US EPA ARCHIVE DOCUMENT

2/7/90

"DPX-V9360"

(ACCENT^{TM}; Sulfonylurea Herbicide)

Registrant: E.I. du Pont de Nemours and Company

Shaughnessy Number: 129008

DISCUSSION OF INDIVIDUAL STUDIES
(Environmental Fate)

Reviewer: Silvia C. Termes, Chemist
Environmental Fate and Ground Water Branch
Environmental Fate and Effects Division
Office of Pesticide Programs

Review of Studies Completed on February 7, 1990

"DPX-V9360"
(ACCENT^{TM}; Sulfonylurea Herbicide)

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Introduction

"DPX-V9360" is the code name for the new sulfonylurea herbicide 3-pyridinecarboxamide((((4,6- dimethoxypyridin-2-yl)aminocarbonyl)-aminosulfonyl))-N,N-dimethyl. The Chemical Abstracts Registry Number for this chemical is 111991-9-4.

The trade name for the formulated pesticide is ACCENT, which is a water dispersible granule containing 75% of the active ingredient "DPX-V9360" by weight. It is a selective herbicide developed to control annual and perennial grass weeds and selected broadleaf weeds when applied postemergence in field corn. ACCENT is not to be used on popcorn, sweet corn, or corn grown for seed production.

Foliar absorption is the primary means of ACCENT uptake by plants. ACCENT should be applied prior to the 10-leaf stage of corn. The application method recommended is by ground spraying. The pesticide should not be applied through any type of irrigation system. Maximum single application rate is 1 oz ai/acre. If split applications are to be made they should not exceed a total of 1 1/3 oz ai/acre in any crop per year (split applications of 2/3 oz each are recommended).

"DPX-V9360"- ACCENT^{TM} Herbicide
Shaughnessy #: 129008

Study 1- Hydrolysis of DPX-V9360

The review of the original study (MRID #40924220) was included in the EFGWB review dated 5/1/89. In a letter dated 11/14/89 the registrant addressed the deficiencies and/or questions noted in the 5/1/89 review. The registrant's response is included in the EFGWB review of 11/29/89.

The registrant clearly explained the reasons for the formation of the minor degradate "DPX-V9360 Ipso Precursor". Formation of this degradate is favored by electronic and steric factors inherent to the parent DPX-V9360 molecule. However, the data provided with the letter was considered confidential by the registrant and, therefore, will not be presented here.

This additional information does not affect the conclusions of the earlier review, but with this additional information the data requirements for the hydrolysis study were considered fulfilled.

February 19, 1990

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DATA EVALUATION RECORD

CASE GS -- 129008 STUDY 1 PM 25

CHEM DPX-V9360 (Sulfonylurea herbicide; common name not yet assigned)

BRANCH Environmental Fate and Ground Water; 161-1

FORMULATION 00-Radiolabeled active ingredient

MRID NO. 40924220

McFetridge, R. 1988. <u>Hydrolysis of [pyrimidine-2-^{14}C] DPX-V9360 and [pyridine-2-^{14}C] DPX-V9360 in buffer solutions of pH 5, 7, and 9</u>. Conducted and submitted by E.I. du Pont de Nemours and Company, Inc., Agricultural Products Department, Wilmington, DE. Laboratory Project ID: AMR-1104-88. Study completed on November 2, 1988.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EFGWB/HED/OPP
TEL: (703)557-2243

SIGNATURE: April 24, 1989

CONCLUSIONS:

The study is basically acceptable and may fulfill data requirements if the registrant can provide an explanation of: a) which factors influence SO_2 elimination and subsequent bridge contraction to form the "DPX-V9360 Ipso Precursor" degradate; b) what is the fate of the eliminated SO_2 and of the "Ipso Precursor"; c) what is known about the phytotoxicity of the "Ipso Precursor," if any.

The reported results indicate that, in the buffered solutions, the stability of DPX-V9360 increases with increasing pH. At pH 5, the major degradation pathway involves the cleavage of the sulfonylurea bridge to form pyrimidine amine and pyridine sulfonamide. A minor degradation pathway involves bridge contraction brought about by elimination of SO_2 to form the "DPX-V9360 Ipso precursor." The half-life for the degradation of DPX-V9360 in pH 5 buffer is 15 days.

MATERIALS AND METHODS

Test materials: [Pyrimidine-2-^{14}C]DPX-V9360, radiochemical purity 97% and specific activity of 25.5 mCi/mol (62.2 uCi/mg) and [pyridine-2-^{14}C]DPX-V9360, radiochemical purity of 95% and specific activity of 25.8 mCi/mole (62.9 uCi/mg).

Stock solutions: 10.01 mg of the pyrimidine-labeled material and 9.98 mg of the pyridine-labeled material were transferred to separate 100-mL volumetric flasks, diluted to volume with Milli-Q water and the pH adjusted to about 9.5 with NaOH/HCl.

Reference standard solutions: Reference solutions (0.1 mg/mL) of DPX-V9360, N-desmethyl DPX-V9360, pyridine sulfonamide, and pyrimidine amine were prepared by dissolving 1 mg each in 1 mL of acetonitrile and diluting to 10 mL with water adjusted to pH 7 with NH_4OH.

Equipment: The hydrolysis apparatus is depicted in Figure 1. Glassware and apparati were sterilized by autoclaving.

Test solutions: For each pH (5, 7, 9), separate solutions containing the pyrimidine- and pyridine-labeled material were prepared by dilution of 0.5 mg of the corresponding stock solution to 100 mL with the pH buffer solution. The buffers used were 0.01 M acetate buffer for pH 5, 0.01 M phosphate buffer for pH 7, and 0.01 M borate buffer for pH 9. Test solutions were sterilized through a sterilization filter.

Sampling: For each test solution, 5-mL aliquots were removed with sterilized syringes and needles at 1, 3, 5, 7, 14, 21, 28, and 30 days. NaOH traps were collected and analyzed at sampling interval (except on days 2 and 3 for the pH 5/pyridine-labeled sample). All samples were analyzed within 24 hours of sampling and stored frozen. Zero-day samples were analyzed by LSC to determine initial concentrations. Initial concentrations for the pyrimidine- and pyridine-labeled solutions were: 5.6 and 5.4 ppm (pH 5); 5.7 and 5.5 ppm (pH 7); and 5.7 and 5.6 ppm (pH 9). For degradate identification purposes only, additional 5 ppm pyridimine-label and pyridine-labeled solutions in pH 5 buffer were prepared.

Experimental procedure: Test solutions were kept in darkness at a temperature of 25 ± 1°C. Sterility (glucose-yeast extract medium) was checked on days 0, 14, and 30.

Immediately after sampling, total radioactivity was determined by LSC. Composition of radioactivity was determined by HPLC radiochromatography. Radioactivity in trap solutions was determined by LSC.

Parent and hydrolysis products were confirmed/determined by LC/MS after appropriate extraction procedures were performed.

REPORTED RESULTS

pH 5: The calculated half-life was approximately 15 days (first-order reaction rate, 0.046 day^{-1}). The major degradation products were pyrimidine amine (from the pyrimidine-labeled experiments), which reached 64% at 30 days and pyridine sulfonamide (from the pyridine-labeled experiments) which reached 63% at 30 days. Thus, the major degradation pathway was cleavage of the sulfonylurea bond.

The "Ipso precursor" (that is, the product of bridge contraction by the loss of SO_2) increased throughout the study and reached 11-12% at the end of the study. N-desmethyl DPX-V9360 was a minor impurity (1%), which decreased with time.

Material balances for the pyrimidine and pyridine labeled DPX-V9360 are shown in Tables I and II, respectively. The decomposition of parent and formation of products as a function of time for the pyrimidine and pyridine labeled materials are shown in Figures 2 and 3, respectively.

pH 7: At this pH, DPX-V9360 was relatively stable; its concentration decreased only 3-4% over a 30-day period. The increase in pyrimidine amine and pyridine sulfonamide was slow and reached 6 and 5% at the end of the study. The "Ipso precursor" only increased to 1-2% of the total radioactivity. Table III and Figure 4 show the material balance and the decline of parent/formation of degradates for the pyrimidine labeled material. The same are shown in Table IV and Figure 5 for the pyridine labeled material.

pH 9: DPX-V9360 was relatively stable at pH 9. During the 30-day experimental period, the decrease in DPX-V9360 concentration was less than 5%. Pyrimidine amine increased to about 3% while pyridine sulfonamide levels changed very little. The increase in "ipso precursor" was less than 2%. The material balance and decline of parent/formation of degradates for the pyrimidine labeled material are shown in Table V and Figure 6, respectively; for the pyridine-labeled material, the results are shown in Table VI and Figure 7.

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The results indicate that at pH 5 the main degradation pathway is cleavage of the sulfonylurea bridge to yield pirimidine amine and pyridine sulfonamide. The other minor pathway is elimination of SO_2 and subsequent bridge contraction to form the DPX-V9360 Ipso Precursor. The author also concluded that CO_2 may be also formed during cleavage of the sulfonylurea bridge. However, this reaction was not detected because the carbonyl carbon was not radiolabeled.

The hydrolytic pathway of DPX-V9360 is shown in Figure 8.

REVIEWER'S COMMENTS

1. Note that in the Table showing the material balance of the [pyridine-2-^{14}C]DPX-V9360 at pH 9, the reaction product written as "pyrimidine sulfonamide" should read "pyridine sulfonamide."

2. Did the author actually detected the eliminated SO_2 (in traps or in solution as a sulfur oxyanion?

3. What factors lead to the elimination of SO_2 and subsequent rebridging?

4. Is there any information on the reactivity of the "Ipso Precursor"? Is it mobile? Is it toxic (including phytotoxicity)?

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Accent environmental fate review

Page ______ is not included in this copy.

