities plus another unknown (minor).

Temik sulfone was stated to have a t-1/2 of 48 minutes with 2-methyl-2-methylsulfonyl propionaldehyde oxime (major) and 2-methy-2-methyl sulfonyl propionitrile, an unknown, temik sulfone, and 1,3-demethyl urea (minor) metabolites (organo phase). Water phase showed all of the above plus 4 other unknowns (minor).

No raw data was provided, temperatures of 100°C are not conducive to where the compound is applied in the field, pH of the solutions not given, material balance not

provided, radiolabeled material preferred. This study cannot be used to support any proposed use of temik and does not satisfy the hydrolysis data requirement where this type of data is required. The above deficiencies need not be addressed because we have an acceptable hydrolysis study (Section 4.0).

The data can be used to support the acceptable study in Section 4.0 and does give additional degradation information.

4.3.6 Acc# 096670. Book II. Ref. 45.

Tobler, E., "TEMIK Aldicarb Pesticide. Thermal Decomposition and Base and Acid-Hydrolysis of TEMIK," UCC Project Report, File No. 14185, July 28, 1970.

4.3.7 Materials and Methods

Temik in a 50/50 mixture of methanol/H_2O was used to evaluate the reactions of temik to weak and strong acids/bases (H_2SO_4, CCl_3CO_2H, H_3PO_4, Ac OH; KOH, NaOH, Na_2S, $NaCN$, No_2CO_3, Polyamine D) at ambient to 77°C temperature variations.

Temik was also evaluated to straight thermal decomposition in different reaction mediums (Toluene, Na_2CO_3/50% ag MeOH, Na_2 1+POμ , KH_2 POμ + K_2H POμ, NaOAc, AcOH, KCℓ, potassium hydrogen thalate).

Samples were quenched with dilute acid (base hydrolysis) or water (acid hydrolysis), extracted with chloroform, separation of layers, washing organic phase, drying, and infrared, GLC analysis for Temik nitrile and temik oxime.

4.3.8 Results

Temik displays rates and product distribution of thermal degradation as well as the base and acid catalyzed hydrolysis of Temik.

4.3.9 Conclusions

The major degradation product of the base hydrolysis of temik is temik oxime, which is always accompanied by varying amounts of nitrile. The oxime/nitrile ratio is dependent on the base-solvent combination

as well as the temperature - stronger the base and higher the temperature the larger the oxime ration (room temp. KOH 70/30, Na_2CO_3 44/56/77°C Na_2CO_3 66/34 Pyredine 49/51). All basic chemicals evaluated reported half-lives of <24 hours.

Acid hydrolysis is much slower (from previous studies at ~25°C and a pH of 5-7 the compound is stable for up to 30 days. Elevating the temperatures to 71°C enhances the degradation, so that half-lives are reported in minutes.

Temik is most stable at pH values of 2-5.

Temik degradation results in the formation of temik nitrile and (methyl-ammonium salt of N-methyl carbamic acid) [111]. It is theorized that as the concentration of [111] increases that its basic properties would enhance the degradation and both thermal and hydrolytic decomposition would occur.

This study is not practical to degradation in aquatic habitats, because of the use of solvent/water systems. We could not use this study to support any proposed uses of temik where hydrolysis data is required. This study can be used to support the acceptable study in Section 4.0. The above deficiencies need not be addressed because we have an acceptable hydrolysis study in Section 4.0.

Note: This data could be very useful in the case of a spill - strong bases would readily decompose the compound in minutes.

4.4 Photolysis

Acc# 096671. Book 1, Ref #5.

Andrawes, N. R., "Photochemical Transformation of Aldicarb," UCC Project Report No. 22335, July 26, 1976.

4.4.1 Materials and Methods

S-methyl-^{14}C labeled aldicarb was incorporated into Clark & Lubs buffer solutions at pH 5 (max. stability) at a concentration of 5 ppm. Reaction was carried out with ACE Glass reqction vessel at 20-25°C with

a 200-watt Hanovia emission lamp (wavelength from 222.4 to 1367.3 NM). Aerobic conditions were employed throughout the study. Sampling was at 24 hour intervals.

At each interval the sample was counted by direct scintillation with volatile lost determined by difference from 0-time measurement. Each sample was then partitioned with Chloroform-acetonitrile, the organo fractions combined, dried over sodium sulfate, and filtered. Radioassy of both organo and water soluable portion was determined. The organo phase was then concentrated and subjected to TLC analysis (two dimensional).

A final study was done with a 2% acetone solution as a sensitizer.

4.4.2 Results

Photolysis of S-methyl-^{14}C aldicarb was found to occur with the formation of photolytic products. Photo-degradation was enhanced by the use of an acetone sensitizer.

4.4.3 Conclusions

At the 7 day interval parent aldicarb was present at 52.7% of applied activity. An extrapolated t-1/2 would be >7 but <.16 days.

Two phases (0-2 days) in which 24% of the parent has degraded and (2-7 days) in which 19% is lost.

Major photoproduct was aldicarb sulfoxide which was 7.5% of applied activity at 7 days.

Minor phoroproducts were aldicarb sulfoxide nitrile, aldicarb sulfone nitrile and aldicarb sulfone alcohol, which were all <1% of applied activity at day 7.

Water soluable accounted for 9.9% of applied activity.

Volatilized activity (not characterized) was the largest amount of activity (28% at 7 days) found.

From a special chart in our files and the reporting that little or no energy below 280-287 NM wavelength

ever reaches the earth, we wonder the results of the study using a lamp with ∿10% of the WATTAGE <280 NM. The half-life and one sample beyond that was not reached/evaluated.

This compounds use is incorporation and it is felt that the above descrepancies need not be addressed; because photodegradation will not be a significant degradative pathway. For this use, this study is acceptable and can be used to support any proposed incoprated use. It is felt more data on the effect of the wavelength below 280 NM is needed if a foliar type use is ever proposed for aldicarb.

4.4.4 Acc#096671. Book 1. Ref 6.

Andrawes, N. R., "Photostability of Aldicarb Sulfoxide," UCC Project Report No. 22325, July 22, 1976.

4.4.5 Materials and Methods

S-methyl-^{14}C labeled aldicarb sulfoxide was used in the study. All other experimental procedures were the same as in 4.4.1.

4.4.6 Results

Aldicarb sulfoxide is stable to photolysis for 14 days.

4.4.7 Conclusions

After 14 days parent aldicarb sulfoxide accounted for 92% of applied activity, water soluables accounted for 5.6%, and no detectable amount of aldicarb sulfoxide nitrile.

This study was not conducted with parent material and would not support any proposed use of aldicarb where photodegradation data is required.

The above deficiencies need not be addressed because we have an acceptable study in Section 4.4.1. This study does support Section 4.4.1 and has been used in that context.

4.4.8 Metabolism

Soil Aerobic

Acc# 096670 Book II Ref. 33.

Richey, F. A., Jr. and H. H. Moorefield, "TEMIK Aldicarb Pesticide. Metabolism by Soils, Laboratory Studies" UCC Project Report, File No. 17507, August 16, 1972.

Acc# 096670 Book II Ref. 34.

Richey, F. A., W. J. Bartley and K. P. Sheets, "Laboratory Studies on the Degradation of the (pesticide) Aldicarb in Soils," J. Agr. Food Chem. 25: 47-51 (1977).

Note: Ref. 33 and 34 are both one and the same - Ref. 33 being the original company report and Ref. 34 the published report. We will review both as one.

4.4.9 Materials and Methods

Three soils, Lufkin fine sandy loam, Lakeland fine sand, and Norfolk sandy loam, aged from 6 days to 2 years.; moist to dry, were treated with ^{14}C-labeled aldicarb in three separate positions (S-methyl, tertiary carbon, and N-methyl) in each soil at a rate of 5.6 kg/ha (25.6 ppm ai/A). After treatment, additional soil was added to cover the aldicarb (2.5-3.6 cm) and saturated with water at varying rates (2.5 cm/week/7 wks., 2.5 cm/wk/10 wks., once at 54 d, and none). The samples were placed in a bell jar with inlet and outlet posts to collect volatiles in a series of traps: Drierite (remove H_2O from air)→ ascarite (remove CO_2) → metabolism chamber → trap at -15°C (retains H_2O)→ 100ml - gas washing bottle with ethylene glycol monoethyl ether - ethanol amine (CO_2 trap) → trap at -5°C → flowmeter→vacuum manifold. Contents of traps and gas washing bottle were periodically assayed for activity. $^{14}CO_2$ identity proof trapped in gas-washing bottle was made by treating aliquots of the three labels and authenic $^{14}CO_2$ with 0.2M $Ba(OH)_2$ - rate of precipitation followed by withdrawing aliquots and determining activity in the supernatant ethanolamine and water showed the reaction-same experiment run with $^{14}CO_2$ authentic in the solvent mixture.

