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8-18-88
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Shaughnessy No.: 103801

Date Out of EAB: AUG 18 1988

To: Dennis Edwards
Product Manager #12
Registration Division (TS 767)

From: Paul Mastradone, Acting Chief
Environmental Chemistry Review Section #1
Exposure Assessment Branch/HED (TS-769C)

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

Attached, please find the EAB review of:

Reg./File Symbol: 352-372, 352-400

Chemical Name: Oxamyl

Type Product: Insecticide-Nematicide

Product Name: Vydate

Company Name: E.I. du Pont de Nemours

Purpose: Review hydrolysis, photodegradation in water, and leaching

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Date Received: 06/14/88

Action Code: 50?

Date Completed: 08/04/88

EAB #(s): 80817, 80818

Monitoring Study Requested: _____

Total Reviewing Time: 3.0 days

Monitoring Study Voluntarily: _____

Deferrals To:

_____ Ecological Effects Branch

_____ Residue Chemistry Branch

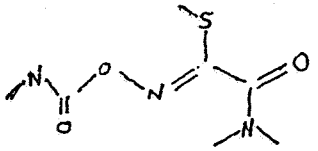
_____ Toxicology Branch

1. CHEMICAL: Oxamyl

Trade Name: Vydate

Chemical Name: Methyl N'N'-dimethyl-N-[(methylcarbamoyl)oxyl]-1-thiooxaminidate

Structure:



2. TEST MATERIAL: see individual studies.

3. STUDY/ACTION TYPE: The registrant has submitted 3 studies in response to the Registration Standard (6/87): hydrolysis, photodegradation in water, and leaching (unaged and aged).

4. STUDY IDENTIFICATION:

Study 1: Hydrolysis of [1-^{14}C] Oxamyl. Mary Ellen Mc Nally and Julia Wheeler. March 30, 1988. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Accession #406065-16.

Study 2: Photodegradation of [1-^{14}C] Oxamyl in Buffer Solution pH 5. Mary Ellen P. Mc Nally and Julia R. Wheeler. March 30, 1988. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Accession #406065-15.

Study 3: Soil Column Leaching Studies with [1-^{14}C] Oxamyl. B. C. Rhodes, R. A. Hughes, and J. R. Nolker. November 20, 1987. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Accession #406065-14.

5. REVIEWED BY:

Pat Ott
Chemist
EAB/HED/OPP

Signature: Pat Ott
Date: 8/11/88

6. APPROVED BY:

Paul Mastradone
Acting Chief
Environmental Chemistry Review Section #1

Signature: Paul J. Mastradone
Date: AUG 18 1988

7. CONCLUSIONS:

Hydrolysis is an important degradative pathway for oxamyl at pH 7 and 9, but oxamyl is stable under acid (pH 5) conditions. The only major degradate is the oxime.

Oxamyl and its degradates (oxamohydroxamic acid and oxamic acid) leach readily through soil (silt loam, loamy sand, sandy loam, and loam soils) that is unaged. For silt loam soil that has been aged 7 or 18 days, oxamyl residues still leach appreciably, though to a lesser degree than with fresh soils.

[The results from the photodegradation in water study are not reported here because the study could not be fully evaluated.]

Study 1:

This study satisfies Subpart N data requirements for hydrolysis by providing information on the rate of hydrolysis of oxamyl at pH 5, 7, and 9 and identification of degradates.

Study 2:

This study can not be fully evaluated until the missing information is provided: a UV-VIS spectrum (300-800 nm) for the xenon burner used in this study and a reference spectrum for sunlight.

Study 3:

This study satisfies Subpart N data requirements for unaged and aged leaching (Section 163-1) by providing information on the leaching behavior of oxamyl and its degradates.

The registrant reported "K_d's", which are soil column distribution coefficients, and are a function of the volume of water required to elute 50% of the applied amount. These are not the same K_d's as those obtained from adsorption/desorption (batch equilibrium) studies. The agency would be interested in seeing data comparing batch equilibrium K_d's with these soil column distribution coefficients.

8. RECOMMENDATIONS:

EAB recommends that the registrant be informed that the hydrolysis (§161-1) and leaching (§163-1) data requirements are satisfied. EAB recommends that the registrant submit the information cited in the CONCLUSIONS Section, so that the agency can fully evaluate the photodegradation in water study.