Pages 9 through 24 are not included in this copy.

The material not included contains the following type of information:

___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product 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

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DATA EVALUATION RECORD

SH#129008 STUDY 2 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Photodegradation in water 161-2

FORMULATION: Radiolabeled active ingredient

MRID #41082620

McFetridge, R.D. 1989. Photodegradation of [Pyrimidine-2-^{14}C]DPX-V9360 and [Pyridine-2-^{14}C]DPX-V9360 in water. Laboratory Project AMR-1173-88; completed on January 10, 1989. Performed and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

February 19, 1990

SIGNATURE:

CONCLUSIONS:

This study is basically acceptable to fulfill Subdivision N Guidelines since the study was satisfactorily conducted at the pH of maximum hydrolytic stability (pH 9). The study was also conducted at pH 7 and 5.

Additional data is being requested for the study conducted at pH 5. This requested information includes:

a. Data on the chemical species (and their percentage) present at each sampling interval for both the irradiated and nonirradiated solutions.

b. Hydrolysis study indicate that a minor mechanism (SO_2 elimination followed by bridge contraction) leads to the formation of the "Ipso Precursor." Was this product detected in the irradiated/nonirradiated solutions?

c. Was the "Photoproduct 1" (detected at less than 10%) also detected in the pH 5 tests? Is there any evidence that "Photoproduct 1" is/is not the "Ipso Precursor."

SUMMARY OF DATA

"DPX-V9360" degraded slowly at pH 7 and 9, under 1-month exposure to early summer sunlight. The estimated half-lives were 200-250 days at pH 7 and 180-200 days at pH 9. By the end of x 30-day study, 8-11% of the parent "DPX-V9360" had degraded. The major photoproduct (at less than 10%, and not further characterized) was "Photoproduct 1" which appears to contain both the pyridine and the pyrimidine rings.

At pH 5, hydrolytic degradation could not be distinguished from photodegradation, because the half-lives of both irradiated and nonirradiated solutions were about the same (ca. 14 days). No degradation products identification/quantitation was presented for the pH 5 studies. This information is being requested from the registrant.

Sunlight: June 7, 1988-July 7, 1988 in Wilmington, DE (39° 40' N latitude; 75°, 36' W longitude). The cumulative exposure at the end of the 30-day study was 207,668 watt-hr/m^2.

MATERIALS AND METHODS

Test materials:	a) [Pyrimidine-2-^{14}C]DPX-V9360, radiochemical purity 98.8%, specific activity 62.2 uCi/mg (25.5 mCi/mmol). b) [Pyridine-2-^{14}C]DPX-V9360, radiochemical purity 99%, specific activity 62.9 uCi/mg (25.8 mCi/mmol).
Stock solutions:	100 ppm stock solutions of each the pyrimidine- and the pyridine-labeled DPX-V9360 were prepared by dissolving 5 mg of the test substance in 50 mL of 0.1% NH_4OH (v/v) solution.
Test solutions:	Test solutions for each labeled at each pH were prepared at a concentration of 5 ppm by dissolving diluting 12.5 mL of the stock solution to 250 mL with the pH 5, 7, and 9 buffer solutions. The 0.01 M buffer solutions were: a) pH 5, acetate buffer; b) pH 7 phosphate buffer; c) borate buffer.
Experimental method:	All the irradiated experiments were conducted in sunlight (early summer). The photolysis vessels consisted of water-jacket beakers connected to a constant temperature water bath (25C). The configuration of the photolysis vessels is shown in Figure 1. The vessels were equipped with parts that allowed a stream of air to be drawn by vacuum over the test solutions and then passed through a 1N NaOH solution scrambler to trap any $^{14}CO_2$. Control samples were also maintained at the same temperature in a dark incubator. All glassware was autoclaved prior use. <u>Sunlight</u>: 39° 40'N latitude and 75° 36' W longitude, Wilmington, DE, from June 7, 1988 to July 7, 1988. The total radiation striking the samples was monitored continuously, the output was collected every 30 min (in watt-hour/m^2) and expressed as the total accumulation of energy since 12:01 am.
Sampling:	5-mL aliquots of irradiated and nonirradiated (dark) test solutions were removed for analysis on days 0, 1, 3, 7, 14, 21, and 30.
Analytical Methods:	Total amount of radioactivity at each sampling interval was analyzed by LSC. Composition of radioactivity was determined by HPLC and components were identified by cochromatography (HPLC and TLC)

with unlabeled standards. Quantification was done by HPLC. Mass spectrometry (MS) was also used for confirmation of components. Sodium hydroxide traps were analyzed by LSC.

REPORTED RESULTS

The cumulative exposure at the end of the 30-day experimental period was 207,668 watt-hr/m^2.

At pH 5, photodegradation could not be distinguished from hydrolysis. At this pH, the half-lives of degradation under irradiation and under dark conditions were 14-19 days and 14 days, respectively.

At pH 7 and 9, DPX-V9360 degraded slowly (8-11% of the applied radioactivity degraded in irradiated solutions; less than 3% in nonirradiated solutions). Estimated half-lives were 200-250 days at pH 7 and 180-200 days at pH 9. In irradiated solutions, a minor product ("Photoproduct 1") was detected at 4-7% after 30 days of exposure; "Photoproduct 1" apparently contains both the pyridine and the pyrimidine rings, but it was not further characterized. No significant $^{14}CO_2$ formation was observed.

The predominant hydrolysis reaction in the pH range 5-9 is cleavage of the sulfonylurea bridge to yield pyrimidine amine and pyridine amine. Exposure to sunlight slightly increases the degradation rate of DPX-V9360 in aqueous solution and the formation of the minor degradation product "Photoproduct 1." Degradation pathway is shown in Figure 2.

REVIEWER'S COMMENTS

The study is basically acceptable to fulfill Subdivision N Guidelines but the registrant must provide the following additional information.

1. Although Subdivision N Guidelines require that the photodegradation in water studies be conducted at the pH(s) of maximum hydrolytic stability (which the registrant has done acceptably), a study at pH 5 was also conducted. For this study (for which hydrolytic degradation could not be distinguished from photodegradation) no data were included showing which chemical species (and the percent of each) were present at each sampling interval. According to the hydrolysis study, a minor degradation pathway also occurs in aqueous media, more predominantly at pH 5. This mechanism leads to the formation of a bridge-contraction product identified as the "Ipso Precursor." Was this species also detected in the irradiated samples? If so, provide this information including the percent of "Ipso Precursor" found for both irradiated and nonirradiated samples at pH 5.

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2. A degradation product identified as "Photoproduct 1" was detected in irradiated samples at pH 7 and 9 and it is believed to contain both the pyrimidine and pyridine rings. The product was identified at less than 10% of the applied. Do the registrant have any further evidence as what this photoproduct is? Was it also detected in the pH 5 studies.

Accent environmental fate review

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The material not included contains the following type of information:

___ Identity of product inert ingredients

___ Identity of product impurities

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___ Description of product quality control procedures

___ Identity of the source of product ingredients

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___ The product confidential statement of formula

___ Information about a pending registration action

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DATA EVALUATION RECORD

SH#129008 STUDY 3 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Photodegradation on soil 161-3

FORMULATION: Radiolabeled active ingredient

MRID #41082621

Dietrich, R.F. 1988. Photodegradation of ^{14}C-DPX-V9360 on a corn belt soil in sunlight. Laboratory Project AMR-862-87; completed on June 23, 1988. Performed and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

SIGNATURE: February 19, 1990

CONCLUSIONS:

This study is acceptable and fulfills data requirements for photodegradation of DPX-V9360 on soils.

DPX-V9360 applied to loam soil (Paris, IL; 4.9% organic matter, pH 6.2, and 29.2 CEC) degraded under midsummer sunlight (39° 40' N latitude; 75° 36' W longitude) and total cumulative solar exposure of 184,569 watts-hrs/m^2 with half-lives of 60-67 days (about three times faster than under dark conditions). The major degradates found at higher concentration after the 30-day period of the study were the hydrolytic degradates Pyrimidine Amine and Pyridine Sulfonamide. Minor degradates (less than 6%) were isolated and identified as N-Desmethyl DPX-V9360 and Pyrimidine Urea.

MATERIALS AND METHODS

Test materials:

a) [Pyrimidine-2-^{14}C]DPX-V9360, 99% radiochemical purity and specific activity 62.2 uCi/mg

b) [Pyridine-2-^{14}C]DPX-V9360, radiochemical purity 99% and specific activity 62.9 uCi/mg.

Soil:

The soil was a loam soil from Paris, IL, containing 4.9% organic matter, pH 6.2, CEC 29.2 meq/mg. Other soil characteristics are shown in Table 1. The same soil was used in the aerobic soil metabolism study (41082622). Soil was air dried and screened through a 1-mm sieve. A thin layer (about 1 min thick) of the soil was formed on plates by spreading a thick slurry of the soil (2:1 g soil:mL water), after which the plates were air-dried for several days at room temperature. The soil area on each plate was approximately 16.3 cm^2.

Treatment solutions:

Solutions containing 53.8 ug [Pyrimidine-2-^{14}C] DPX-V9360/mL acetonitrile and 53.9 ug [Pyridine-2-^{14}C] DPX-V9360/mL were prepared. Each plate received an even application of 0.303 mL of the desired solution, giving a deposition of 16 ug of DPX-V9360 on each soil plate equivalent to 1.4 oz ai/acre (100 g ai/ha).

Experimental method:

Each soil plate was assembled as shown in Figure 1. Heat exchangers in each photolysis box were connected to a circulating water bath kept at 25C. Soil temperatures of both dark and irradiated samples were monitored throughout the study. Provisions were made to trap evolved $^{14}CO_2$. Experiments were conducted under sunlight (Wilmington, DE; 39° 40' N latitude and 75° 36' W longitude) from July 21, 1987 to August 20, 1987. Local climatological data was collected and provided, solar radiation striking the photolysis equipment was continuously monitored to allow measurement of the cumulative energy to which the samples were exposed.