Soil samples extracted with Acetone-water-phosphoric acid. Eluted water from soil treated first extracted with acetonitrile, then partitioned with methylene chloride. After separation the aqueous layer extracted with methylene chloride. Acetonitrite -methylene chloride samples were combined, dried over sodium sulfate and filtered. Sample assayed by lcs, organic phase concentrated and subjected to two dimensional TLC.

Unextractable residue was determined by oxidation with potassium dichromate in sulfuric - phosphoric acid. Soil organic matter was also subjected to extraction by sulfuric acid and sodium hydroxide with enzyme treatment of others using B-glucosidase and cellulase.

4.5 Results

Aldicarb was found to metabolize in soil with degradates and volatiles formed.

4.5.1 Conclusions

At 63 days in Norfolk sandy loam (N-SL), S-me- ^{14}C-label resulted in 7.0% of applied dose as CO_2, 74.0% as sulfoxide + sulfone (of which sulfoxide is major), 16.0% others, 4.0% as water soluable, and 4.0% unextractable. The soil had been dried for two years.

At 63-75 days in Lufkin fine sandy loam (LFSF), S-me^{14}C-label resulted in 83.0% of applied dose as CO_2, 8.0% as sulfoxide + sulfone, 2.0% others, 0.5% water soluable, and 16.0% unextracted. The soil had been moist 15 days and then air dried. At 63 days for LFSF aged moist 40 days and then air dried, the S-me-^{14}C-label showed 43% of applied dose as CO_2, 20% as sulfoxide + sulfone, 3.0% others, 5.0% water soluables, and 80% unextracted. The N-me and test - ^{14}C labels exhibited similar results except the N-me label gave higher CO_2 values, 61.0%, of applied dosage, while the test exhibited more unextractables 12.0% than the S-me label.

At 69 days Norfolk sandy loam (NSL) aged moist 10 days, then used, the N-me- ^{14}C-label showed 36.0% of applied dose as CO_2, 39.0% as sulfoxide + sulfone, 4.0% as

others, 4.0% as water soluable, and 6.0% as unextractable.

At 69 days NSL aged moist 10 days then air dried, S-me, N-me, and tert- C-labels gave similar results, except the N-me gave higher CO_2, 54.0% and lower sulfoxide + sulfone 18.0%; the tert label showing higher unextractables 16.0% and sulfoxide + sulfone 40.0%.

At 12 & 19 days Lakeland fine sand (LFS) aged moist 6 days, then used, the S-me label, slowed 10% as CO_2, 19.0% sulfoxide + sulfone, 23.0 % others, 38.0% water soluables, and 4% unextractables. N-me and tert-^{14}C labels did not behave similarly as last time. N-me resulted in higher CO_2 53.8% and higher unextractable 11.6%. Tert exhibited lower unextractables, 5% , but higher water soluables 38.0% and others 21.2%.

Radioactivity precipitated with Ba CO_3 indicated volatile products were 95% (average) actual $^{14}CO_2$.

The use of B-glucosidase and cellulase on the humic portion of a soil extract resulted in liberation of radioactivity, but resolution was poor on TLC and identification could not be attempted.

Approximately half of the unextractable residues were stated to be further extracted by sequential extraction with 0.05 N H_2SO_4 and 0.1N NaOH solutions. Half of the recovered activity was in the humic acid raction and half was in the fulvic acid fraction.

Soil characteristics of pH, moisture content, and organic matter; as well as soil sample age, pretreatment, and treatment during experimentation all reflect the rate of aldicarb degradation.

Differences in label positions result in different recoveries of various isolated fractions. The N-me-^{14}C-label gives the highest unextractable residue value, while the S-me-^{14}C-label shows the highest $^{14}CO_2$ value. The tert label gives the most even distribution.

LFS soil exhibited a substantially greater amount of water soluables than the other soils, owing to the pH of the soil (7.1) and hydrolysis data - this may be a physico-chemical phenomena and may be the occurrence

in basic soils types.

Parent compound breaks down rapidly with an estimated half-life of <14 days. The two major metabolites sulfoxide and sulfone are much more persistent with half-lives of 50-70 days.

The two studies #33234 combined make an acceptable soil metabolism (aerobic) study and could be used to support any proposed use of aldicarb where this data is required at the rates evaluated.

Note: Previous review 1016-69, 78/9-7-77 also contains an acceptable soil metabolism (aerobic study). The data of each does agree with each other. This study will have an impact on the past review and conclusions (see final conclusions Section 6.8).

4.5.2

Characteristics of Soils Used in Aldicarb Degradation Tests

Soil type	pH	% organic matter	Mechanical anal.		
			Sand, %	Silt, %	Clay, %
Lufkin fine sandy loam	7.1	1.74	59.7	22.0	17.9
Lakeland fine sand	4.6	1.32	97.5	1.2	0
Norfolk sandy loam	4.8	1.56	82.6	8.5	7.4

Summary of Radiolabel Recoveries (as Percent of Applied Dose) from Experiments 1 through 4

Expt no.	Soil	^{14}C label	^{14}C recoveries							Total time, days
			CO_2	Extracted				Unextracted	Total	
				TTR[a]	Others	H_2O soi.	Total			
1	NSL[b]	S-Me	7.1	73.7	15.8	4.1	93.6	4.3	104.0	63
	LFSL[c]	S-Me	82.3	7.9	2.2	0.5	10.6	15.8	109.2	63
2	LFSL	S-Me	42.8	20.1	3.4	4.8	28.3	8.4	79.6	75
	LFSL	N-Me	60.8	22.6	4.4	4.8	31.8	6.9	99.5	75
	LFSL	Tert.	45.1	15.6	5.3	6.8	27.7	11.8	84.6	75
3	NSL	S-Me	22.2	46.1	5.3	3.7	55.1	5.5	85.8	69
3	NSL	N-Me	35.9	38.7	3.6	3.6	46.1	6.1	88.1	69
3	NSL	N-Me[d]	53.9	18.3	0.9	2.8	22.0	6.8	82.7	69
3	NSL	Tert.	21.4	40.0	5.8	6.7	52.3	16.4[e]	90.1	69
4	LFS[f]	S-Me	8.6	21.8	25.1	39.2	86.1	3.1	95.8	12
4	LFS	S-Me	13.2	16.0	22.8	37.2	75.8	3.6	92.6	19
4	LFS	N-Me	53.8	13.7	2.9	5.1	21.7	11.6	87.1	19
4	LFS	Tert.	10.4	16.2	21.2	38.3	75.7	5.1	91.2	19

[a] TTR = total toxic residue = aldicarb + aldicarb sulfoxide + aldicarb sulfone. [b] NSL = Norfolk sandy loam. [c] LFSL = Lufkin fine sandy loam. [d] Soil was briefly air-dried. [e] 9.4% removed by sequential acid-base extraction leaving 7.8%. [f] LFS = Lakeland fine sand.

4.8.9 Metabolism

Soil Anaerobic

Acc# 096670 Book II Ref. 38.

Sheets, K. P.and D. H. Hirsh, "TEMIK Aldicarb. Metabolism of Aldicarb in Muskingum Silt Loam Soil," UCC Project Report, File No. 22196, June 23, 1976.

4.9.0 Materials and Methods

Aldicarb [2-methyl-2-(methyl-^{14}C-thio) propion-aldehyde-O-(methylcarbomoyl) oxime] was added to Muskingum Silt Loam (pH [5.4], OM [1.3], CEC [5.6], moisture % 1/3 bar [20.5], sand [9.0%], silt [42%], Clay [20%], NO_3-[24 ppm] and NO_2-[0 ppm]) at a rate of 2.7 ppm (air dry soil-75% field capacity for study). Field moisture (75% capacity) was maintained for 30 days then divided, with anaerobicity established by purging with nitrogen. Sampling was 30 and 60 days post aerobic sampling at 30.

Samples were extracted with acetone/methnol followed by a subsequent acetone/water + 1 drop phosphoric acid extraction and concentrated. The concentrates were each extracted with acetonitrile and chloroform to separate organo and water soluables. Aqueous phase estracted with chloroform to further separate organo and water soluables. Cleanup of organo phase was accomplished by elution with methanol, acetone and concentrating and treating with lead acetate. Activity determined by LCS and metabolites by TLC. Unextractables determined by oxidation.

4.9.1 Results

Aldicarb degrades under anaaerobic conditions.

4.9.2 Conclusions

At 30 days under anaerobic conditions 65% of applied activity was characterized by being volatilized $^{14}CO_2$. A total of 12.6% of applied activity was in the organo phase and 13.5% in the acqueous phase.