9. BACKGROUND:

Oxamyl is an acutely toxic insecticide/nematicide used on a variety of field and vegetable crops. It is a restricted use pesticide, and the label indicates its use is prohibited in Suffolk and Nassau Counties (NY). It is on the list of analytes to be monitored in the National Pesticides in Ground Water Survey. It was on the GW Data Call-In list and the registrant submitted all required data; the data was screened by the GW team. A registration standard was issued in June, 1987.

Data gaps include: photodegradation in water, anaerobic soil metabolism, terrestrial field dissipation, confined rotational crop, glove permeability, spray drift, and reentry data. Rotational crops intervals range from 4-6 months.

The acceptable data are: aerobic soil metabolism, hydrolysis, and leaching. Oxamyl had a half-life of 14-28 days (silt loam). The major degradate was CO_2. Also formed were the oxime and N-N-dimethyloxamic acid. See Section #7 for other data.

10. Review of Individual Studies: see Data Evaluation Records

11. Completion of One-Liner: Yes

12. CBI Appendix: N/A

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DATA EVALUATION RECORD

Oxamyl | Study 1 (Hydrolysis)

Hydrolysis of [1-^{14}C] Oxamyl. Mary Ellen McNally and Julia Wheeler. March 30, 1988. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Lab Project ID #AMR-961-87. Accession #406065-16.

Reviewed By: Patricia Ott Signature: Pat Ott
Title: Chemist Date: 8/11/88
Org: Environmental Chemistry Review Section #1

Approved By: Paul Mastradone Signature: Paul J Mastradone
Title: Acting Chief Date: AUG 18 1988
Org: Environmental Chemistry Review Section #1

Conclusions:

This hydrolysis study satisfies Subpart N data requirements by providing information on the rate of hydrolysis of oxamyl at pH 5, 7, and 9 and the identity of degradates.

At pH 5, oxamyl is stable to hydrolysis. At pH 7, the half-life is 8 days, and at pH 9, the half-life is 3 hours. The only major degradate (formed at >10% of applied radioactivity) was the oxime [methyl 2-(dimethylamino)-N-hydroxy-2-oxo-ethanimidothioate].

Materials and Methods:

The hydrolysis of ^{14}C-oxamyl (#1 carbon radiolabel and 98% pure) in millipore filtered and buffered water at 18.4 ppm was studied at pH 5, 7, and 9. Sterilized glassware was used.

Fortified solutions were incubated in the dark at 25°C for up to 31 days. Sub-samples were analyzed on day 0, 1, 3, 5, 7, 9, 14, 16, 21, 26, and 31 (pH 5), day 0, 0.5, 1, 2, 4, 5, 8, 13, 15, 20, 25, and 30 (pH 7), and 0, 1, 2, 3, 4, 5, 6, 7 hours and 5, 11, and 15 days (pH 9).

The sterility of solutions was checked at day 0 and 30 by incubating an aliquot with sterile soy broth medium. No microbial growth was observed.

Total radioactivity was measured by liquid scintillation counting and individual compounds were analyzed by HPLC (UC detector). Confirmation was by GC-MS. Two degradates were monitored: the oxime [methyl 2-(dimethylamino)-N-hydroxy-2-oxo-ethanimidothioate and 1,3-dimethylurea.

Reported Results:

Mass balances were 96-106% during the study. Oxamyl at pH 5 was stable (half-life >31 days), and at pH 7, the half-life was 8 days, while the half-life at pH 9 was only 3 hours. At pH 7 and 9, the oxime (methyl 2-(dimethylamino)-N-hydroxy-2-oxo-ethanimidothioate) was the major hydrolysis product. For the pH 7 test, the oxime accounted for 93% of the total radioactivity on day 30 of the experiment. At pH 9, the oxime accounted for 104% of the total radioactivity within 5 hours. Only this degradate was formed at greater than 10% of the applied radioactivity.

RIN 3755-96

Oxamyl EF

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____ Identity of product impurities.

____ Description of the product manufacturing process.

____ Description of quality control procedures.

____ Identity of the source of product ingredients.

____ Sales or other commercial/financial information.

____ A draft product label.

____ The product confidential statement of formula.

____ Information about a pending registration action.

✓ FIFRA registration data.

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DATA EVALUATION RECORD

Oxamyl | Study 2 (Photodegradation in Water)

Photodegradation of [1-^{14}C] Oxamyl in Buffer Solution pH 5. Mary Ellen P. McNally and Julia R. Wheeler. March 30, 1988. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Lab Project ID #AMR-960-87. Accession #406065-15.

