Shaughnessy No.: 100101

Date Out of EAB: MAR 18 1987

To: Robert Taylor
Product Manager #25
Registration Division (TS-767C)

From: Emil Regelman, Supervisory Chemist
Review Section #3
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the EAB review of...

Reg./File # : 201-298

Chemical Name: Cyanazine

Type Product : Herbicide

Product Name : Bladex

Company Name : Shell Oil Company

Purpose : Partial response to groundwater data-call-in.
Hydrolysis, aerobic and anaerobic soil metabolism and leaching data.

ACTION CODE: 660

EAB #(s) : 70024 and 70025

Date Received: 12/09/86

TAIS Code: 56

Date Completed: _____

Total Reviewing Time 3.0 day

Monitoring study requested: _____

Monitoring study voluntarily: _____

Deferrals to: _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

1. CHEMICAL: Common name:

Cyanazine

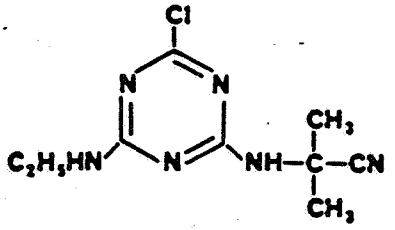
Chemical name:

2-[[4-Chloro-6-(ethylamino)-s-triazin-2-yl]amino]-2-methylpropionitrile

Trade name(s):

Bladex, SD 15418, WL 19805, Fortrol

Structure:



Formulations:

80% WP, 43% 4 lb/gal FlC, and 90% DF

Physical/Chemical properties:

Molecular formula: ~~$C_6ClH_{13}N_6$~~ $C_9H_{13}N_6Cl$
Physical state: White crystalline solid
Melting point: 167.5-169°C

2. TEST MATERIAL:

Triazine ring-labeled [^{14}C]cyanazine. Radiochemical purity 99%.

3. STUDY/ACTION TYPE:

Review of partial submission of ground-water call-in data.

4. STUDY IDENTIFICATION:

(1) Woodward, M.D., E.L. Holloway, and S.F. McEuen. 1986. The hydrolytic stability of ^{14}C-SD 15418 in buffered aqueous solution. RIR-22-004-86 Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 263542. Reference 1.

(2) Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under aerobic conditions. RIR-22-019-086. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265358. Reference 2.

(3) Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under anaerobic conditions. RIR-22-008-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265359. Reference 3.

(4) McEuen, S.F. and M.D. Woodward. 1986. Mobility of SD 15418 and degradation products in soil measured by soil thin-layer chromatography. RIR-22-007-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265360. Reference 4.

5. REVIEWED BY:

A. Schlosser
Chemist
EAB/HED/OPP

Signature: Arthur O. Schlosser

Date: March 19, 1987

6. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #3, EAB/HED/OPP

Signature: E. Regelman

Date: 3/20/87

7. CONCLUSIONS:

Study 1: Cyanazine was stable to hydrolysis at 25° C at pH 7and 9. At pH 5 a hydrolysis half-life of about 148 days was calculated. The major product was identified as N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylanaline.

Study 2: Under aerobic conditions at 25°C cyanazine degraded with a half-life of 14-21 days in a sandy loam soil kept at a field moisture content of 75%. Four major degradates were identified. The study was conducted for only six months.

Study 3: Under anaerobic conditions at 25°C cyanazine degraded with a calculated half-life of about 108 days. Three major degradation products were identified.

Study 4: Soil TLC studies showed cyanazine to be mobile (Rf 0.49-0.55) in sandy loam, silty clay loam, and loam soils, and very mobile (Rf 0.75) in a silt loam soil. All three of the degradation products tested were rated as either mobile or very mobile in the soil types tested. Rf values from 0.47 to 1.00 were determined.

8. RECOMMENDATIONS:

We can accept the hydrolysis and anaerobic soil metabolism studies included in this submission as completely fulfilling respective data requirements. The leaching data submitted when taken together with previously accepted data also completely fulfill requirements. The aerobic soil metabolism study is incomplete in that it was only conducted for six months. A one year study is required.

Acceptance of the following data which are currently under rewiew in EAB will be needed to further assess the potential for groundwater contamination by cyanazine: photodegradation studies in water and in soil, and monitoring studies in surface and groundwater. Additional field dissipation studies are also required.
Confined accumulation studies in rotational crops and if needed field accumulation studies have been identified as data gaps in the registration standard.

9. BACKGROUND:

Cyanazine has been previously reviewed by Dyanamc for the Registration Standard. See Task 2 March 17, 1983 and addendums of Aug. 6, 1985 and Aug. 16, 1985.