At 60 days under anaerobic conditions 77% of applied activity was characterized by being volatilized $^{14}CO_2$.

A total of 9% of applied activity was in the organo phase and 4.9% in the aqueous.

Consolidated results gave two major metabolities: aldicarb sulfoxide alchohol and aldicarb sulfone acid 5 and 18% of applied activity at 30 days ~~and~~ and 2.2 and 0.2% at 60 days, respectively. The figure is higher if the origin amount of 8.4 and 7.2% are added to the above numbers respectively (identification of origin material showed it to be principally the above two acids).

Compounds found but were all less than 3.5% at both 30 and 60 days were identified as:

aldicarb sulfoxide amide
aldicarb sulfoxide oxime
aldicarb sulfone amide
aldicarb sulfone
unknown 1
aldicarb sulfone alcohol
aldicarb sulfone nitrile
aldicarb sulfone oxime
aldicarb sulfoxide nitrile
unknown 2
unknown 3
aldicarb parent
methane sulfonic acid

Unextractable residues at 30 and 60 days anaerobic incubation were 8.6 and 9.2% respectively.

This compound will degrade under anerobic conditions to a variety of metabolites - rates between aerobic/anaerobic degradation are about equal to slightly faster under anerobic than aerobic conditions.

This study is an acceptable anaerobic soil metabolism study and can be used to support any use of aldicarb where this type of data is required.

4.9.3 Metabolism

Microbes Effects on Pesticides

Acc# 096670 Book 1 Ref. 23.

Jones, A. S., "metabolism of Aldicarb by Five Soil Fungi," J. Agr. Food Chem. 24: 115-117 (1976).

4.9.4 Materials and Methods

^{14}C-methylthio labeled aldicarb was incorporated into sterile Czapek-Dox Broth pH 7.3 at a concentration of 0.05 mg/50 ml of medium (0.2 lb. ai/A) Flasks were then innoculated with Cunninghamella elegans, Gliocladium catenulatum, Penicillium multicolor, Rhizoctonia sp, and Trichoderma harzianum. Flasks were shaken and incubated at 25°C and sampled at 7, 14, 21 and 28 days.

Flash containing ^{14}C-aldicarb sulfoxide were prepared as above and innoculated with C. elegans, G. catenulatum and T. herzianum and treated as above.

Samples were homogenized and centrifuged to remove mycelial fragments and counted for activity. Aqueous supernatants were extracted with chloroform/acetonitrile. Organic extracts were concentrated, aqueous freeze-dried and activity counted. Metabolites were characterized by TLC.

4.9.5 Results

The five species of fungi evaluated were found to degrade aldicarb. Metabolites were found.

4.9.6 Conclusions.

Distribution of activity between the organic and water soluable products increased from 7, 14, 21 and 28 days incubation. At day 7 the ratio of organic/water was 96:4; at day 28 it was ~70:30 (range of 86:14 to 68:32).

At day 21 metabolites found in the organo phase were: aldicarb sulfoxide (50% of total activity) as the major metabolite. Minor metabolites identified were aldicarb sulfone, oxime sulfoxide, nitrile sulfoxide, oxime sulfone and nitrik sulfone (all <10% of total activity).

Only a trace of activity was reported in the mycelial pellet.

Water soluable metabolites identified were: alcohol and amide sulfoxides and sulfones (major) with acid sulfoxide and sulfone and an unknown as minor metabolites (no percentages given for major or minor).

Incubation with Beta-glucosidase or glucuronidase was reported not to alter TLC pattern, indicating metabolites were not present as glucose or glucuronic acid conjucates.

Degrading potentiol is G. catenulatum > P. multicolor = C. elegans > Rhizoctonia sp > T. harizianum.

Aldicarb sulfoxide was found to degrade to oxime and nitrile sulfoxide (major metabolites ~10 and 10% respectively of total activity). Aldicarb sulfone, oxime sulfone, and nitrile sulfone as (minor) metabolites (Trace -3% of total activity). Water soluables not characterized.

Degradative potential G. catenulefum > C. elegans > T. harzianum.

Although this study used rates far less than the recommended 5-10 lbs ai - we believe that we can say microbial degradation will occur at these rates, because of support from soil metabolism studies at the higher rate. In addition since fungi are the most likely susceptible species, and they are found to degrade aldecarb; bacteria and actinomycetes which are much more resistant would degrade appreciably more and faster.

The study is an acceptable Effect of Microbes on Pesticides study and can be used to support any proposed use for aldecarb where this data is required.

4.9.7 Metabolism

Microbes Effects on Pesticides

Acc# 096670 Book I Ref. 23.

Kaufman, D. D., "Pesticide Metabolism," in Pesticides in the Soil: Ecology, Degradation and Movement. International Symposium on Pesticides in the Soil February 25-27, 1970, Michigan State University, East Lansing.

4.9.8 This study is not data per se, but rather a discussion of pesticide metabolism by soil microorganisms in general. It refers to similarly related OP's and the different microbial modes such as deakylation,

reduction, amide or ester hydrolysis, oxidation, etc. We have used this data to help in validating previous studies, but will not validate it for registration purposes because of it not being germane data to EC.

4.9.9 Metabolism

Effect of Pesticides on Microbes.

Acc# 096670. Book II Ref. 41.

Spurr, H. W., Jr., and A. A. Sousa, "Potential Interactions of Aldicarb and Its Metabolites on Nontarget Organisms in the Environment," J. Environ. Quality, 3(2): 130-133 (1974).

5.0 This study has been reviewed in previous 1016, 69, 78/9-7-77 review. We will not review it again per Dr. Rogoff's memo to Mr. Campt of 8/12/77.

5.1 Metabolism

Effect of Pesticides on Microbes.

Acc# 096670. Book II Ref. 44.

Verstraete, W. and J. P. Voets, "Impact in Sugarbeet Crops of Some Important Pesticide Treatment Systems on the Microbial and Enzymatic Constitution of the Soil."

5.1.1 Materials and Methods

A loamy soil texture field was treated with a herbicide (Avadex) at 3.5 l/ha^{-1} (0.6 ppm ai/A), which was then followed by temik at 10 and 20 kg ha^{-1} (1 and 2 ppm ai/A). One Plot had a herbicide bentanal applied at the end at a rate of 0.6 ai/A. Each treatment was repeated 6 times.

Soil samples to a depth of 5 cm (2") were taken and homogenized (storage at 4°C before analysis). Total numbers of bacteria were determined by medium of Bunt and Rovira (1955) and fungi on Martin's agar. Saccharase, phosphatase, urease, and dehydrogenase activity were determined by method of Hoffmann and Hoffmann (1966) and Glathe and Thalman (1970). Protease was also evaluated using the method of Ladd and

Butler (1972). Results were examined by analysis of variance and by the Duncan test.

Results

Using analysis of variance and the Duncan test no inhibition of microbial functions could be observed.

Conclusions

Cumulative biological indexes in upward ranking for spring, summer, and fall for the aldicarb treatment was, 99, 99, 90; indicating no inhigition of the soil functions described previously. Analysis of variance was not significant for all parameters tested. The Duncan test ranked the Temik treated test 9th and 7th for upward ranking. Correlation between the cumulative biological rank index and crop production is in positive agreement, except leaf yield.

This is an actual field study and not a laboratory, however, that is not our objection.

There is evidence that Eureopean soils are much more advanced microbially, showing more resistance. We would expect much faster degradation and the use of much higher rates before any effect could be observed. We have little knowledge on the synergism effects of combination pesticide application as performed here (whether one alone would inhibit - can not be evaluated). We also note that in 1972, a significant response to N_2-fixation was seen, yet in 1973, this was not evaluated. No objections to statistical method-this reviewer having done this type of analysis before.

The study is not acceptable to support any U. S. proposed use of temik. However, it could be used in that context if the company wishes to analyze both Belgium-U. S. Equivalent soils to match microbial populations

5.1.2 Metabolism

Effect of Microbes on Pesticides

Acc# 096670 Book II Ref. 39.

Skrentry, R. F. and J. A. Ellis, "Control of Aphis fabae on Broad Beans (Vicia faba) by the Systemic Action of Gamma-BHC, Thionazin and Aldicarb," Pest. Sci. 1: 45-48 (1970).

5.1.2 This is not a microbial study as such, but a comparison of yields between the application of two pesticides (Temik and/or thionazin). The company claims that higher yields resulted from no effect on the soil micro-flora. However, the paper suggests aldicarb persists longer, thus giving better control. This is not EC data.

5.1.3 Metabolism

Effect of Pesticides on Microbes

Acc# 096670 Book I Ref. 26.