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Sampling: Day 0 samples were collected for both labels (dark and irradiated conditions). Soil slides were removed from the sample box at 3, 7, 14, 21, and 30 days after the study was initiated.

Extraction of radioactivity: Soil coatings from each slide were scraped, placed in centrifuge tubes and extracted three times with 25-ml portion of acetone/0.1 M ammonium carbonate (90/10) and then further extracted with 0.1 M ammonium carbonate and acetone washes.

Analytical methods: Extracts were analyzed by LSC for total radioactivity. Composite of extracts were concentrated in vacuo and analyzed by TLC. Unextracted radioactivity in soils was determined by combustion.

Tentative identification of components in extracts was done by TLC (cochromatography with standard parent and degradates). The 30-extracts were also analyzed by HPLC (cochromatography) to confirm identity of major degradates. Radioactivity trapped in the NaOH traps were analyzed to confirm that it was associated with $^{14}CO_2$ evolution.

Further isolation and characterization of degradates was done by treating soil plates with a larger (1 mg) dosage of each label of parent DPX-V9360 and exposed from 7/21/87 to 8/27/87. The extraction method was the same as the one used for the study, but each final extract was further partitioned to isolate degradates. Isolated degradates were identified by LC/MS.

REPORTED RESULTS

DPXV-9360 degraded under midsummer sunlight (39° 40' N latitude; 75° 36' W longitude) and total cumulative solar exposure of 184,569 watts-hrs/m^2 with half-lives of 60-67 days (204-210 days for nonirradiated samples). The major degradates in both irradiated and nonirradiated samples were Pyrimidine Amine (maximum 8% at 30 days) and Pyridine Sulfonamide (maximum 10% at 30 days) both of which are known to be hydrolytic products of DPX-V9360. "Polars" (10-12% after 30 days) were identified to be a mixture of degradates none of which individually comprised more than 6% of the total recovered radioactivity. Minor degradation products isolated and characterized were N-Desmethyl DPX-V9360 and Pyrimidine Urea. Evolution of $^{14}CO_2$ was detected only when the pyrimidine-labeled DPX-V9360 was used (1% of the recovered radioactivity at the completion of study).

REVIEWER'S COMMENTS

Note that in the heading on page 18, "Mass Spectral Confirmation of Pyridine Sulfonamide and Triazine Urea as DPX-V9360 Degradates", "Triazine Urea" actually denotes "Pyrimidine Urea." There is no triazine ring present in DPX-V9360.

Soil should have been sieved through a 2 mm-mesh screen and not through a 1-mm mesh screen.

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___ A draft product label

___ The product confidential statement of formula

___ Information about a pending registration action

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DATA EVALUATION RECORD

SH#129008 STUDY 4 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Metabolism in soil, aerobic 162-1

FORMULATION: Radiolabeled active ingredient

MRID #410822622

Rhodes, B.C. 1989. Aerobic soil metabolism of ^{14}C-DPX-V9360 in a corn belt soil. Laboratory Project AMR-855-87; completed on April 6, 1989. Performed and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

SIGNATURE:

February 19, 1990

CONCLUSIONS:

This study does not fulfill data requirements at this time. Although the study is scientifically sound and it does address the microbial degradation of DPX-V9360 in soil under aerobic conditions, the degradation of the major metabolites/degradates Pyridine Sulfonamide and Pyrimidine Amine is not addressed. The duration of the study was 8 months and at 6 and 8 months the maximum concentrations of these degradates (> 80%) were found. Thus, from the study it is not possible to determine how persistent or how these metabolites/degradates are further metabolized/degraded.

The registrant must provide acceptable experimental evidence as to how these major metabolites/degradates are further metabolized/degraded (that is the pattern of decline of these metabolites/degradates must also be established).

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SUMMARY

DPX-V9360 degraded in nonsterile silty clay loam soil from Paris, IL (pH 6.1, 5.1% organic matter, 30.4 meq/100 g CEC) with a half-life of 26 days. In sterile soils, the degradation half-life was ca. 6 months. Thus microbial degradation under aerobic conditions is a significant factor in the breakdown of DPX-V9360.

The main degradation pathway appears to involve cleavage of the sulfonylurea bridge to produce Pyridine Sulfonamide and Pyrimidine Amine (93% and 81% respectively, after 8 months). Formation of bound radioactivity increased with time (ca. 7% and 18% after 8 months when the [pyridine-^{14}C]DPX-V9360 and [pyridimine-^{14}C]DPX-V9360 were used respectively].

However, the study was not carried on beyond 8-months and, therefore, the decline of these two major degradates could not be established.

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MATERIALS AND METHODS

Test materials:

a) [Pyridine-2-^{14}C]DPX-V9360, radiochemical purity 99% and specific activity 62.9 uCi/mg

b) [Pyrimidine-2-^{14}C]DPX-V9360, radiochemical purity of 98.8% and specific activity of 62.2 uCi/mg.

Soil:

Silty clay loam soil from Paris, IL (pH 6.1, 5.1% organic matter, 30.4 meq/100 g CEC), Table 1. The soil was sieved through a 2-mm mesh sieve and homogenized and characterized. Activity of soil microorganisms was checked with ^{14}C-starch. Soil for sterile studies was autoclaved.

Treatment solutions:

Separate test solutions were prepared for the nonsterile and sterile studies.

Nonsterile soil studies: a) 2.02 mg [pyridine-2-^{14}C] DPX-V9360 plus 2.0 mg of the radiolabeled analytical standard in 50 mL of acetonitrile (total specific activity 2.5 uCi/mL and total test substance concentration of 0.08 mg/mL; b) 2.01 mg [pyrimidine-2-^{14}C]DPX-V9360 and 2.0 mg of nonradiolabeled analytical standard in 50 mL acetonitrile (total specific activity 2.5 uCi/mL and total test substance concentration 0.08 mg/mL).

Sterile soil studies: a) 0.97 mg of [pyrimidine-2-^{14}C]DPX-V9360 plus 2.03 mg [pyridine-2-^{13}C]DPX-V9360 plus 1.06 mg of nonradiolabeled analytical standard in 64 mL acetone (specific activity 0.95 uCi/mL and total test substance concentration of 0.06 mg/mL; b) 1.11 mg of [pyrimidine-2-^{14}C]DPX-V9360 plus 2.06 mg of [pyrimidine-2-^{13}C]DPX-V9360 plus 0.95 mg nonradiolabeled test material (specific activity of 1.06 uCi/mL and total test substance concentration of 0.06 mg/mL.

Application rate:

0.4 mL-aliquots of the solutions used in nonsterile soil studies delivered 0.64 ppm of test substance which is equivalent to 70 g ai/ha (maximum proposed application rate). For the sterile soil studies, 0.50 mL aliquot delivered a total substance concentration of 0.64 ppm.

Experimental procedure:

A. Nonsterile soil study. 50-g oven dry weight of soil were placed in each of the 20 individual glass incubation flasks. Deionized water was mixed into the soil to 75% of its moisture-holding capacity at 0.33 bar. The 0.4 mL aliquots of the [pyridine]- or the [pyrimidine]-labeled DPX-V9360 were evenly applied with a syringe. After the organic solvent evaporated, the flasks were gently shaken to mix the soil. The gas outlet of each flask was connected to a 1N NaOH trap for CO_2, the gas inlet of each flask was opened to the atmosphere. Samples were placed in the dark in a 25C incubation room.

B. Sterile soil study. Soil samples (50 g oven-dry weight) in 8 individual glass barometer flasks and brought to 75% moisture holding capacity at 0.33 bar were autoclaved. Four flasks were treated with the [pyridine-^{14}C] labeled solution and the other four with the [pyrimidine-^{14}C] labeled solution. After the organic solvent evaporated, the flasks were gently shaken, sealed, and each sidearm of the barometer connected to a 20 mL in NaOH solution. Flasks were placed in the dark in a 25C incubator.

Sampling:

a) Nonsterile soil - 0, 1, 3, 7, 14, 21, 30, 60, 90, 120, 180, and 240 days.

b) Sterile soil - 0, 60, 90, 180 days. Extraction and analyses began within 3 days or immediately upon collection. Those that were not extracted immediately were stored at -10 °C.

Analytical method:

Radioactivity in traps was analyzed by LSC. Radioactivity in soil was extracted by the method outlined in Figure 1. The concentrated solutions (triplicate) were then analyzed by LSC for total radioactivity and by HPLC to separate individual components and the components tentatively identified by comparison of retention times of reference standards. Soil extracts were also analyzed by TLC (methylene chloride/methanol/concentrated ammonium hydroxide, 165/30/5, v/v/v) along with reference standards. Radioactive degradates whose identities could not be confirmed were isolated by HPLC/fractionation, and further purified for spectral characterization (MS, ir, and proton nmr).

Total unextractable radioactivity was determined by combustion followed by LSC. This bound radioactivity was characterized by the soil fractionation procedure outlined in Figure 2.

REPORTED RESULTS

Material balance tables are shown in Tables II and III for nonsterile soils treated with [pyridine-^{14}C]DPX-V9360 and [pyrimidine-^{14}C]DPX-V9360, respectively. Table IV shows the results for sterile soil experiments. $^{14}CO_2$ formation was less than 1% of total radioactivity and thus is not an immediately significant degradation pathway for DPX-V9360.

After 6 months of incubation, DPX-V9360 was not detected in extracts of nonsterile soil, but was 40-50% of the radioactivity in sterilized soils incubated for the same period.