10. DISCUSSION OF INDIVIDUAL TESTS OR STUDIES:

See Dynamac Tasks I and 2 of February 18, 1987.

11. COMPLETION OF ONE-LINER:

Not done at this time.

12. CBI APPENDIX:

All data reviewed here are considered CBI by the registrant and must be treated as such.

DYNAMAC
CORPORATION

CYANAZINE ADDENDUM

Final Report

Task 1: Review and Evaluation of Individual Studies

Task 2: Environmental Fate and Exposure Assessment

Contract No. 68-02-4250

FEBRUARY 18, 1987

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
Dynamac Corporation
The Dynamac Building
11140 Rockville Pike
Rockville, MD 20852

CYANAZINE

Table of Contents

INTRODUCTION

Cyanazine is a pre- or postemergent herbicide registered for use on corn, cotton, grain sorghum, winter wheat, and fallow crop land. Approximately 22-24 million pounds of the active ingredient are applied annually in the United States. Of the domestic use, ~92, 4, and 2% is applied to corn, cotton, and grain sorghum, respectively. Application rates of the single active ingredient range from 0.6 to 5 lb ai/A. Cyanazine may be formulated with other pesticides and fertilizers. Single active ingredient formulations consist of 80% WP, 43% 4 lb/gal FlC, and 90% DF. These formulations may be applied to corn and fallow cropland by using ground or aerial equipment and to sorghum and cotton by using ground equipment only. One and one-half to 2 inches of moisture (rainfall or irrigation) are required within 10 days after cyanazine application to activate the herbicide. If no moisture occurs within the 10-day period, a shallow incorporation is recommended on labels. The specific type of equipment and method of incorporation is determined by site and equipment availability. Applicators need not be certified or under the direct supervision of applicators certified to apply cyanazine.

CASE GS -- CYANAZINE STUDY 1 PM --

CHEM 100101 Cyanazine

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Woodward, M.D., E.L. Holloway, and S.F. McEuen. 1986. The hydrolytic stability of ^{14}C-SD 15418 in buffered aqueous solution. RIR-22-004-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 263542.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

REVIEWED BY: P. Perreault
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ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: A. Schlosser
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-7709

SIGNATURE: DATE:

CONCLUSIONS:

Degradation - Hydrolysis

1. This study is scientifically valid.

2. Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at ~10 ppm, was stable for 30 days in the dark at 25°C in sterile aqueous solutions buffered at pH 7 and 9. At pH 5, [^{14}C]cyanazine degraded slowly with a half-life of >30 days (calculated ~148 days). One major degradate, N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223; 13.5% of the applied at day 30), and one minor degradate, tentatively identified as 2-([4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-amino)-2-methylpropanamide (DW 4512), were detected.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the hydrolysis of [^{14}C]cyanazine at 25°C in sterile solutions buffered at pH 5, 7, and 9.

MATERIALS AND METHODS:

Sterile aqueous solutions buffered at pH 5, 7, and 9 were treated with

triazine ring-labeled [^{14}C]cyanazine (SD 15418, radiochemical purity >99%, specific activity 20,400 dpm/µg, Shell Agricultural Chemical Co.) dissolved in acetone, at 10 ppm. The treated solutions were shaken, placed in sealed vials, and stored in the dark at 25°C. Samples were taken for analysis at days 0, 7, 14, 21, and 30 posttreatment. The pH of the test solutions was measured at each sampling interval.

Samples taken at days 0, 7, 14, and 21 were analyzed for total radioactivity using LSC and for [^{14}C]cyanazine and its degradates using HPLC and LSC. Each day 30 sample was divided into three parts. The first part was analyzed for total radioactivity using LSC. The second part was analyzed for [^{14}C]cyanazine and its degradates using HPLC and LSC. The third part was extracted three times with chloroform. The concentrated extracts were analyzed using TLC on silica gel plates developed in toluene:ethyl acetate (1:1) and heptane:dioxane (1:1). Radioactive areas were visualized by autoradiography, identified by comparison to standards, and quantified by LSC. In addition, day 30 pH 5 samples were further analyzed for degradates using gradient elution HPLC and LSC. Aliquots of these samples were then extracted three times with chloroform. The concentrated extracts were separated using TLC as described previously, except that the plates were developed in ethyl acetate:water:formic acid (7:1:1). The isolated degradate was methylated with diazomethane and purified on TLC plates developed in heptane:dioxane (1:1). The identity of the major degradate was further confirmed by GC/MS of the methylated material.