Lin, S., B. R. Funke and J. F. Schulz, "Effects of Some Organophosphate and Carbamate Insecticides on Nitrification and Legume Growth," Plant Soil 37 (3): 489-496 (1972).

5.1.4 Materials and Methods

Bearden loam soil was treated with 5, 50, and 500 ppm ai/A and adjusted to 60% moisture, with 31 ml of 1 mg/ml ammonium sulfate solution for nitrification. Samples at 0, 3, 6, 11 and 30 days were taken with nitrate and nitrite determined as described by Bremmer.

Pure cultures of Rhizobium melilote, leguminosarum, trifolu, and japonicum were evaluated by sensi disc (2.20 µl/disk 95% technical) method.

Sweet clover and alfalfa were grown with 5,50 and 500 ppm aldicarb. At 30 days average dry weights were determined.

5.1.5 Results

No effect on nitrification was observed, except at the 500 ppm level. All Rhizobium species evaluated showed an inhibition with sensi disk, except japonicum at the lowest rate. No effect on alfalfa or clover seedlings, except for the 500 ppm level.

5.1.6 Conclusions

At day 6 ppm NO_3-N for the control was 52.5 ppm; for 5, 50, 500 ppm aldicart the results were 49.5, 43.0, and 15 ppm respectively. At day 11, the control was 59.0 ppm; 5, 50, 500 ppm aldicarb the results were 56.5 51.0, and 4.0 ppm. At 30 days the control was 46 ppm; the 500 ppm aldicarb 1.0 ppm.

At 2 µl/disk(≈2ppm) Rizobium meliloti, japonicum, leguminosarum, and trifolii exhibited zones of inhibition of 11.0, 0.0, 22.0, and 29.0 mm respectively. For 20 µl/disk(≈20 ppm) zones of inhibition for these same organisms were 17.5, 6.5, 34, and 29.0 mm respectively.

Alfalfa plant weight (in milligrams) of 5, 50, and 500 ppm concentrations and the control were 9.4, 6.5, and 3.5 mg respectively. For sweetclover these same parameters exhibited 8.1, 6.1, 2.0 and 5.6 mg respectively.

Nitrification and phytotoxicity are not severely inhibited until concentrations of 50-500 ppm aldicarb were evaluated. This is 5-50 x the normal rate used for aldicarb.

Indications are that N_2-fixation may be impaired at ≈ 2ppm, all Rhizobium species, except japonicum were inhibited. The inhibition was not severe if we use 15 mm as a base for significance in sense-disc method. At ≈20ppm results are severe, except for japonicum, which was not inhibited. No correlation between the nodulating bacteria tested and legume growth can be made.

This study did not address N_2-fixation directly, protein, starch, or cellulose degradation. This study is not acceptable by itself and would not support any proposed use of aldicarb.

By combining the soil metabolism studies, the microbes effect on pesticide studies, and parts of previous effects of pesticides on microbes data (with the Belgium soil as a back-up) this study can be made acceptable.

5.1.7 Metabolism

Microbes Effects on Pesticides

Acc# 096670 Book Ref. I.

Anderson, J. P. E., "Factors Influencing Insecticide Degradation by a Soil Fungus, Mucor alternans," Diss. Abstr. Int., 32 (6): 3414B-3415B (1971).

5.1.8 The data submitted was an abstract of the 118 page total paper. It was stated that Temik did not effect the growth of Mucor alternans. We will not review this abstract unless raw data pertaining to Temik/ Mucor alternans is sumbitted.

5.1.9 Mobility

Leaching

5.2 In review 1016, 69, 78 and 9/7/77 an acceptable leaching study combination was reviewed. We have (5) new leaching studies submitted, they support the previous studies showing aldicarb and metabolites to leach in sandy type soils, to a less extent in loam soils, and nil in muck-type soil. One study (ref. 32) of upward movement in soil is germane to EC. We will review it for comparison to downward column.

The following are the titles of the new leaching studies:

Borash, A. J. and J. A. Kramer, Jr., "Experiments Designed to Trace Movements of Aldicarb in Soil," UCC Project Report 17959, January 9, 1973.

Coppedge, J. R., D. L. Bull and R. L. Ridgway, "Movement and Persistence of Aldicarb in Certain Soils," Arch. Environ. Cont . Toxicol. 5: 129-141 (1977).

Richey, F. A., Jr., "TEMIK Aldicarb Pesticide. Water leaching of Aldicarb, Aldicarb Sulfoxide, Aldicarb Sulfone and Internal Standard Chloride Ion in Columns of Four Soil Types," UCC Project Report File No. 16669, January 7, 1972.

Romine, R. R., "TEMIK Aldicarb Pesticide Leaching of A ldicarb into Sandy Soil with Irrigation of a "TEMIK" Treated Sugar Beet Field," UCC Project Report, File No. 17079, April 11, 1972.

The following will be reviewed for comparison with downward columns:

Richey, F. A. Jr., "TEMIK Aldicarb Pesticide. Upward Movement of Aldicarb through Soil During Water Evaporation," UCC Project Report File No. 17526, August 18, 1972.

S-methyl ^{14}C-labeled temik was applied to the top of a six-inch column of Blanton fine sand soil at 4 lbs. ai/6"A. An additional 4-inch layer was applied over the temik to make the total depth 10". Water was added and the column held at room temperature for 16 hrs., then heated by sunlamp to 38° C (surface) for 7 days. A stream of air was also blown over the top during the 7-day interval. Soil was analyzed in 1" segments.

Of the 93.1% recovered activity, ≈40% was found in the top 1" soil layer, 15% in the 1-2" layer, ≈10.2% in the 2-3" layer and ≈6% in the top 1/4" layer. Of the activity ≈75% was aldicarb sulfoxide, ≈8.5% aldicarb sulfone, ≈14% others, ≈2.0% water soluables, and ≈1% parent.

This upward leaching study supports the previous acceptable downward leaching columns, in that aldicarb and its metabolites will leach in certain type soils. The 38°C temperature is high, but since this was on the surface, it is felt that temperatures could reach 38°C on a hot day. This is another acceptable leaching study.

5.2.1 Mobility

Adsorption.

Acc# 096670 Book I Ref. #20.

Hough, A., I. J. Thomason and W. J. Farmer, "Behavior of Adlicarb in Soil Relative to Control of Heterodera schachtii," J. Nematol. 7: 214-221 (1975).

5.2.2 Materials and Methods

Two soils: Holtville clay (sand [6.4%], silt [42.1%], clay [51.5%], O. M. [1.4%], pH [7.6], C.E.C.[32.7]) and Buren silt loam (sand [37.7%], silt [51.3%], clay [11.0%], O.M. [1.4%], pH [7.2%], and C.E.C. [10.8%], were used to evaluate adsorption isotherms of aldicarb sulfoxide at concentrations of 0.1, 0.3, 1.0, 3.0, 10.0, and 100 µg/ml in 0.01M $CaCl_2$. Adsorbent and solution were separated by centrifugation for 20 min. at 22C. A 10ml aliquot was analyzed for aldicarb sulfoxide and the amount adsorbed per gram absorbent was calculated. The amount absorbed was plotted against the equilibrium concentration on a log-log scale.

5.2.3 Results/Conclusions

Freundlick K values for aldicarb sulfoxide in Holtville clay is 3.3 and for Buren silt loam 0.34, indicating much more adsorption of the sulfoxide moiety to clay soil than loam, yet both soils have low enough values to indicate high mobility.

This type of data is not required for this use and we will not validate the data, but have included it for reference.

5.2.4 Mobility

Adsorption.

Acc# 096670 Book I Ref #8

Bromilow, R. H., "Breakdown and Fate of Oximecarbamate Nematicides in Crops and Soils," Annals. Appld. Biol. 75 (3): 473-479 (1973).

5.2.5 Materials and Methods

A sandy soil (under grass) was evaluated for Q values; Chemical concentration in the soil O.M. ÷ Chemical concentrations in the soil water, for aldicarb, aldicarb sulfoxide, and aldicarb sulfone.

5.2.6 Results/Conclusions

Q values for aldicarb, aldicarb sulfoxide, and aldicarb sulfone were 10, 1, and 2 respectively. The

above three compounds do not exhibit a tendency to adsorb.

This data is not required for this use and we will not validate it, but present it as reference.

5.2.7 Mobility

Volatility

5.2.8 Acc# 096670 Book 1 Ref #10

Bull, D. L. R. A. Stokes, J. R. Coppedge and R. L. Ridgway, "Further Studies on the Fate of Aldicarb in Soil," J. Econ. Entomol. 63: 1283-1289 (1970).

5.2.9 This data has been reviewed in the previous 1016-69, 78 and 9/7/77 (pg. 29-oranges review), and we will not review it again per Dr. Roggoff's memo to Mr. Campt of 8/12/77.