In nonsterile soil, pyrimidine amine was 84% after 6 months and ca. 81% after 8 months. Bound radioactivity found when the [pyrimidine-^{14}C] DPX-V9360 was used reached 18% after 6 months. Pyridine sulfonamide reached 94% after 6 months and was 93% after 8 months; bound radioactivity found when the [Pyridine-^{14}C]DPX-V9360 was used reached 6.9% after 8 months.

In sterile soils, Pyrimidine amine reached 24.3% after 6 months and "Pyridine sulfonamide" reached 34% after 6 months.

The degradation product labeled as "Pyridine sulfonamide" is a combination of Pyridine sulfonamide and an artifact formed during extractions with ammonium carbonate. This artifact was not detected when ammonium carbonate was not used in the extraction process. Identification of this artifact was attempted by MS, ir, proton-nmr and cochromatography with suspected metabolites of DPX-V9360.

There was also a minor radiolabeled product designated as "Intact Unknown," which was detected in both nonsterile and sterile soils and with both labels. Thus, this compound is believed to contain both rings. In nonsterile soils it reached a maximum by 120 days (4 months), but was not detected in later samples. In sterile samples, it reached 9-10% of total radioactivity after 6 months. This "Intact Unknown" did not cochromatograph with N-desmethyl DPX-V9360, DPX-V9360 carboxamide, O-Desmethyl DPX-V9360, and DPX-V9360 Ipso Precursor.

The calculated first half-life of DPX-V9360 in nonsterile soil was 26 days; in nonsterile soils it was 178 days (ca. 6 months). This indicates that microbial degradation under aerobic condition is a significant factor in the breakdown of DPX-V9360, in which cleavage of the sulfonylurea bridge is apparently the primary route of degradation of DPX-V9360.

REVIEWER'S COMMENTS

1. The study was conducted over an 8-month period. Although it does show the pattern of decline of parent DPX-V9360, the pattern of decline of the major degradation products "Pyridine Sulfonamide" and Pyrimidine Amine cannot be established clearly as the maximum concentration of these degradates are found towards the end of the study (at 6- and 8-month sampling). The registrant should address the pattern of decline of these two major metabolites.

2. It is not clear from the experimental description as to why acetonitrile was used as a solvent in the solutions prepared to treat nonsterile soils and, why acetone was used for sterile soils.

3. In sterilized soil studies it is said that one solution was prepared with "[pyrimidine-2-^{14}C]DPX-V9360 plus [pyridine-2-^{14}C]DPX-V9360 plus nonanalytical standard." The other solution was prepared with both the [pyrimidine-2-^{14}C] plus the analytical standard. The Table reporting the results of this study (Table IV) refers to "[pyridine-2-^{14}C]DPX-V9360." Thus, it appears that the description of the first solution is not correct and that the author meant "[pyridine-2-^{14}C]DPX-V9360" instead of "[pyrimidine-2-^{14}C]DPX-V9360."

4. N-desmethyl DPX-V9360, O-desmethyl DPX-V9360, DPX-V9360 Carboxamide, and the DPX-V9360 Ipso PRecursor were used as reference standards to identify the degradate labeled as "Intact Unknown," but this compound did not cochromatograph with the standards. What is the possibility that a fully desmethylated product (the DPX-V9360 carboxamide without the two O-methyl groups) or a fully desmethylated "Ipso Precursor" or other partially desmethylated products (such as "N-desmethyl and O-desmethyl" or the "carboxamide O-desmethyl, etc.) are identified as the "Intact Unknown"?

Accent environmental fate review

Page ______ is not included in this copy.

Pages 66 through 76 are not included in this copy.

The material not included contains the following type of information:

___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product 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

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

SH#129008 STUDY 5 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Metabolism in soil, anaerobic 162-1

FORMULATION: Radiolabeled active ingredient

MRID #41082623

Rhodes, B.C. 1989. Anaerobic soil metabolism of ^{14}C-DPX-V9360. Laboratory Project AMR-851-87; completed on April 6, 1989. Prepared and submitted by E.I. du Pont de Nemours, Wilmington, DE.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

SIGNATURE:

February 19, 1990

CONCLUSIONS:

This study is acceptable and fulfills Subdivision N data requirements for this type of study.

SUMMARY

The calculated half-life under anaerobic conditions is 63 days. After 60 days under anaerobic conditions (90-days from the beginning of the study) parent DPX-V9360 declined to ca. 30% of the applied (under aerobic conditions, ca. 10% remained after 90 days). The main degradates were "Pyridine Sulfonamide" and Pyrimidine Amine at 59% and 47% after 60 days of anaerobic incubation (90-days from the beginning of the study), at 90-days under aerobic conditions these degradates were detected at 88% and 73% of the applied, respectively.

A minor (< 10%) degradate labeled as "Intact Unknown" was also detected, but attempts to identify it by several spectroscopic methods were not successful.

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MATERIALS AND METHODS

Test Material:	a) [Pyridine-2-^{14}C]DPX-V9360, specific activity 62.9 uCi/mg and radiochemical purity 99%; b) [pyrimidine-2-^{14}C] DPX-V9360, specific activity 62.2 uCi/mg and radiochemical purity of 98.8%.
Soil:	The soil used was the same silty clay loam soil from Paris, IL (pH 6.1, 5.1% organic matter, 30.4 meq/100 g CEC) used in the aerobic soil metabolism study. The soil ws sieved through a 2-mm mesh sieve, and homogenized prior characterization. Presence of microorganism in soil was demonstrated by using ^{14}C-starch.
Test solutions:	Two test solutions were prepared. Each of the solutions delivered 0.032 mg ai to the 50-g sample of soil (or 0.64 ppm, equivalent to 70 g ai/ha). One of the solutions contained 1.0 mg and 2.0 mg of ^{14}C- and ^{13}C-pyridine labeled DPX-V9360 plus 1.0 mg of nonradiolabeled material, all dissolved in 31 mL of acetone. The other solution was prepared in a similar manner, but using the ^{14}C and ^{13}C-pyrimidine labeled DPX-V9360.
Experimental procedure:	50-g oven dry weight equivalent of soil were placed in each of 12 individual incubation flasks and deionized water was added to 75% of its moisture holding capacity at 0.33 bar. The desired aliquot of test solution (0.25 mL) was applied evenly to the soil surface the organic solvent allowed to evaporate. The gas outlet of each flask was connected to two traps in series (one containing ethylene glycol to trap organic volatile material and the other NaOH (1N) to trap $^{14}CO_2$). The gas inlet was opened to the atmosphere. The flasks were incubated at 25 °C, in darkness, for 30-days. After 30 days each flask was purged with nitrogen and the purge with nitrogen continued for the 60-day anaerobic phase of the study, where the samples remained in darkness at 25 °C. Moisture loss was compensated by addition of water.
Sampling:	For each radiolabel, duplicate soil samples and traps were analyzed for days 0, 30 (initiation of anaerobic phase), 45, 61, 79, and 90.

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Analytical methods: Total radioactivity in traps was analyzed by LSC. Soil radioactivity was determined after extraction by the method outlined in Figure 1. Total radioactivity of extracts was analyzed by LSC. Components of radioactivity were analyzed by HPLC and tentatively identify by comparison of the retention time of the components with those of known standards. TLC was also used to confirm identity of radioactive components by cochromatography with known standards. Unextracted soil radioactivity was determined by combustion followed by LSC. HPLC/fractionation was used to isolate unidentified components, which were then identified by spectroscopic techniques.

REPORTED RESULTS

At day 30 (end of aerobic incubation), the parent DPX-V9360 was 59% for the [pyridine-^{14}C]DPX-V9360 study and 64% for the [pyrimidine-^{14}C]DPX-V9360 study. The major degradates "Pyridine sulfonamide" and Pyrimidine amine were 32% and 25% after 30 days.

After anaerobic conditions were established, parent DPX-V9360 declined to 29% (pyridine-labeled study) and 33% (pyrimidine-labeled study) after 60 days (90 from the beginning of study). After 60 days (90 from the beginning of the study), 47% Pyrimidine Amine and 59% "Pyridine Sulfonamide"* were detected. Bound radioactivity was 7% (pyridine labeled study) and 12% (pyrimidine labeled study). An unidentified material labeled as "Intact Unknown" was detected after 90 days at a maximum of 7% (pyrimidine-labeled material).

The calculated half-life under anaerobic conditions was 63 days in contrast to 26-days under aerobic conditions, but the degradation pathway appears to be identical as the one under aerobic conditions.

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*"Pyridine Sulfonamide" is used to label the artifact formed by extraction with ammonium carbonate, which is only formed once Pyridine sulfonamide has been formed.

REVIEWER'S COMMENTS

1. "Anaerobic" conditions were attained by purging with nitrogen after aerobic incubation. A flooding/purging method would have been preferred, for which dissolved oxygen content and/or redox potential should have been monitored throughout the duration of the experiment. However, because current Subdivision N Guidelines allows purging with an inert gas after completion of the aerobic phase, the anaerobic study can be considered acceptable to fulfill data requirements.

Accent environmental fate review

Page ______ is not included in this copy.

Pages 81 through 91 are not included in this copy.

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___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product 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

X FIFRA registration data

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"DPX-V9360"- ACCENT^{TM} Herbicide
Shaughnessy #" 129008

Study 6- Mobility in soil:
Batch-equilibrium adsorption/desorption
and soil thin-layer chromatography studies.

The review of the original study (MRID #40924222) was included in the EFGWB review dated 5/1/89. In a letter dated 7/5/89, the registrant addressed the deficiencies/questions noted in the 5/1/89 review. The registrant's response is included in the EFGWB review of 10/20/89.

The registrant satisfactorily responded to all of EFGWB questions. In the 10/20/89 review the registrant was informed that data requirements for mobility in soil studies were partially satisfied and that batch-equilibrium adsorption/desorption studies conducted with the major degradates Pyridine Sulfonamide and Pyrimidine Amine might be requested at a later date.