Reviewed By: Patricia Ott
Title: Chemist
Org: Environmental Chemistry Review Section #1
Signature: Pat Ott
Date: 8/11/88

Approved By: Paul Mastradone
Title: Chemist
Org: Environmental Chemistry Review Section #1
Signature: Paul J Mastradone
Date: AUG 18

Conclusions:

This study can not be fully evaluated until the following points are addressed:

1. A UV-VIS spectrum (300-800 nm) for the xenon burner used in this study and a reference spectrum for sunlight should be provided.

Materials and Methods:

A photodegradation in water study at 20 ppm for ^{14}C-oxamyl (labelled in the #1 carbon position and 98% pure) was conducted at pH 5 (the pH of minimal hydrolysis).

Fortified, buffered, sterilized solutions were exposed to simulated sunlight continuously for 16 days. Identical sterilized control solutions were incubated in the dark, and all solutions were maintained at 25°C.

The photolysis vessels were water-jacketed beakers covered with glass plates. The radiation source was a xenon burner (Suntest) equipped with a filter to eliminate wavelengths less than 290 nm. Spectra for the xenon lamp and sunlight were provided only for the 300-384 nm part of the UV-VIS spectrum. The integrated light intensity of the xenon lamp for this spectral range was equal to 96% of the corresponding energy of sunlight at 1 ppm on June 17, 1986 in Wilmington, DE. The lamp was 9 and 1/4" above the sample.

Total radioactivity was determined by liquid scintillation counting. Individual compounds were analyzed by HPLC (UV detector) and the samples were monitored for 2 degradates: the oxime and 1,3-dimethylurea. GC-MS was used to confirm identity of compounds.

Solutions were sampled on day 0, 1, 3, 5, 7, 9, 14, and 16.

Reported Results:

The degradation of ^{14}C-oxamyl occurred more rapidly in the irradiated solutions than the non-irradiated solutions.

The estimated half-life (calculated from first-order rate constants) of ^{14}C-oxamyl at pH 5 was 7 days and >30 days for non-irradiated oxamyl.

The principle degradation product was the oxime (methyl 2-(dimethylamino)-N-hydroxy-2-oxo, methyl ester). After 16 days of continuous irradiation, the oxime accounted for 75% of the applied radioactivity. Mass balance throughout the study was $\geq$97% of the applied radioactivity.

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DATA EVALUATION RECORD

Oxamyl Study 3 (Unaged and Aged Soil Column Leaching Study)

Soil Column Leaching Studies with [1-^{14}C] Oxamyl. B.C. Rhodes, R.A. Hughes, and J.R. Nolker. November 20, 1987. Performed and Submitted By: E. I. du Pont de Nemours and Company, Inc., Wilmington, DE. Lab Report ID #AMR-865-87. Accession #406065-14.

Reviewed By: Patricia Ott Signature: Patricia Ott
Title: Chemist Date: 8/11/88
Org: Environmental Chemistry Review Section #1

Approved By: Paul Mastradone Signature: Paul J Mastradone
Title: Acting Chief Date: AUG 18 1988
Org: Environmental Chemistry Review Section #1

Conclusions:

This study satisifes the Subpart N data requirements for unaged and aged leaching (Section 163-1) by providing information on the leaching behavior of oxamyl and its degradates.

Oxamyl residues leach readily through unaged silt loam, loamy sand, sandy loam and loam soil columns and, to a lesser but still appreciable degree, through silt loam soil aged for 7 and 18 days.

Three compounds were found both in the eluates and throughout the soil column of unaged and aged soil: oxamyl, oxamohydroxamic acid, and oxamic acid.

The registrant reported K_d's; however, these are not the same K_d's which are obtained from adsorption/desorption (batch equilibrium) studies, but are a variation of the work by Swoboda and Thomas (1968)*. The registrant used a ^{36}Cl marker and the K_d's reported in this study are a function of the volume of water required to elute 50% of the applied amount from the column. K_d's for fresh soil columns for the 4 soils and the 7 day aged silt loam soil column ranged from -0.06 to 0.52, indicating oxamyl is highly mobile in soil, which supports the finding of oxamyl in ground water (Long Island, NY). The agency would be interested in seeing data comparing batch equilibrium K_d's with these soil column distribution coefficients.

Materials and Methods:

Unaged Study

^{14}C-Oxamyl (labelled at the #1 carbon position and 92% pure) was added to soil columns (2" i.d. x 12" h), each containing 1 of 4 soils: silt loam (Keyport), loamy sand (Fayetteville), sandy loam (Sassafras) and loam (Tama). See Table 1 for soil characteristics. The test solution added contained 0.06 mg ^{14}C-oxamyl and 0.10 mg unlabelled oxamyl.