5.3.0 Mobility

Volatility

Acc# 096670 Book 2 Ref #43

The Volatilization, Degradation, Adsorption, and Desorption Characteristics of Aldicarb [2-Methyl-2-(Methylthio) Propionaldehyde O-(Methylcarbamoyl) Oxime] in Soils and Clays, Supak, James R., PhD, Texas A&M University, 1972.

5.3.1 No data from the article submitted, just a cover abstract. We cannot make a review of an abstract. This does appear to answer why aldicarb is found to stop its upward movement in soil at the 1" level. We will require that this be submitted, however, this data is not required for this use.

5.3.2 Mobility

Volatility

Acc# 096670 Book II Ref #40

Sprengler, H. T., J. E. Griffith and W. S. Tamplin, "TEMIK and TEMIK Metabolites Vapor Pressure Data," UCC Project Report File No. 10819, October 24, 1968.

5.3.3 Vapor pressure data for Temik and Temik metabolites was obtained by the gas transpiration method. Results are as follows:

"TEMIK" INSECTICIDE AND SOME METABOLITES VAPOR PRESSURE DATA (a)

Sample Designation		Vapor Pressure, mm Hg, at: 0°C (b)	25°C	50°C
I.	TEMIK oxime sulfone	3×10^{-5}	3×10^{-4}	2×10^{-3}
II.	TEMIK oxime sulfoxide	3×10^{-5}	3×10^{-4}	2×10^{-3}
III.	TEMIK Insecticide	1×10^{-5}	1×10^{-4}	7×10^{-4}
IV.	TEMIK sulfone	8×10^{-6}	9×10^{-5}	6×10^{-4}
V.	TEMIK sulfoxide	1×10^{-5}	7×10^{-5}	5×10^{-4}
VI.	TEMIK nitrile sulfone	2×10^{-4}	3×10^{-3}	3×10^{-2}
VII.	TEMIK nitrile sulfoxide (liquid sample)	1×10^{-4}	2×10^{-3}	4×10^{-2}

(a) Considered precise within the order of magnitude indicated by the exponent of the pressure value

(b) Extrapolated

This type of data is not required for this use, however, it is being reviewed for reference and to support a change of conclusions from 1016-69, 78 of 9/7/77.

Note: One reference indicates values of $\approx 1.0 \times 10^{-4}$ mm Hg is not considered valatile material.

5.3.4 Field Dissipation

Soil

Acc# 096670 Book I & II, Ref. 2, 9, 13, 21, 24, 47 (8, 39 additional from England).

5.3.5 Two studies, numbers 9 and 13 were reviewed in the previous 1016, 69, 78 of 9/7/77. We will not review these again per Dr. Rogoff's memo to Mr. Campt of 8/12/77. Two studies, numbers 8 and 39 are on English

soils, we will not review these, except only for comparison, because of not being done under actual use conditions.

Ref. number 9 & 13, which were reviewed previously did not evaluate the compound from four agricultural soils. The references cited above combined give us enough data to make an acceptable field dissipation soil review. All four will be presented as one acceptable study.

5.3.6 Materials and Methods

Study No.	Soil	Rate
2	Norfolk sandy loam North Carolina	S-methyl-^{14}C ≈3 lbs. ai/A
9	Lufkin fine sandy Texas	^{35}S-labels 2mg/100 g. ai/A
21	California	2.5, 5.0 10.0, 20.0 lbs. ai/A
24	Gulpin fine loam Penn.	0.5, 1.0, and 2.0 lbs. 10% ai/12 trees
47	Sandy loam Texas	1.5 lbs ai/A
13	Norfolk sandy loam North Carolina	10 lbs. ai/A

5.3.7 Results/Conclusions

Study #2 -- Sample depth 8"

~~Table II~~. Relative Concentration of Radiolabeled Components Present in the Soil after In-Furrow Application of S-Methyl-^{14}C Aldicarb during the Summer of 1967[a]

	% of Recovered Readioactivity at Indicated Days After Treatment[b]				
Transformation Products	0	7	14	60	90
Aldicarb	82.6	34.7	6.5	ND[c]	ND
Aldicarb sulfoxide	12.7	48.6	66.9	31.1	13.1
Aldicarb sulfone	1.4	4.4	11.6	50.0	41.5
Oxime sulfoxide	1.2	1.8	0.9	2.0	2.8
Nitrile sulfoxide	ND	0.8	1.3	1.2	0.9
Nitrile sulfone	ND	1.2	0.5	3.0	4.8
Origin of tlc	0.9	3.4	2.5	3.2	13.3
Water-solubles	1.2	5.0	9.8	9.6	23.6
Total ppm ± S.D.[d]	13.1± 0.24	3.47± 1.30	2.49± 1.56	0.17± 0.07	0.07± 0.03

[a]Aldicarb applied at the rate of 3.4 kg/ha at the time of planting potatoes.
[b]Based on triplicate samples and duplicate analyses for each sample.
[c]ND—none detected.
[d]Total parts per million of ^{14}C-aldicarb equivalents recovered ±standard deviatio

5.3.7 Study #9

~~Table 1~~ - Relative concentrations of S^{35} - labeled UC-21149 and its metabolites recovered from soil that was treated and then exposed to seasonal field conditions.

Compound	% of applied dose at indicated weeks after treatment			
	0	1	2	8
Unknown A	0.2	0.7	0.7	0.1
Unknown B	.0	.1	.2	.1
Unknown C	.1	.2	.1	.0
Unknown D	.0	.0	.9	.0
Sulfoxide	8.0	36.8	14.4	.8
Oxime sulfoxide	.7	.7	1.2	.1
Sulfone	.0	4.6	3.8	1.0
Nitrile sulfoxide	.0	1.5	.7	.1
Unknown E	.0	1.3	1.1	.2
UC-21149	76.6	1.6	.2	.1
Unknown F	.0	.2	.4	.1
Unextracted	14.4	13.8	15.9	11.1
Lost	.0	38.5	60.4	86.3

Sample depth 4-6"

Study #24

~~Table 1~~ - Recovery of aldicarb at 4 time intervals from soil treated at 3 different rated by broadcast application in 1966.

Treatment (lb/12 trees)	Soil depth (in.)	Ppm of aldicarb found indicated days after application			
		1 day	15 days	36 days	63 days
0.5	6	0.38	0.18	0.00	0.00
	12	.00	.02	.04	.00
1.0	6	.85	.24	.10	.00
	12	.00	.04	.02	.00
2.0	6	.92	.61	.29	.07
	12	.00	.07	.04	.04

5.3.7 Study #13

RESIDUES OF TEMIK AND ITS CARBAMATE METABOLITES IN SOIL

Days After Treatment	Sampling Date	Total TEMIK Residue ppm	pH
	Treated Area		
0 (pretreatment control)	6/21/68	0.06	6.00
0	6/21	9.4	5.98
3	6/24	7.2	5.90
7	6/28	5.5	5.91
5.0" irrigation water applied 6/28			
8	6/29	0.66	
14	7/5	0.66	
21	7/12	1.1	
28	7/19	0.19	6.01
5 weeks	7/26	0.09	
7 weeks	8/9	0.20	
8 weeks	8/16	0.13	6.08

Sample depth 6"

Study #21

Total Carbamate Residues (ppm) in Soil, after Soil Treatment with Aldicarb (March 1975)[a]

Substrate	Sample	10 lb AI per acre (four-side) Range	Mean	1974[b] mean	20 lb of AI per acre (four-side) Range	Mean	mean 197-
Soil	Pretreat	<0.01-0.01	<0.01		<0.01-0.14	0.04	
	35-day	0.26-0.69	0.52	1.02	0.94-1.45	1.20	2.45
	118-day	0.12-0.36	0.20	0.14	0.19-0.52	0.42	0.21

Substrate	Sample	20 lb of AI per acre (two side) Range	Mean
Soil	Pretreat	<0.01	<0.01
	35-day	0.27-1.16	0.69
	118-day	0.10-0.37	0.23

[a] Applied March 19, 1975, to soil in a Valencia orange grove located on the Irvine Ranch, Tustin, Calif; sprinkler irrigation for 24 h on March 20 and again on March 22; four replicate plots.

[b] Applied April 8, 1974. These values are the data used to construct Figures 1, 2, and 3 and Table I.