After evaluation of all the data submitted with the Section 3 registration package, EFGWB is requesting that batch-equilibrium adsorption/desorption studies be conducted with Pyridine Sulfonamide and Pyrimidine Amine.

The results of the original study show that parent DPX-V9360 is very mobile in the sandy loam and silt loam soils used in the study ($K_{ad} < 2$). Data from the soil thin-layer chromatography studies indicate that the degradate Pyridine Sulfonamide is more mobile than parent DPX-V9360; the degradate Pyrimidine Amine was less mobile than parent DPX-V9360.

Feb. 19, 1990

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DATA EVALUATION RECORD

CASE GS — 129008 STUDY 6 (Study 3 of 5/1/89 review) PM 25

CHEM

BRANCH Environmental Fate and Ground Water; 163-1

FORMULATION 00-Radiolabeled active ingredient

MRID NO. 40924222

Priester, T.M.; Sheftic, G.D. 1988. Batch equilibrium (adsorption/desorption) and soil thin-layer chromatography studies of [^{14}C] DPX-V9360. Conducted and submitted by E.I. du Pont de Nemours Company, Inc., Agricultural Products Department, Wilmington, DE. Laboratory Project ID: AMR-842-87. Study completed on November 22, 1988.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EFGWB/HED/OPP
TEL: (703) 557-2243

SIGNATURE: April 24, 1989

CONCLUSIONS:

The mobility in soil studies are basically acceptable. However, the registrant should provide additional information to clarify the following:

A. Batch-equilibrium adsorption/desorption studies

An equilibration time "between 16-21 hrs" was used. However, no reason was given why this time period was chosen or data provided showing the equilibration time was adequate. Data for the terbacil and diuron standards should also be included.

B. Soil thin-layer chromatography

Indicate the temperature at which the plates were developed.

Batch-equilibrium adsorption/desorption studies indicate that parent DPX-V9360 was more weakly adsorbed onto the sandy loam soils than onto the silt loam soils. However, the correlation between percent organic matter and sorption coefficients was low and suggests that other soil properties such as pH and cation exchange capacity may be significant in the adsorption/desorption behavior of DPX-V9360.

Soil thin-layer chromatography results showed that DPX-V9360 was more mobile in the sandy loam soils than in the silt loam soils. The order of mobility (based on R_f values) was pyridine sulfonamide > DPX-V9360 $\sim$ terbacil > pyrimidine amine $\sim$ diuron. Pyridine sulfonamide and pyrimidine amine are major degradates of DPX-V9360; terbacil and diuron were used as references.

MATERIALS AND METHODS

A. Batch-equilibrium adsorption/desorption studies

Soils: Four different soils (Woodstown sandy loam, Cecil sandy loam, Flanagan silt loam, and Keyport silt loam; characteristics on Table I) were air-dried, screened through a 2-mm mesh screen, and thoroughly mixed by hand.

Test material: [pyrimidine-2-^{14}C]DPX-V9360, radiochemical purity of 94%, specific activity of 25.5 Ci/mole (62.2 uCi/mg).

Test solutions: Aqueous solutions of the ^{14}C-labeled DPX-V9360 (as well as of ^{14}C-labeled terbacil and diuron) in 0.01 N calcium sulfate solution) were prepared at nominal concentrations of 0.2, 0.5, 1, 2.5, and 6 ppm. Actual concentrations were determined by LSC (Table II).

Experimental Procedure

a) Adsorption phase: 20 mL aliquots of each test solution were mixed with 20 g of each soil type (in duplicate; 4-oz screw cap bottles). The capped bottles were shaken for 16-21 hours at $25^{o}C$ (constant-temperature water bath) at a shaker speed of about 70 oscillations/min. After the equilibration period, soil/aqueous phase were separated by centrifugation (10 min at ~ 2000 rpm). The radioactivity in the decanted, filtered supernatant was determined by LSC (three 1-mL aliquots).

b) Desorption phase: After the supernatants of the highest concentration solutions were decanted, 0.01 N calcium sulfate solution was added to reestablish original total weight and 1:1 (w/v) soil-to-water ratio. The capped bottles were shaken in a constant-temperature water bath ($25^{o}C$) at approximately 70 oscillations/min for 16-21 hrs. Aliquots (1 mL) of the filtered supernatant were analyzed (in triplicate) for total radioactivity. The desorption procedure was repeated five times.

Analytical methods: Aqueous solutions (decants) from the adsorption and desorption phases were analyzed by HPLC (Zorbax column; acetonitrile/0.0005 M KH_2PO_4 (adjusted to pH 2.3 with HCl as the mobile phase).

Radioactivity remaining in soils after the desorption phase was completed was determined by HPLC of extracts. Extractions were done by slurrying the soils with 0.1 M ammonium carbonate adjusted to pH 9.6 with NH_4OH for a 16-hour period and reextracting the remaining soil 3-to-4-times with pH 9.6, 0.1 M ammonium carbonate/acetone (10/90) for 1 hr. Triplicate 0.5 mL aliquots of the composite extracts were analyzed for total ^{14}C by LSC. The organic solvent was removed by rotary evaporation and the remaining aqueous phase reduced in volume. Final aqueous extracts were analyzed by HPLC.

Calculations: Sorption coefficients were obtained from Freundlich isotherms. For the adsorption phase, $\log S = 1/na \cdot \log W_2 + \log K_a$ where W_2 is the concentration in aqueous phase after equilibration, S is the concentration adsorbed onto the soil after equilibration (obtained by substracting W_2 from the initial concentration W_1). For the desorption phase, the concentration of radioactivity after each subsequent equilibration (w_{2a}) was determined by substracting the concentration prior equilibration from the concentration after equilibration and S in the soil by substracting W_{2a} from the previous day's value.

Sorption coefficients per unit of organic matter value ($K_{a/d,om}$) were calculated by:

$$K_{a/d,om} = \frac{K_{a/d} \times 100\%}{\%\ om}$$

REPORTED RESULTS

Tables II through V show the initial and after equilibration concentration for the adsorption phase. For the desorption studies, this data is shown in Tables VI-IX. Corresponding isotherms are shown in Figures 3 through 5.

Sorption coefficients are summarized in Tables X (adsorption) and XI (desorption) and are shown compared to those of terbacil and diuron [no actual data were presented for terbacil and diuron; these values were taken from a referenced report].

The K_a values for the two sandy loam soils, which have 1.1 and 2.1% organic matter were 0.16 and 0.28; these values indicate that DPX-V9360 were weakly adsorbed to these soils. For the two silt loam soils with 4.3 and 4.7% organic matter, the K_a values were 1.73 and 0.61, respectively. The low correlation between percent of organic matter and K_a values indicates that other soil properties such as pH and cation exchange capacity may be significant in the adsorption behavior of

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DPX-V9360 onto soil particles. Likewise, desorption also appeared to correlate poorly with the percent organic matter content.

Recovered radioactivity ranged from 96-98%, of which 87-90% was recovered as parent DPX-V9360, < 5% pyrimidine amine, about 1% N-desmethyl DPX-V9360, and unknown (less than 1%), as shown in Table XII.

REVIEWER'S COMMENTS

1. It is not clear from the report if a preliminary study was performed aimed to determine the necessary equilibration time. It also is not clear the reason for expressing the equilibration time as between 16 to 21 hrs rather than giving the actual equilibration time.

2. In Table XII (identification of components in aqueous and soil), both columns corresponding to Flanagan soil experiments appear labeled as "Flanagan (soil)". We assume that the first column refers to "Flanagan (Aqueous)".

3. From the data in Table XII, it can be seen that the percent of parent DPX-V9360 is lower in the aqueous phase of the more acidic (and higher CEC) Flanagan and Keyport than in the Woodstown and Cecil soils. The percent of parent DPX-V9360 extracted from the Flanagan and Keyport is however, higher in these soils than in the Woodstown and Cecil soils, which again indicate that pH and/or CEC of the soil determines the sorption behavior of DPX-V9360.

4. The total amount of pyridimine amine detected was also higher in the Flanagan and Keyport soils, particularly in the extracts from the soil.

5. Did the authors measure the pH of the test solutions (freshly made), of the aqueous phase in contact with the soil (at the beginning and end of the equilibration period)? If so, did they observe any drastic changes in pH?

6. Results for terbacil and diuron were included, but no isotherms were provided for these compounds. Although the terbacil study appears referenced (but not for diuron), the data for these two compounds should have also been included in the present report.

7. Reference 6 cites an aerobic soil metabolism study that was used to select the degradates to be studied. However, this study has not been submitted to the Agency yet. Instead, the registrant has requested a waiver based on other preliminary, earlier studies.

B. Soil thin-layer chromatography

Soils: The same four soils used in batch-equilibrium adsorption/desorption study (see Table I of such study for soil characteristics).

Soil plates were 400-um layer of soil spread onto 20 cm x 20 cm glass plates.

Test materials: ^{14}C-DPX-V9360 (radiochemical purity 94%; specific activity 25.5 Ci/mole) and the radiolabeled degradates pyrimidine amine (radiochemical purity 94.2%; specific activity 22.0 Ci/mole) and pyridine sulfonamide (radiochemical purity 93.6%; specific activity 25.8 Ci/mole) were studied against reference [2-^{14}C] terbacil (95% radiochemical purity; 10.6 Ci/mole specific activity) and [carbonyl-^{14}C]diuron (99% radiochemical purity; 0.96 Ci/mole specific activity).

Experimental procedure: 3-uL aliquots of the sample and reference standards (0.1 to 1.0 mg compound/mL acetone) were spotted 3-cm from the bottom of each plate. The acetone was allowed to evaporate and the lower 0.5 cm of each plate was submerged in water (water temperature unspecified). The water was allowed to ascend 10-cm above the origin. The plates were air-dried for 24-hrs and then exposed to X-ray film for 2-weeks.