REPORTED RESULTS:

[^{14}C]Cyanazine was stable for 30 days in the dark at 25°C in sterile aqueous solutions buffered at pH 7 and 9 (Table 1). At pH 5, [^{14}C]cyanazine degraded slowly with a half-life of >30 days (calculated half-life ~148 days). One major degradate, SD 31223, and one minor degradate, tentatively identified as DW 4512, were detected.

The pH of the test solutions remained constant throughout the experiment.

DISCUSSION:

Method detection limits were not reported.

Table 1. Distribution of radioactivity (% of the applied) in aqueous buffers treated with [^{14}C]cyanazine at ~10 ppm and incubated in the dark at 25°C.

Sampling interval (days)	Cyanazine	SD 31223[a]	Unidentified compounds[b]
		pH 5	
0	99.5	<0.1	0.5
7	96.6	2.6	1.3
14	93.6	6.1	1.0
21	90.0	9.5	1.1
30	86.7	13.5	0.9
		pH 7	
0	99.4	ND[c]	0.6
7	98.3	ND	0.5
14	95.5	ND	0.5
21	98.5	ND	0.8
30	98.5	ND	0.5
		pH 7	
0	99.3	ND	0.7
7	97.8	ND	0.7
14	94.1	ND	0.9
21	97.7	ND	1.6
30	98.5	ND	1.6

a N-[4-(Ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine.

b Consisting primarily of 2-([4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-amino)-2-methylpropanamide (tentative).

c Not detected; detection limit not reported.

CASE GS — CYANAZINE STUDY 2 PM —

CHEM 100101 Cyanazine

BRANCH EAB DISC —

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under aerobic conditions. RIR-22-019-086. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265358.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

REVIEWED BY: P. Perreault
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TEL: 468-2500

APPROVED BY: A. Schlosser
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-7709

SIGNATURE: Arthur A. Schlosser DATE: March 19, 1987

CONCLUSIONS:

Metabolism - Aerobic Soil

1. This study is scientifically valid.

2. Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at 20 ppm, degraded with a half-life of 14-21 days in sandy loam soil maintained at 75% of field moisture capacity under aerobic conditions at 25±1°C in the dark. Four major degradates, identified as 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide (SD 20258), N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196), N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223), and N-(4-amino-6-chloro-1,3,5-triazin-2-yl)-2-methylalanine (SD 33104), comprised up to 77.6% of the applied (day 90 posttreatment).

3. This study partially fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of cyanazine in aerobic soil for a period of six months. The study must be extended to twelve months to fully elucidate the patterns of formation and decline of cyanazine degradation products.

MATERIALS AND METHODS:

Hanford sandy loam soil (66% sand, 21% silt, 13% clay, organic matter content 1.1%, pH 6.5, CEC 6.0 meq/100 g) was sieved (<2 mm), air-dried, and treated with triazine ring-labeled [^{14}C]cyanazine (SD 15418, radiochemical purity >99%, specific activity 2.25 μCi/mg, Shell Agricultural Chemical Co.), dissolved in acetone, at 20 ppm. The acetone was allowed to evaporate, and the treated soil was thoroughly mixed, placed in either glass bottles or flasks, and adjusted to 75% of field moisture capacity with deionized water. The bottles containing treated soil were placed in a dessicator, and humidified compressed air was continuously passed through the system. The bottles were incubated in the dark at 25°C for up to 180 days, and the soil was watered frequently to maintain its initial moisture content. In order to quantify volatilization, the flasks containing treated soil were sealed and connected to a continuous aeration system. Each flask was connected to two traps: one containing ethylene glycol to trap volatile degradates; and one containing ethanolamine to trap $^{14}CO_2$. The flasks were incubated in the dark at 25 ± 1°C for up to 180 days.

Aliquots of the trapping solutions were sampled at 0, 7, 14, 21, 30, 60, 90, 120, and 180 days posttreatment and were directly analyzed for total radioactivity using LSC. Soil samples were taken from the bottles at 0, 7, 14, 21, 30, 60, 90, 120, and 180 days posttreatment and were extracted two times with methanol:water (4:1). The extracts were combined, concentrated, and analyzed for [^{14}C]cyanazine and its degradates using HPLC and LSC. Soil samples were further extracted with water in a Soxhlet extractor for 40 to 66 hours. The aqueous extracts were centrifuged, concentrated, and analyzed by HPLC and LSC. Nonextractable radioactivity in the extracted soil was determined by combustion analysis. In order to characterize the nonextractable portion, the previously extracted 120-day soil samples were further extracted with several organic and aqueous solvents, including hexane, ethyl acetate, chloroform, acetone, methanol, acetonitrile, water, 0.1 N HCl, and 0.1 N ammonium hydroxide, and the extracts were partitioned into organic and aqueous phases. In addition, the ethyl acetate extractable portion, along with a reference standard of [^{14}C]SD 33104, were methylated with diazomethane and purified on TLC plates developed in heptane:dioxane (1:1). The identity of the degradate was confirmed by GC/MS.