Sample depth 12"

5.3.7 Study #47

Total Toxic Aldicarb Residues (as Temik Sulfone) in Soil Treated with Aldicarb 10G in the Texas High Plains (1971)

Sampling location	Treatment date	Sampling date	Residue, ppm[a] Brownsville	Union Carbide	Gulfport
		Dryland			
Row	6/30/71	7/2/71	0.23	0.50	0.28
Row	6/30/71	7/27/71	0.05		
Row	6/30/71	11/22/71	0.00		0.00
Middle	6/30/71	7/2/71	0.00	0.02[b]	
Middle	6/30/71	7/27/71	0.00		0.00
Middle	6/30/71	11/22/71	0.00		0.00
Row	6/25/71	6/28/71	1.49	1.80	1.65
Row	6/25/71	7/27/71	0.39		0.10
Row	6/25/71	11/22/71	0.00		0.00
Middle	6/25/71	6/28/71	0.00	<0.02	
Middle	6/25/71	7/27/71	0.00		
Middle	6/25/71	11/22/71	0.00		
	Untreated	6/25/71	0.00	<0.02	0.00
	Untreated	7/27/71	0.00		0.00
	Untreated	11/22/71	0.00		
		Irrigated			
Row	6/10/71	6/28/71	0.07	0.12	0.10
Row	6/10/71	11/22/71	0.00		0.00
Middle	6/10/71	6/28/71	0.00	<0.02	
Middle	6/10/71	11/22/71	0.00		0.00
Row	6/16/71	6/28/71	0.43	0.37	0.27
Row	6/16/71	7/27/71	0.06		0.00
Row	6/16/71	11/22/71	0.00		0.00
Middle	6/16/71	6/28/71	0.00	<0.02	
Middle	6/16/71	7/27/71	0.00		
Middle	6/16/71	11/22/71	0.00		0.00
East Creek[c]	6/16/71	7/14/71	0.00		
East Creek[d]	6/16/71	7/14/71	0.00		
Creek Bottom[e]	6/16/71	7/14/71	0.00		
Row	6/15/71	6/28/71	0.78	0.78	0.54
Row	6/15/71	7/27/71	0.00		0.00
Row	6/15/71	11/22/71	0.00		0.00
Middle	6/15/71	6/28/71	0.00	<0.02	0.00
Middle	6/15/71	7/27/71	0.00		
Middle	6/15/71	11/22/71	0.00		0.01[b]
Row	6/14/71	6/25/71	0.35	0.61	0.23
Row	6/14/71	7/20/71	0.06		
Row	6/14/71	7/26/71	0.00		
Row	6/14/71	11/22/71	0.00		0.00
Middle	6/14/71	6/25/71	0.00	<0.02	
Middle	6/14/71	7/20/71	0.00		
Middle	6/14/71	7/26/71	0.00		
Middle	6/14/71	11/22/71	0.00		0.00
	Untreated	6/25/71	0.00	<0.02	
	Untreated	7/26/71	0.00		0.00
	Untreated	11/22/71	0.00		0.00

[a] residues were corrected for moisture content and for aldicarb recovery from fortified samples. [b] Lower limit of sensitivity. [c] One-fourth mile down from Field no. 3. [d] One mile down creek from Field no. 3. [e] Even with and North of Field no. 3.

Soil sample depth 6 inches

5.3.7 Aldicarb parent compound dissipates rapidly with an estimated half-life of 1-14d and forms two major metabolites; aldicarb sulfoxide and sulfone. The two metabolites are much more presistent showing estimated estimated half-lives of 60-90 and >90d respectively and accounting for ≈81% of the activity at d 60. Oxime sulfoxide, nitrile sulfoxide, nitrile sulfone are minor metabolites identified (all <5% at day 90). Water soluable and the origin fractions are significant at day 90 (≈13 & 24%) respectively. Leaching to the 12" depth occurs in the sandy type soils evaluated.

5.3.8 Accumulation

Fish

Acc# 096670 Book II. Ref#36.

Romine, R. R., "Accumulation of Aldicarb Residues in Fish Tissues from Chronic Exposure to Aldicarb, Aldicarb Sulfoxide, and Aldicarb Sulfone in Aquaria Water," UCC Project Report, File No. 19009, December 10, 1973.

5.3.9 Methods and Materials

Bluegill su-fish were exposed to equal-molar concentration of aldicarb, aldicarb sulfoxide, and aldicarb sulfone at levels of 0.1 and 0.01 ppm for 30-60 days.

Method of analysis for water was aldicarb-FPO-water and fish-FPO-fish,method consists of extracting total residues of parent, sulfoxide, and sulfone; and oxidizing to aldicarb sulfone with peracetic acid. Clean-up via Florisil column and analyzed by GLC.

5.4.0 Results/Conclusions

0.1 ppm

Date	Days exposure	Cone Fish (ppm) Tank 1	Cone Fish (ppm) Tank 2	Cone Water (ppm) Tank 1	Cone Water (ppm) Tank 2	Accumulation Factor Tank 1	Accumulation Factor Tank 2	Average
12-11-72	7	0.45	0.47	0.102	0.108	4.4	4.4	4.4
12-18-72	14	0.55	0.44	0.069	0.078	7.9	7.0	7.45
12-20-72	16	0.53	0.47	0.075	0.064	7.0	8.3	7.65
12-26-72	22	0.46	0.45	0.089	0.082	5.1	5.6	5.35
1-2-73	29	0.43	0.42	0.035	Not Analyzed	12.2	-	12.2
1-8-73 #	35	0.52	0.04	0.099	Not Analyzed	5.2	-	5.2
1-15-73	42	0.39	0.04	0.048	Not Analyzed	8.1	-	8.1
1-22-73	49	0.41	Not Detectable	0.081	Not Analyzed	5.0	-	5.0
1-29-73	56	0.28	Not Detectable	Not Analyzed	Not Analyzed	-	-	-

\# Fish placed in clean water in Tank 2 Residues calculated as Aldicarb Sulfone

5.4.0 Results/Conclusions

0.01 ppm

Date	Days exposure	Cone Fish (ppm) Tank 1	Cone Fish (ppm) Tank 2	Cone Water (ppm) Tank 1	Cone Water (ppm) Tank 2	Accumulation Factor Tank 1	Accumulation Factor Tank 2	Average
12-11-72	7	0.022	0.034	0.015	0.015	1.4	2.2	1.8
12-18-72	14	0.028	0.03	0.008	0.012	3.5	2.5	3
12-20-72	16	0.032	0.022	0.007	0.011	4.5	2	3.25
12-26-72	22	0.029	0.026	0.008	0.012	3.6	2.1	2.85
1-2-73	29	0.027	0.032	0.007	Not Analyzed	3.8	-	-
1-8-73 #	35	0.26	0.019	0.01	Not Analyzed	2.6	-	-
1-15-73	42	0.42	Not Detectable	0.009	Not Analyzed	4.6	-	-
1-22-73	49	0.02	Not Detectable	0.02	Not Analyzed	1	-	-
1-29-73	56	Not Detectable	Not Detectable	Not Analyzed	Not Analyzed	-	-	-

\# Fish placed in clean water in Tank 4 Residues Calculated.

Accumulation peaks at day 29 (12x) and declines thereafter to day 56 (5.0x). Residues in fish when taken out of the treated water decline from 0.42 ppm at 29 days to 0.04 ppm at day 35; finally to not detectable at day 49. Silimar results are seen at the 0.01 ppm concentration, except accumulation factors are lower (3.8x) and 1x) respectively.

A flow-through system was not evaluated, because the participating laboratory could not maintain fish colonies under flow-through conditions.

The method used for evaluation was not radioisotopic, did not analyze all metabolites formed both in soil and water, and analyzed the compunds in question collectively.

The method however, does exhibit recoveries from both water and fish at >90%. The fish lose the residues accumulated when placed into fresh water- indicating that residues will decline once the fish is removed from exposure. Data to indicate what is in the water to start from both hydrolysis and soil are excellent. Normal river water is normally of pH values so that the parent will breakdown. In conclusion, the method is adequate for the residues described in the material and method section.

From hydrolysis, soil metabolism (anaerobic), photolysis, and microbial metabolism data, we can predict the following residues in water, besides the ones mentioned previously; these being:

1. Aldicarb sulfoxide alcohol (major)
2. Aldicarb sulfone acid (major)
3. Aldicarb sulfoxide amide (minor)
4. Aldicarb sulfoxide oxime (minor)
5. Aldicarb sulfone amide (minor)
6. Aldicarb sulfone alcohol (minor)
7. Aldicarb sulfone nitrile (minor)
8. Aldicarb sulfone oxime (minor)
9. Aldicarb Sulfoxide nitrile (minor)
10. Methane sulfonic acid (minor)
11. Parent (minor)
12. Unknowns (1, 2, 3) (minor)

The method used did not have or was not evaluated to identify these residues in fish. The method did not or was not evaluated to identify potential fish metabolites.

We defer to Environmental Safety as to the need for data on the above metabolites. If they do not need this data, then Environmental Chemistry can accept this study.