Calculations: R_f values were calculated from the equation $R_f = \frac{d}{S}$, where d = the average distance traveled by the test compound at the end of the development and S = the distance between the point where the test compound was applied and the end of the solvent front after development.

REPORTED RESULTS

Table XIII summarizes the soil TLC results. The R_f values for parent DPX-V9360 were lower in the Flanagan and Keyport silt loam soils (0.40 and 0.41, respectively) than in the Woodstown and Cecil sandy loam soils (0.60 and 0.61, respectively). The pyridine sulfonamide and pyrimidine amine and the referenced terbacil and diuron R_f values were also lower in the silt loam soils.

The order of mobility (based on R_f values) was pyridine sulfonamide > DPX-V9360 $\sim$ terbacil > pyrimidine amine $\sim$ diuron. Mobility appears to be inversely proportional to the percent of organic matter content (Figure 6).

REVIEWER'S COMMENTS

The registrant should clarify the temperature at which the plates were developed.

Accent environmental fate review

Page ______ is not included in this copy.

Pages 99 through 116 are not included in this copy.

The material not included contains the following type of information:

___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product 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

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DATA EVALUATION RECORD

SH#129008 STUDY 7 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Terrestrial field dissipation 162-1
(steel cylinders)

FORMULATION: ACCENT 26DF Formulation prepared with radiolabeled active ingredient

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MRID #41082624

Priester, T.M. 1989. Terrestrial field soil dissipation of [pyridine-2-^{14}C]DPX-V9360 and [pyrimidine-2-^{14}C]DPX-V9360 in Newark, DE; Greenville, MS; and Rochelle, IL. Study Project AMR-843-87; Completed April 6, 1989. Prepared and submitted by E.I. du Pont de Nemours and Company, Wilmington, DE. Low dose samples were analyzed by Agrisearch, Inc., Frederick, MD (Study No. 1703).

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

SIGNATURE: February 19, 1992

CONCLUSIONS:

This study is unacceptable at the present time and, thus, data requirements for terrestrial field dissipation studies are not satisfied. The registrant must submit additional, acceptable information to the Agency in order to reevaluate the study.

In the reviewed study the author has attributed the loss of total radioactivity observed to extensive degradation of the pyrimidine and pyridine rings to $^{14}CO_2$ and other volatile degradates. However, in the reviewed aerobic soil metabolism study (41082622) no substantial evolution of $^{14}CO_2$ and other volatile degradates was noted during the 8-month duration of the study. Moreover, it was at 6 to 8 months that the maximum concentrations (>80%) of the Pyridine Sulfonamide and Pyridine Amine degradates were found, but beyond 8-months (time at which the study was terminated) no data is available showing the degradation pathway of these main degradates.

It is also known from mobility in soil studies that the Pyridine Sulfonamide degradate is more mobile than parent DPX-V9360. Because the depth of the cylinders was 14 inches, it is possible that the "lost" radioactivity may have moved below 14-inches.

The "lost" radioactivity may be due (as claimed by the author) to formation of $^{14}CO_2$/other volatiles movement to below 14-inches, or a combination of both. The registrant has been requested in the review of the aerobic soil metabolism study to provide convincing experimental evidence on the pattern of decline of the major degradates. Therefore, the registrant should also provide experimental evidence showing that no significant radioactivity had moved below 14-inches.

Other information requested is:

a) Explanation as to why a study was conducted in a soil with a pH higher than the recommended 7.5 upper limit.

b) Clarify how the pHs of the soils were determined.

c) Expand the description of the test plots (size, depth of water table, pattern of placing the cylinders throughout the plot).

d) Provide actual data in support of the reported storage stability of samples.

e) For the Newark, DE and Rochelle, IL provide a comparison (on a monthly basis) of normal, average rainfall for the area with the rainfall measured during the course of the study.

In the study conducted in Greenville, MS it was noted that, in general, the actual rainfall was below the average. In this study, less radioactive residues were observed in the lower segments.

SUMMARY OF REPORTED DATA

Three different sites (Newark, DE; Rochelle, IL; Greenville, MS) were selected for the study. Stainless steel cylinders, driven into the soils to a 14-inch depth, were placed throughout the field and treated with [pyridine-2-^{14}C]DPX-V9360 and [pyrimidine-2-^{14}C]DPX-V9360 at a dose of 1 oz ai/acre (a formulated product was used); in the Newark, DE additional studies were performed at a dose of 10 oz ai/acre.

The estimated first half lives were as follows:

Newark, DE	3±1 week (based on first 17-weeks)
Rochelle, IL	6±2 weeks for the pyridine-labeled study
	8±1 week for the pyrimidine-labeled study (based on first 17 weeks)

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Greenville, MS . . . . 2±1 week (based on first 4-weeks).

Major degradates found (>10% of applied) were Pyridine Sulfonamide, Pyrimidine Amine, N-Desmethyl Pyridine Sulfonamide, Pyridine Acid Sulfonamide, and O-Desmethyl Pyrimidine Amine.

MATERIALS AND METHODS

Test material(s): Radiolabeled DPX-V9360 was used to prepare the 26 DF formulation containing the inert ingredients used in the commercial ACCENT formulation. Separate ACCENT formulations containing [pyridine-2-^{14}C]DPX-V9360 or [pyrimidine-2-^{14}C]DPX-V9360 were prepared from [pyridine-2-^{14}C]DPX-V9360 of 62.9 uCi/mg specific activity and 96% radiopurity and from [pyrimidine-2-^{14}C]DPX-V9360 of 62.2 uCi/mg specific activity and radiopurity greater than 92%.

Sites: Three test sites were selected: a) Newark, DE; b) Greenville, MS; c) Rochelle, IL. Soil characteristics for these sites are shown in Table I. No pesticide was used in any of these sites for at least three years prior application of DPX-V9360. Untreated soil from 0-3 inches, 3-6 inches, 6-9 inches and 9-14 inches were collected at each site, air dried, sieved through a 2-mm mesh sieve and homogenized prior to characterization.

Plots: Bare ground plots were prepared. At each site 22-stainless steel cylinders (4-in id x 15 x in long) (11 cylinders per radiolabel) were driven into the soil. At the Newark site 20 extra cylinders were driven into the soil to conduct studies at high dose.

Application rates: In the three sites the 22 cylinders were treated at an application rate equivalent to 1 oz ai/acre (70 g ai/ha). In the 20 extra cylinders placed in the Newark, DE study a dosage ten times higher was used.

Application dates: a) Newark, DE: 6/2/87; b) Rochelle, IL: 6/4/87; c) Greenville, MS: 6/5/87.

No other pesticides, intentional irrigation, tilling or weeding were employed during the course of these studies. Duration of the study was 52-weeks.

Sampling: One cylinder of each radiolabeled study from each test plot was removed at preselected time intervals of 0 days, 1 week, 2 weeks, 4 weeks, 8 to 9 weeks, 17 weeks, 35 to 43 weeks, and 52 weeks. After removal, cylinders were frozen at approximately -20 C.

Sample preparation:	Prior to analysis the cylinders were allowed to thaw at room temperature and segmented (from the top down) in increments of 0-3, 3-6, 6-9, and 9-4 inches. Each soil segment was lyophilized or air dried for 3-days and homogenized and weighed before and after drying.
Meteorological data:	Weather data (including soil and air temperature and precipitation data) were obtained as follows: a) Newark, DE from the site; b) Greenville, MS site from the National Weather Service Center in Stoneville, MS; Rochelle, IL, from the field station.
Analytical methods:	Total radioactivity in soil was determined by combustion followed by LSC. Extraction of radioactivity in each soil increment was performed as shown in Outline 1. Concentrated soil extracts were then analyzed by RPLC; an alternative HPLC method was used on the 52-week high-dose Newark, DE samples. Retention times of radiolabeled compounds were compared with those of reference standards. Components were isolated and characterized by LC/MS analyses.

REPORTED RESULTS

I. The distribution and concentration of total ^{14}C radioactivity are tabulated as follows:

A. Newark, DE Studies:

a) Table IV and V, [pyridine]- and [pyrimidine]-labeled experiments, respectively, conducted at 10 oz ai/acre. Note that with aging total radioactivity can be detected in the deeper soil increments.

b) Table VI and VI, [pyridine]- and [pyrimidine]-labeled experiments, respectively conducted at 1 oz ai/acre. Note again that with aging total radioactivity can be detected in the deeper soil increments.

In general, most of the radioactivity remained in the 0-3 and 0-6 inches for both the high and the low dose studies.

B. Rochelle, IL studies:

Tables VIII and IX show the distribution of total radioactivity for the [pyridine-2-^{14}C]DPX-V9360 and [pyrimidine-2-^{14}C]DPX-V9360 studies, respectively. Movement of radioactivity to the lower segments with increasing aging can be observed. Most of the radioactivity remained in the 0-3 and 3-6 in segments.

C. Greenville, MS studies:

Tables X and XI show the distribution of total radioactivity for the [pyridine-2-^{14}C]DPX-V9360 and [pyrimidine-2-^{14}C] DPX-V9360 studies, respectively. No radioactivity below 0.0005 ppm was detected in the 9-14 in segment at any time. Most of the radioactivity remained in the 0-3 and 3-6 in segments.

Total radioactivity (based on soil combustion data) declined to 39-62% in [pyridine-2-^{14}C]DPX-V9360 and 46-55% in the [pyrimidine-2-^{14}C]DPX-V9360. The loss of radioactivity was attributed to extensive degradation of the pyridine and pyrimidine rings to $^{14}CO_2$ and other volatile degradates.