*Allen R. Swoboda and Grant W.Thomas. Movement of Parathion in Soil Columns. J. Agr. Food Chem. 16, No. 6, pp 923-927, 1968.

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Soils were air dried, sieved, and added to column chromatography film tubes. In addition to the ^{14}C-oxamyl solution, a $Na^{36}Cl$ solution was added as a reference compound. The columns were then eluted with 1000 ml and 20 ml fractions were collected.

Total radioactivity in each fraction was counted with a scintillation counter calibrated for both ^{14}C and ^{36}Cl.

After the column was eluted, the soil inside was divided into 2" segments, dried and weighed. Aliquots were combusted and analyzed for total radioactivity with LSC. Any segment containing at least 10% of the total applied ^{14}C radioactivity was extracted and analyzed. The remaining segments were pooled, extracted and analyzed.

The extraction and cleanup method involved extraction with methanol (3x) and then water (2x), followed by centrifugation. The supernatants were analyzed with HPLC (UV detector) and TLC. The solid residue was combusted and analyzed by LSC.

For the HPLC analysis, 5 reference standards were injected, and each was adequately separated by the Du Pont Zorbax® ODS column. The compounds were: oxamic acid, N,N-dimethyloxamide, oxamohydroxamic acid, oxamyl, and 1-cyano-N,N-dimethylformamide.

TLC plates were streaked with soil extracts and reference compounds, developed in methanol/ethyl acetate/acetic acid (20/80/1), and compounds were quantified with a linear scanner.

Aged Study

Two columns of silt loam soil were prepared for the aged study. The ^{14}C test solution was mixed into each of two plugs (2"h x 2" i.d., 21.7% (w/w) water) of silt loam soil, then stored in the dark (25°C) for either 7 or 18 days' incubation.

At the end of the aging period, the ^{36}Cl-test solution was mixed with the soil plug and the 2" plug was immediately added atop a 10" column of fresh silt loam and the column was prepared and leached as in the unaged study.

Reported Results:

Distribution Coefficients

The following soil-water distribution coefficients were reported for the unaged and aged soils used in this study:

	Soil					
	Silt Loam 1	Silt Loam 2	Sandy Loam	Loamy Sand	Loam	Silt Loam (aged 7 days)
K_d	-0.06	-0.05	0.05	0.08	0.41	0.52

Column Elution Behavior

Total recovery of ^{14}C from all fresh soil columns averaged 100%; however, only 65% and 89% of the applied ^{14}C radioactivity was recovered from the aged columns.

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The remaining radioactivity is assumed to be $^{14}CO_2$, a known aerobic soil metabolite. Recovery of ^{36}Cl-radioactivity averaged about 100% for fresh columns and 92-98% for the aged columns.

During elution of the fresh soil columns, 89-95% of the applied ^{14}C radioactivity was eluted in 1000 ml water. When the treated silt loam soil was aged, the amount of radioactivity which eluted decreased to 67% and 37% of the total applied ^{14}C when the soil was aged for 7 and 18 days before elution, respectively.

The concentration of ^{14}C radioactivity was greatest in the top 2" segment and rather evenly distributed throughout the remainder of the column. The exception was the silt loam column aged for 18 days, which retained most of the ^{14}C radioactivity in the top 4" of soil.

In the leachate of fresh soil columns, the % of applied ^{14}C radioactivity as oxamyl ranged from <1 to 83%, <1 to 80% for oxamohydroxamic acid, and 12-17% for oxamic acid.

The eluate from the 7 day aged silt loam column contained 50% of the applied ^{14}C radioactivity as oxamyl and 17% as oxamic acid. For the soil aged 18 days after oxamyl application, oxamyl concentration in the column leachate was 21% of applied ^{14}C, while oxamic acid and oxamohydroxamic acid were present at 14% and 2% of applied ^{14}C, respectively.

Radiaoctivity Retained on Soils

After elution with 1000 ml water, fresh soil columns contained only 5-11% of the applied ^{14}C-radioactivity, consisting of 2-3% oxamyl, 1-7% oxamic acid and 1% unextracted/bound residue.

For the 7 day aged silt loam column, ^{14}C residues remaining on the column accounted for 22% of the applied ^{14}C. Of this total, 11% was oxamic acid, 4% was oxamyl and 7% was bound.

For the 18 day aged silt loam column, ^{14}C residues remaining on the column accounted for 28% of the applied ^{14}C. Oxamic acid was the major component, comprising 6%, while oxamyl was 5% and bound residues accounted for 17% of the applied.

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