5.4.1 Accumulation

Rotational Crops

Acc# 096677 Book I Ref. #19

Hirsh, D. H. and K. P. Sheets, "Aldicarb Subsequent Crop Studies," UCC Project Report No. 23520, April 21, 1977.

5.4.2 Materials and Methods

^{14}C-methyl aldicarb was applied to Norfolk sandy loam (pH[5.7], OM[1.1%], CEC [4.0], H_2O 1/3 bar [20.5%], sand [82%], silt [8%], and clay [10%]) at a rate of 5 lbs. ai.A, and incorporated to a depth of 6 inches. Crops was planted 119 and 365 days after last application. Residues found as ^{14}C were subjected to analysis by GLC flame-photometric detector selective for sulfur, with parent, sulfoxide, and sulfone moieties being detected.

5.4.3 Results/Conclusions

Subsequent Crop Plantings (a) Crop	PPM Residues Calculated as Aldicarb 119-Day C-14 (b)	119-Day Carbamate (c)	1-Year C-14 (b)	1-Year Carbamate (c)
Lettuce (a)	0.06	0.02	0.013	<0.02 (d)
Turnip tops	0.25	0.04	0.045	<0.02 (d)
Peeled turnip	0.03	<0.02 (d)	nil (f)	-
Turnip peelings	0.04	0.14 (e)	0.007	-
Unpeeled turnip	-	-	-	<0.02 (d)
Barley heads	0.24	0.04	0.033	<0.02 (d)
Barley green plants	0.24	0.05	0.060	<0.02 (d)
Barley straw	1.35	0.72	-	-
Soil at planting	0.37 (g)	-	0.26	-
Soil at harvest	0.25	-	0.31	-

(a) Time to planting of crops after application of aldicarb to soil. Lettuce planted 150 days after application.

(b) Radioanalysis via combustion.

(c) Residue method of analysis by gas chromatography using sulfur detector to determine aldicarb, aldicarb sulfoxide and aldicarb sulfone.

(d) Limit of detection, none detected.

(e) Possibly soil was not completely washed form turnip before peeling, resulting in high assay in peelings.

(f) Less than blank (untreated sample).

(g) Five pounds per 10-inch acre in Norfolk sandy loam is approximately 3 ppm.

As can be seen, there is a vast difference from total ^{14}C values and carbamate values. The identity of carbamates with this method will identify parent, sulfoxide, and sulfone moieties; collectively as the sulfone. A method using S-Methyl-^{14}C Aldicarb in a field study identified 3 more degradates (oxime sulfoxide, nitrile sulfoxide, nitrile sulfone) plus two unknowns (which are substantial at 90 days (water soluables and the origin fractions) #

Source. J. Agr. and Food Chemistry, Vol. 19, No.4, page 727/July/Aug-71. (Ref.#2).

A method used by the J. Agr. Food Chem., (Vol. 21, No. 2, 1973) which was basically the U.C. 1970 method, determined that oxime type compounds interfere in the methods detection of aldicarb, aldicarb sulfoxide and sulfone. There is also evidence from plant metabolism data that the oxime type compounds are introduced into the plants natural metabollic pathway as glocoside conjugates. This data also indicates the water soluable fraction reduces to form alcohol sulfoxide, which is further introduced into the plants natural metabollic pathway, as glucoside conjugates.

Based on the above comments and data, a 12 mo. crop rotation interval can be supported. If the applicant wishes a six month or no crop rotation interval we need either:

1. Data on the other metabolites identified to show these are not present or,

2. A statement or data indicating the above metabolites in question are conjugated residues in the plant.

#Ref. #47.

5.4.4 Ancillary

Coppedge, J. R., D. A. Lindquist, D. L. Bull and H. W. Dorough, "Fate of 2-Methyl-2-(methythio)propionaldehyde O-(methylcarbamoyl) oxime (TEMIK) in Cotton Plants and Soil," J. Agr. Food Chem. 15: 902-910 (1967).

This data has been reviewed in previous 1016-69,78 of 9/7/77, we will not review it per Dr. Rogoff's memo to Mr. Campt of 8/12/77. Further details, see page 45 of 1016 -69,78 of 9/7/77.

5.4.5 U. S. Environmental Protection Agency, "Substitute Chemical Program. Initial Scientific and mini-economic Review of Aldicarb," EPA-540/1-75-013 (1975).

Same as above (see page 46 of above for further details).

6.0 General Conclusions/Environmental Profile

6.0.1 Hydrolysis

Aldicarb is stable to hydrolysis at pH values ≤7.0 at ambient temperatures. Its most stable pH is 5.5 with 1-1.2% degradation at a 28 d interval. At pH values > 7.0 aldicarb is subject to hydrolysis and an extrapolated t-1/2 would be ≃8.0 days (pH 9.0). Hydrolysis products identified were:

1. Aldicarb oxime (major)
2. Aldicarb sulfoxide (minor)
3. Aldicarb sulfoxide oxime (minor)
4. Aldicarb nitrile (minor)

Aldicarb exhibits temperature dependency to hydrolysis at acid, neutral, basic pH values at elevated temperatures (50-100°C). A basicity dependency is also shown.

Aldicarb sulfoxide is stable to hydrolysis at pH values of ≤7.0 (2.3% in 28d). At pH values of ≥7.0 hydrolysis is rapid with an extrapolated t-1/2 of ≃2 d (pH9). Degradates identified were:

1. Aldicarb sulfoxide oxime (major)
2. Aldicarb sulfoxide nitrile (major)
3. Water soluables and unknowns (minor)

At acid conditions the slow hydrolysis from the nitrile moiety, with the oxime moiety formed at basic conditions. Aldicarb sulfoxide exhibits temperature dependency to hydrolysis at acid, neutral, basis pH values at elevated temperatures (50-100°C).

Aldicarb sulfone will hydrolyze at elevated temperatures of 50-100°C with a t-1/2 extrapolated as ≃48 mins. Degradates identified were:

1. Aldicarb sulfone oxime (Major)
2. Aldicarb sulfone nitr-le (minor)
3. Unknown (minor).
4. 1, 3-dimethylurea (minor).

No other data presented for this moiety, however, we would speculate very similar results to the sulfoxide moiety.

Hydrolysis data requirement has been fulfilled and will support any proposed use of aldicarb.

6.0.2 Photolysis

Aldicarb will phorodegrade with an extrapolated t-1/2 of >7 but <15 days in water at 20-25°C. Photoproducts identified were:

1. Aldicarb sulfoxide (major)
2. Aldicarb sulfoxide nitrile (minor)
3. Aldicarb sulfone nitrile (minor)
4. Aldicarb sulfone alcohol (minor)

Volatilyzed material at day 7 was 28% of applied activity (not characterized).

No data on soil surfaces and artificial sun lamp, which had special lines below 280-NM (10% of total wattage). It is speculated that the special line below 280 NM would shorten the half-life and not pose a great significant difference.

This data will support any proposed incorporated use of aldicarb (photolysis will not be a major pathway in this type of use), but will not support any foliar use until soil data and effect of wavelength below 280 NM is determined. Photolysis data requirement for this use (oranges incorporated) is satisfied.

Note: Aldicarb sulfoxide is stable to photolysis for 14 days.

6.0.3 Metabolism

Soil Aerobic

Aldicarb will metabolize in clay, fine sand, sandy loam, fine sandy loam, clay loam, and muck type soils, with varying pH values (4.0-810) moisture (3-100%), and organic matter (1-78%). An extrapolated half-life range is from ≤1 week to 56 days. Degradates identified were:

1. Aldicarb sulfoxide (major)
2. Aldicarb sulfone (major)
3. Nitrile sulfoxide (minor)
4. Oxime (minor).
5. Oxime sulfoxide (minor).
6. Nitrile sulfone (minor).

7. Oxime sulfone (minor)
8. Unknowns 1, 3, 5, 6, 7 (minor)
9. Water soluables (major, ninor) depending on label.

Soil characteristics of pH, moisture content, organic matter, as well as soil sample age, pretreatment and treatment during experimentation, all reflect the rate of aldicarb degradation. Differences in label positions (S-me, N-me, Tert) result in different recoveries of various isolated fractions. N-me-^{14}C gives the highest unextractable residue values, S-me^{14}C gives the highes $^{14}CO_2$ value, with tert ^{14}C giving the most even distribution. Sandy soils form the highest water soluable extracts.

Bound residues range from 4-16.4% of applied dose depending on label.

Volatilization is quite substantial and of the volatilized material 95% was identified as $^{14}CO_2$.

The soil metabolism (aerobic) data requirement has been fulfilled and this soil metabolism data will support uses in terrestrial and terrestrial/aquatic (forest) type applications. It will not support the aerobic aquatic data requirement and will not substitute for uses requiring the data (aquatic and aquatic impact uses).