II. Concentration of parent DPX-V9360 and metabolites/degradates.

A. Newark, DE studies:

Tables XII and XIII show the distribution of parent DPX-V9360 and degradates for the studies conducted at 10 oz ai/acre with the [pyridine-2-^{14}C]DPX-V9360 and the [pyrimidine-2-^{14}C]DPX-V9360 respectively, while for the studies conducted at 1 oz ai acre, the results are shown in Tables XIV and XV.

The degradation (dissipation profile) of DPX-V9360 are shown in Fig. 9 and 10. There appears to be no significant effect of initial application in the dissipation profile of parent DPX-V9360. The average half-life for both labels was 3±1 week, assuming a first-order degradation rate during the first 17 weeks.

B. Rochelle, IL studies

The results of these studies are shown in Tables XVI and XVII and the dissipation profiles are shown in Figure 11. Again assuming a first-order degradation rate during the first 17 weeks, the estimated first half-life was 6±2 weeks for the pyridine-labeled study and 8±1 week for the pyrimidine-labeled study.

C. Greenville, MS studies

Tables XVIII and XIX show the results for these studies. Assuming a first-order degradation rate during the first 4 weeks, the estimated half-life for each of the radiolabeled studies was 2±1 week.

Table XX summarizes the kinetic data. DPX-V9360 appear to have degraded more rapidly in the Greenville, MS studies.

III. Degradation pathways under field conditions

The initial degradation pathway is hydrolysis to produce the sulfonylurea-bridge cleavage product Pyridine Sulfonamide and Pyrimidine Amine. These initial degradates undergo subsequent degradation (N-demethylation and O-demethylation).

Major radiolabeled degradates at > 10% at any sampling intervals were Pyridine Sulfonamide, N-Desmethyl Pyridine Sulfonamide, Pyridine Acid Sulfonamide, Pyrimidine Amine, and O-Desmethyl Pyrimidine Amine. The maximum concentration of these degradates occur in the 4 to 9 week samples.

Other degradates detected at < 0.009 ppm and < 9% were N-Desmethyl DPX-V9360, O-Desmethyl DPX-V9360, Pyrimidinyl Urea and other minor degradates. They appear, to occur throughout all time periods of the study, but not at significant concentrations. The more polar degradates (Pyridine Sulfonamide, N-Desmethyl Pyridine Sulfonamide, and Pyridine Acid Sulfonamide) were detected at the lower soil segments.

REVIEWER'S COMMENTS

1. The loss in total radioactivity was attributed by the author to extensive degradation of the pyridine and pyrimidine rings to $^{14}CO_2$ and other [unspecified] volatile degradates. From the aerobic soil metabolism study, little $^{14}CO_2$ or volatile degradates evolution was noted during the 8-months duration of the study. A major deficiency found in the soil metabolism study was that the pattern of decline of the major degradates Pyridine Sulfonamide and Pyrimidine Amine was not addressed. The maximum concentration (> 80%) of these degradates peaks after 6 to 8 months but beyond 8-months no data was presented showing the subsequent degradation of these major degradation products. Thus, the author's explanation is not valid without any further experimental evidence showing that the major metabolites are extensively mineralized to $^{14}CO_2$.

   Mobility in soil studies indicate that Pyridine Sulfonamide is more mobile than parent DPX-V9360. Since the depth of soil cylinders was only 14 inches, there is also the possibility that the "lost" radioactivity (as parent DPX-V9360 and/or other degradates) has moved below the 14-inch depth.

2. According to the proposed label, it is recommended that ACCENT be not applied to soils having a pH higher than 7.5. The soil from Greenville, MS has a pH higher than the upper limit proposed in the label. The registrant should clarify the following: a) how "soil pH" were determined; b) the rationale behind choosing a soil with a pH higher than the recommended upper limit.

3. If CO_2 formation is an important degradation route for the major metabolites, then it should be kept in mind that at higher pHs it is

not CO_2 (gas) the predominant species but HCO_3^-/CO_3^{2-}. That is, inorganic "carbonates" can be formed and incorporated into the soil.

4. Although the report mentions that samples of day 0 (at 1 oz ai/acre) stored at -20 °C at 2-, 4-, and 11.5-months were stable no actual data showing storage stability was submitted with the report.

5. Cumulative rainfall for the Newark, DE study is reported as 25.4 (inches) of rain. However, it is not mentioned how typical is that amount of rainfall for the area.

   For the Greenville, MS study the amount of rainfall was considerably below average in 8 to 12 months of duration of the study. Only in November 1987 and March 1988 the rainfall was significantly above average. No irrigation was used throughout the study. In this study less amount of total radioactivity was detected in the lower segments, which may be related to the less than average overall rainfall.

   For the Rochelle, IL study no information was provided about the average rainfall per month.

6. There was no complete description about the field sites (plot size, placement of cylinders, depth of water table).

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Page ______ is not included in this copy.

Pages 125 through 152 are not included in this copy.

The material not included contains the following type of information:

___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product 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

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The information not included is generally considered confidential by product registrants. If you have any questions, please contact the individual who prepared the response to your request.

DATA EVALUATION RECORD

SH#129008 STUDY 8 PM 25

CHEM: "DPX-V9360" (No common name assigned)

BRANCH: Environmental Fate and Ground Water
Accumulation in confined rotational crops 165-1

FORMULATION: Radiolabeled active ingredient

MRID #41082625

Dietrich, R.F. 1989. Confined accumulation study of ^{14}C-DPX-V9360 on rotational crops. Laboratory project AMR-874-87; completed January 23, 1989. Prepared and submitted by E.I. du Pont de Nemours and Company, Inc., Wilmington, DE.

SUBST. CLASS: Herbicide

REVIEWED BY: S.C. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: (703) 557-2243

SIGNATURE: February 19, 1990

CONCLUSIONS:

This study may be acceptable if the registrant submits further information to clarify the study:

a. Explain why total radioactive residues in unplanted aged soil (30- and 120 days and 10 months) slightly increased when the [pyridine-2-^{14}C]DPX-V9360 was used to treat the soils.

b. Since Pyrimidine Amine has been clearly detected in field studies, is there any possibility that the extraction method used failed to extract this product? On the other hand, the submitted and review aerobic soil metabolism study (41082622) failed to address the further degradation of this main product as well as Pyridine Sulfonamide.

c. The possibility that the "Compounds A, B, and C" formed from Pyridine Sulfonamide (which did not chromatographed with related structures) are formed from a compound(s) in which the -SO_2-group was previously eliminated.

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d. Comment if the presence of the pesticides used to control disease/insect infestations had any interference with the analytical methods or the uptake of DPX-V9360 residues.

e. Provide information about the health and development of the crops throughout the study.

SUMMARY OF REPORTED DATA

Pots containing loamy sand soil (80.8% sand, 12.8% silt, 6.4% clay; pH 6.4, CEC 3.4, meq/100 g) separately treated with [Pyridine-14C]DPX-V9360 or [Pyrimidine-^{14}C]DPX-V9360 at an application rate equivalent to the maximum recommended rate of 70 g ai/ha were aged for 30- and 120-days and 10 months.

Crops were planted as follows: Soybeans (30-, 120-days and 10 months); Lettuce and wheat (120-days and 10 months); Radishes (10-months) and harvest at maturity. From the reported data there is indication that metabolites/degradates containing the pyridine ring are more readily uptaken by plants than those containing the pyrimidine ring. Neither in soils nor in plants the presence of Pyrimidine Amine (which is known to be a major metabolite/degradate of DPX-V9360) was detected.

Maximum total residues were observed in soybean forage/hay and seeds with the pyridine labeled materials, but the amount of residues decreased with increasing aging of the soil. The major metabolite as detected in these samples was Pyridine Sulfonamide.

With the pyrimidine labeled DPX-V9360, total residues were lower and the only identified degradate/metabolite was N-Desmethyl DPX-V9360, which was higher in forage/hay than in seeds.

Maximum total residues were also observed in wheat straw/chaff with the pyridine-labeled material with Pyridine Sulfonamide identified as major metabolite/degradate.

The lowest residues were found in lettuce leaves and radish bulbs.

Results are summarized in the tables below.

RESIDUES IN ROTATION CROPS

Crop/Crop Fraction	Soil aging time	Total radioactive residues, ppm[a] Pyr. ^{14}C	Total radioactive residues, ppm[a] Pyrim. ^{14}C	Parent	Composition, ppm Pyr. Sulf.	Composition, ppm N-Des.	Others[b]
Soybean forage/hay	30-day	0.221	0.060	0.002	0.080	0.025	A
	120-day	0.191	0.056	0.002	0.071	0.022	B
	10 months	0.075	0.014	nd	0.021	0.002	C
Soybean seed	30-day	0.226	0.043	nd	0.023	0.003	D
	120-day	0.157	0.033	nd	0.015	0.002	E
	10 months	0.069	0.012	nd	0.013	nd	F
Lettuce	120-day	0.050	0.015	0.002	0.019	-	G
	10 months	0.011	0.003	nd	0.004	-	H
Wheat forage/hay	120-day	0.112	0.033	ne	ne	-	I
	10 months	0.043	0.009	0.001	0.008	-	J
Wheat straw/chaff	120-day	0.246	0.099	0.004	0.056	-	K
	10 months	0.185	0.056	0.007	0.038	-	L
Wheat grain	120-day	0.025	0.020	0.005	0.003	-	M
	10 months	0.014	0.006	0.005	0.003	-	N
Radish greens	10 months	0.027	0.004	0.001	0.010	-	O
Radish root	10 months	0.006	0.003	na	na	-	P

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[a] Calculated as DPX-V9360 equivalents; nd= not detected; ne= not extracted; na= not analyzed

[b] "Polars", "Bound radioactivity", "Other species resolved by chromatography", "Compounds A, B, and C" (which contain the pyridine ring) and seen in D, E, and F. For details see Tables VII, VII, IX and X.