6.0.4 Metabolism

Soil Anaerobic

Aldicarb metabolizes under anaerobic conditions in silt loam and residues of parent declined from 1.7% of applied activity (day 0 anaerobic or 30 days aerobic) to 0.0 at day 30 anaerobic or 60 days aerobic). Degradation under anaerobic conditions is about the same as the aerobic soil metabolism. Degradates identified were:

1. Aldicarb sulfoxide alcohol (major)
2. Aldicarb sulfone acide (major)
3. Aldicarb sulfoxide amide (minor)
4. Aldicarb sulfoxide oxime (minor)
5. Aldicarb sulfone amide (minor)
6. Aldicarb sulfone (minor)

7. Unknown 1 (minor)
8. Aldicarb sulfone alcohol (minor)
9. Aldicarb sulfone nitrile (minor)
10. Aldicarb sulfone oxime (minor)
11. Aldicarb sulfoxide nitrile (minor)
12. Unknown 2 (minor)
13. Unknown 3 (minor)
14. Methane sulfonic acid (minor)

Bound residues were from 8.6 to 9.2% respectively at 30 and 60 days time.

Volatility is substantial and identified by difference as $^{14}CO_2$. The compound will degrade under anaerobic conditions further to a variety of metabolites. Anaerobic soil metabolism data requirement has been fulfilled and this metabolism data will support uses in terrestrial and terrestrial/aquatic (forest) type applications. It will not support the anaerobic aquatic data requirement and will not substitute for uses requiring this data (aquatic and aquatic impact uses).

6.0.5 Metabolism

Microbes' Effect on Pesticides

Aldicarb will be metabolized by soil fungi when grown in shake flask cultures containing aldicarb. Metabolites formed were:

1. Aldicarb sulfoxide (major)
2. Aldicarb sulfone (minor)
3. Oxime sulfoxide (minor)
4. Nitrile sulfoxide (minor)
5. Oxime sulfone (minor)
6. Nitrile sulfone (minor)

--Organo phase

1. Alcohol and amide sulfoxides and sulfones (major)
2. Acid sulfoxide and sulfone (minor)
3. Unknown (minor)

--Aqueous phase

Degrading organisms in decreasing order of degradation portential were:

1. Gliocadium catenulatium
2. Penicillium multicolor

3. Cunninghamella elegans
4. Rhizoctonia sp.
5. Tricoderma harzianum

Aldicarb sulfoxide will be degraded to:

1. Oxime and nitrile sulfoxide (major)
2. Aldicarb sulfone (minor)
3. Oxime sulfone (minor)
4. Nitrile sulfone (minor)

Degradative potential G. Catenulatium > C. elegans > T. harzianum.

Although the study used rates less than the recommended rates, microbial degradation will occur at these rates (supported by soil metabolism studies at higher rates). In addition since fungi (which are the most susceptable species) did degrade the compound; bacteria and actenomycetes (which are more resistant) would degrade appreciably more.

Microbes effect on pesticides data requirement has been fulfilled and would support any proposed use for aldicarb where this data is required.

6.0.6 Metabolism

Effect of Pesticides on Microbes

Cumulative biological indexes in upward ranking for spring, summer, and fall for aldicarb was 99, 99, and 90; indicating no inhibition of the soil functions saccharase, phosphatase, urease, protease and dehydrogenase; with no inhibition of bacteria or fungi (total populations). Analysis of variance using the Duncan Test was not significant for all parameters tested. This is Belgian soil and cannot be used directly to support the data requirement, but is used to support other studies/conclusions.

Nitrification and phytotoxicity are not severely inhibited until 50-500 ppm (10-50x normal rate) concentrations were evaluated Rhizobium species are not severely inhibited with 20 ppm (2x-5x normal rates) concentrations were evaluated. This is a symbiotic organism and not a-symbiotic (free-living) as the requirement calls for.

By combining the soil metabolism studies, the microbes effects on pesticides studies, parts of previous effects of pesticides on microbes data (1016-67,78 9/7/77) and the Belgian soil as back-up the effect of pesticide on microbes data requirement has been fulfilled. It can be used to support any proposed use where this data is required.

6.0.7 Mobility

Leaching

The ability of temik and its degradates to leach depends on the soil type, particularly the organic matter. In muck soil the sulfoxide degradate leached through 7" of soil; loamy type soil, parent, sulfoxide, and others leached; in clay type soil the same three leached. The sulfone metabolite did not leach and is bound. Since the leaching studies show temik and its degradates to leach, we do not need an aged leaching study.

The leaching data requirement has been fulfilled and can be used to support all uses of aldicarb where this data is required.

Since the parent and degradates leach in sandy soils (this use) a caution should be taken to contamination of ground water tables.

6.0.8 Mobility

Adsorption, Upward movement

Temik and temik sulfoxide, sulfone, others, and water soluables will migrate upward in a soil column to the top 1" layer. Moisture content, relative humidity, temperature, and clay content of the soil seem to be integral to upward movement.

Freandlick K values for aldicarb sulfoxide in Holtville clay and Buren silt loam are 3.3 and 3.4 respectively. A sandy soil gave Q values for aldicarb, aldicarb sulfoxide, and aldicarb sulfone as 10, 1, and 2 respectively. Componds above do not exhibit adsorption tendencies.

0.34 see pg. 3

6.0.9 Mobility

Volatility

Vapor pressure, mm Hg, at 25°C for aldicarb, aldicarb sulfoxide, sulfone, oxime sulfone, oxime sulfoxide, nitrile sulfone, nitrile sulfoxide were: 1×10^{-4}, 7×10^{-5}, 9×10^{-5}, 3×10^{-4}, 3×10^{-4}, 3×10^{-3}, and 2×10^{-3}, respectively. A reference in our files indicates values of $\simeq 1.0 \times 10^{-4}$ mmg Hg STP is not considered volatile material. Soil metabolism data using purified $^{14}CO_2$ standard, accounted for 95% of volatilized material as $^{14}CO_2$. Clay content reported to be significant to the upward movement of the above moieties.

Based on more information received, this time, we change our conclusions from 1016-69,78-9/7/77, that the chemical is volatile to the chemical is not volatile.

This data is not required for this use, unless Tox ~~board~~ BRANCH requires reentry data.

6.1 Field Dissipation

Soil

Aldicarb dissipates in four agricultural use areas (N.C., TX CA, PA) rapidly with extrapolated half-lives of 7-14 d. Aldicarb sulfoxide and sulfone increases with time and account for 66 and 14% of material at 14d interval. Half-life estimates for the sulfoxide and sulfone moieties are≃60 and >90 days respectively. Other metabolites (minor) identified were oxime sulfoxide, nitrile sulfoxide, nitrile sulfone, and 5 unknowns. Bound residues were ≃11-14% at 0-8 wks. Aldicarb was found in the six-inch layer for up to 30 days. Small quantities, 0.04 ppm, were found in the 12-inch layer.

Field dissipation, soil, data requirement can be used to support any proposed use of aldicarb where this data is required.

6.2 Accumulation

Fish

Bluegill

Accumulation peaks at day 29 (12x) and declines thereafter to (5.0x) at day 56 for the 0.1 ppm level. Residues taken from fish when taken out of the treated water decline from 0.42 ppm at 29 days to 0.04 ppm at day 35; to not detectable at day 49. Similar results are seen at the 0.01 ppm concentration. except accumulation factors are lower (3.8x) and (1 x) respectively.

Flow-through system not evaluated because the participating laboratory could not maintain fish colonies under flow-through conditions. All metabolites that may be present in the water were not evaluated, only parent sulfoxide, and sulfone moieties (see section 5.4.0).

The method used, however, does recover the parent, sulfoxide, and sulfone moieties at ≥90% for water and fish. Residues and accumulation as presented are accurate.

If ESS does not require data on the other metabolites then this study can be used to support proposed uses of aldicarb, where this data is required.

6.3 Accumulation.

Rotational Crops

(See Section 5.4.3).

7.0 Recommendations

7.1 P. M. Note

The only data gap may be the fish study. Please co-ordinate with Environmental Safety, if they concur with the limits of the study, then no data gap exists for this use.

7.2 P. M. Note #

Company will have to submit full article from Acc# 096670 Book 2 Ref. #43, entitled The Volatilization, Degradation, adsorption and Desorption Characteristics of Aldicarb in soils and clays. James Raymond Supak, PhD, Texas, A&M Univ., 1972.

This is not substantial enough to deny registration.

7.3 P. M. Note

All questions asked of 1016-69, 78-9/7/77, have been answered.

7.4 Crop rotation interval for Tobacco, Drybeans, Soybeans, in 6F 1849, 6/28/78.

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