MATERIALS AND METHODS

Test materials: a) [Pyrimidine-2-^{14}C]DPX-V9360, with specific activity of 62.9 uCi/mg and 99% radiochemical purity; b) [Pyridine-2-^{14}C]DPX-V9360, with specific activity of 62.2 uCi/mg and 99% radiochemical purity.

Soil: Loamy sand soil (from Pennsgrove, NJ) (80.8% sand, 12.8% silt, 6.4% clay) pH 6.4, CEC 3.4 meq/100 g was used to fill 38 plastic pots (14 3/4 inches diameter) to a depth of 12 inches.

Treatment of pots: (August 10/87); 36-pots were treated with test solutions containing 0.77 mg of radiolabeled material (which is a dose equivalent to 70 g ai/ha), 18 of them with the [pyridine-^{14}C]DPX-V9360 and the other 18 with the [pyrimidine-^{14}C]DPX-V9360. Two additional pots (one with each label were treated at a higher dose of 700 g ai/ha. After application of test substance, the soil in each pot was sampled to a 12-in depth for "Day 0" analyses.

To help determine the origin of radiolabeled residues in soybeans grown in soil treated with [pyridine-^{14}C] DPX-V9360, additional experiments were conducted with ^{14}C-Pyridine sulfonamide at a rate equivalent to 2 log/ha.

Planting of crops: Pots were aged for 30, 120-days, and 10-months. The planting scheme (2 pots per crop per aging period) was:

<u>30-days aging</u>, soybeans
<u>120-days aging,</u> soybeans, wheat, lettuce
<u>10-months aging</u>, soybeans, wheat, lettuce, radishes

During aging the pots were maintained at 15-40 C, watered to keep soil moisture, and weeds removed by pulling them (but left in the corresponding pot).

Crop maintenance: Crops were watered as necessary; a photoperiod of $\geq$ 13 hrs was maintained. Plants stressed by disease or insect infection were treated with the pesticides described in "Appendix I".

Sampling: a) Soil - Besides sampling at Day 0, soil was sampled at each planting and harvest (to $\sim$ 12 in depth). Samples taken at same time were pooled, air-dried, weighed, and homogenized and then stored frozen.

b) Crops - Crops were harvest at maturity.

	Planting time		
	30-days	120-days	10-months
Soybeans, harvest time	140 days	107 days	80-days
Lettuce, harvest time	--	48 days	52-days
Wheat, harvest time	--	120 days	103 days
Radishes, harvest time	--	--	42 days

Samples were freeze-dried immediately after harvest. The freeze-dried samples were then homogenized and kept frozen until analyses.

Analytical methods: a) Total radioactivity of soil/crop fraction samples was determined by combustion followed by LSC.

b) Soil and plant radioactivity were extracted following the schemes described in Figure 1. Total radioactivity of extracts was determined by LSC. Components of plant and soil extracts was determined by HPLC. Soil extract components were also by TLC for Day 0 samples.

Detection limits for individual compounds determined by chromatographic analyses depended on crop and concentration of extractable radiolabeled components. Detection limits ranged from 0.001 to 0.010 ppm.

REPORTED RESULTS

a. Total radioactive residues in nonplanted soils:

For the [pyridine-^{14}C]-labeled study, the total radioactive residues in soil decreased from 0.035 ppm at "Day 0," to 0.009 ppm (30-day aging), to 0.013 ppm (120-day aging), to 0.016 ppm (10 month aging).

For the [pyrimidine-^{14}C]-labeled study, the total radioactivity in soil decreased from 0.031 ppm ("Day 0"), to 0.015 ppm (30-day aging), to 0.008 ppm (120-day aging), to 0.010 ppm (10-month aging).

Table II shows the total radioactivity in soil at planting time together with total radioactivity in soil at harvest time.

The composition of radioactivity (i.e., parent, metabolites, and bound) in soils at planting and harvest time are shows in Table III for the [pyrimidine-^{14}C]-labeled study and in Table IV for the [pyridine-^{14}C]labeled study. Parent DPX-V9360 decreased from 0.29 ppm (Day 0) to

0.010 ppm (30-day aging), to 0.001 ppm (120-day aging), to 0.001 ppm (10-month aging) for the pyrimidine-^{14}C] study. For the [pyridine-^{14}C]-labeled study, parent DPX-V9360 varied from 0.033 ppm (Day 0), to 0.005 ppm (30-day aging), to 0.002 ppm (120-day aging), to 0.001 ppm (10-month aging).

The major extractable degradate was Pyridine Sulfonamide which reached a maximum 0.004 ppm at 227 days posttreatment and remained in that range afterwards. At Day 0, 30-days aging, and 120-days aging the amount of this degradate was 0.001 ppm; at 10-month aging, it was 0.004 ppm. Bound residues with the [pyridine-^{14}C] labeled material were about the same as the degradate label.

No Pyrimidine Amine degradate was detected. Levels of bound radioactivity were about the same as with the pyridine labeled experiment.

b. Crops

1. Soybeans. This crop was planted at 30 and 120-day and at 10-month. Tables V and VI show the total radiolabeled residues for the [pyridine-^{14}C] labeled and [pyrimidine-^{14}C]labeled studies. Total radioactivity residues (pyridine labeled study) in forage/hay was 0.221 ppm, 0.191 ppm, and 0.075 ppm at 30 day, 120 day, and 10-month planting, respectively, while for seeds it decreased from 0.226 to 0.157 to 0.069 ppm.

   For the pyrimidine labeled study, total residues in forage/hay were 0.060 ppm, 0.056 ppm, and 0.014 ppm for 30 days, 120-days, and 10-month planting while for seeds it decreased from 0.043 ppm, to 0.033 to 0.012 ppm.

   The higher residues seen in the pyridine-labeled study indicate that metabolites containing the pyridine ring are more likely to accumulate than those containing the pyrimidine ring.

   The major metabolite in soybeans was Pyridine Sulfonamide (0.080 ppm, 0.071 ppm, and 0.021 ppm in the 30- and 120-day, and 10-month; forage/hay). It was also a major metabolites in mature seeds, but at a lower concentration (Table VII)

   From a study conducted with ^{14}C-Pyrimidine Sulfonamide at least three radiolabeled Compounds (A,B, and C) detected in the mature seeds indicate that these are degradates and/or metabolites of Pyridine Sulfonamide. Their concentration decreased with aging time (Table VII). These compounds were not further characterized, but possible related structures appear in Figure 2.

   The only metabolite/degradate identified in the pyrimidine-labeled study was N-Desmethyl DPX-V9360. Its concentration is higher in forage/hay than in seed, but the concentration decrease with time.

2. Lettuce

For mature lettuce leaf the maximum total radioactivity for the pyridine label study was 0.050 ppm and 0.011 ppm when planted at 120-day and 10-month soil aging. With the pyrimidine labeled treatment, the total radioactive residues were lower (0.015 and 0.003 ppm at 120-day and 10-month soil aging). The maximum level of residue found was Pyridine Sulfonamide at 0.019 ppm (120-day aging) and 0.004 ppm (10-month aging). Maximum parent concentration was 0.002 ppm with both labels at 120-day aging (Table VIII).

3. Wheat

The higher total radiolabeled residues were found in wheat straw/chaff when the pyridine labeled material was used (0.246 ppm and 0.185 ppm) at 120 day and 10-month soil aging. Total residues (both labels) were higher in straw/chaff and it is attributed to concentration of the radiolabeled residues in the foliage as the plant dries out upon reaching maturity (Tables V and VI).

The major metabolite found in straw/chaff was Pyridine Sulfonamide (0.056 ppm and 0.038 ppm at 120-days and 10-month soil aging, respectively).

In wheat grain, total radioactivity was 0.025 ppm and 0.014 ppm for the pyridine-labeled study (120 day and 10 month soil maturity, respectively) 0.020 ppm and 0.006 ppm with the pyrimidine-labeled treatment.

4. Radishes

Radiolabeled residues were higher in soils treated with [pyridine]-labeled DPX-V9360. Radishes were planted only at 10 months. The main degradate found in leaves was Pyridine Sulfonamide at 0.010 ppm.

REVIEWER'S COMMENTS

1. It was noticed in Table II that there is a slight increase in total radioactivity in soil from 0.009 ppm at 30-day aging to 0.013 ppm at 120-day aging to 0.016 ppm at 10-month aging, when the pyridine labeled material was used. Does the author have any evidence that degradates/metabolites containing the pyridine ring tend to be more persistent than those containing the pyrimidine ring?

2. Pyrimidine Amine was not detected in soil even though this degradate has been detected in soil metabolism studies and in field dissipation studies. On the other hand, the aerobic soil metabolism study submitted and reviewed (MRID 410822622) failed to define the pattern of decline of the two major degradates/metabolites of DPX-V9360 (that is, of Pyridine Sulfonamide and Pyrimidine Amine).

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3. Compounds A, B, and C are believed to be metabolites and/or degradates of Pyridine Sulfonamide. None of these compounds chromatographed with the compounds of closely related structures (N-Desmethyl Pyridine Sulfonamide; Pyridine Sulfonamide Carboxamide, "Pyridine Saccharin"). What is the possibility that any of these compounds are related to a "pyridine structure" formed by previous elimination of -SO_2-?

4. It is possible that the presence of any of the other pesticides used to control insects/diseases may have interfered with extraction procedures?

5. No information was provided about the health and development of the plants throughout the study.

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Pages 161 through 181 are not included in this copy.

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___ Identity of product inert ingredients

___ Identity of product impurities

___ Description of the product manufacturing process

___ Description of product quality control procedures

___ Identity of the source of product ingredients

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___ The product confidential statement of formula

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