Additional soil samples were taken for analysis at day 41 posttreatment and were extracted two times with methanol:water (4:1). The concentrated extracts were analyzed using HPLC. Radioactive components were separated using a C-18 column, and the ethyl acetate fractions were combined, concentrated, and then analyzed using TLC on silica gel plates developed in chloroform:ethanol (17:3) and heptane:dioxane:acetic acid (100:100:1). Radioactive areas were visualized by autoradiography and identified by comparison to cochromatographed standards. [^{14}C]Residues identified as parent compound or as the degradate SD 20258 were purified on TLC plates

developed in heptane:dioxane (1:1), and the identity of these components was confirmed by GC/MS. [^{14}C]Residues identified as the degradate SD 20196 and a reference standard of [^{14}C]SD 20196 were methylated with diazomethane and cochromatographed in the heptane:dioxane (1:1) solvent system. The identity of the degradate was confirmed by GC/MS. The eluates from the C-18 column were combined, concentrated, and freeze-dried, and the resulting residue was extracted with methanol. A portion of the methanol extracts and a reference standard of [^{14}C]SD 31223 were methylated with diazomethane, and both samples were purified on TLC plates developed in heptane:dioxane (1:1). The identity of the degradate was confirmed by GC/MS.

REPORTED RESULTS:

Triazine ring-labeled [^{14}C]cyanazine, at 20 ppm in sandy loam soil maintained in glass bottles under aerobic conditions at 25°C in the dark, degraded with a half-life of 14 to 21 days (Table 1). Four major degradates, identified as SD 20258 (amide), SD 20196 (chloro acid), SD 31223 (hydroxy acid), and SD 33104 (des-ethyl chloro acid), were detected. No volatiles and only trace amounts of $^{14}CO_2$ were detected in the trapping solutions of the sealed flasks containing treated soil.

DISCUSSION:

The study was only conducted for six months. A one year study is needed to fully describe the patterns of formation and decline of the degradation products of cyanazine.

Recovery values from fortified samples and method detection limits were not reported.

Table 1. Distribution of radioactivity (% of the applied) in sandy loam soil treated with [^{14}C]cyanazine at 20 ppm and incubated under aerobic conditions in the dark at 25°C.

Sampling interval (days)	Extractable radioactivity[a]								
	Cyanazine	SD 20258[b]	SD 20196[c]	SD 31223[d]	SD 33104[e]	Unidentified compounds[f]	Total extractable [^{14}C][g]	Non-extractable [^{14}C]	Total
0	99.6	ND[h]	ND	ND	ND	0.7	99.8	0.2	100.0
7	77.8	11.4	1.0	3.6	ND	0.8	94.6	3.5	98.1
14	57.5	21.2	3.1	6.7	ND	3.4	91.9	4.9	96.8
21	44.9	27.3	6.4	9.2	ND	3.7	91.5	7.8	99.3
30	29.4	31.3	12.2	12.0	ND	5.1	90.0	9.5	99.5
60	7.3	23.1	28.9	20.7	3.0	3.7	86.7	11.0	97.7
90	2.5	12.3	37.5	22.9	4.9	4.5	84.6	13.9	98.5
120	1.4	6.1	37.0	27.7	6.2	5.7	84.1	15.1	99.2
180	0.9	1.6	33.1	33.7	7.5	7.6	84.4	16.2	100.6

a Includes aqueous methanol and Soxhlet extracts.

b 2-([4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide.

c N-[4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine.

d N-[4-(Ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine.

e N-(4-Amino-6-chloro-1,3,5-triazin-2-yl)-2-methylalanine.

f Includes at least three minor degradates.

g By LSC of extract, not by summing measured concentrations of individual [^{14}C]residues.

h Not detected; detection limit not reported.

CASE GS -- CYANAZINE STUDY 3 PM --

CHEM 100101 Cyanazine

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under anaerobic conditions. RIR-22-008-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265359.

SUBST. CLASS = S.

DIRECT RVW TIME = 8 (MH) START-DATE END DATE

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TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-7709

SIGNATURE: DATE:

CONCLUSIONS:

Metabolism - Anaerobic Soil

1. This study is scientifically valid.

2. Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at 20 ppm, degraded with a half-life of >60 days (calculated half-life ~108 days) in anaerobic sandy loam soil incubated at 25°C in the dark. Three major degradates, identified as 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropanamide (SD 20258), N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196), and N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223), were detected.

3. This study fulfills EPA Data Requirements for Registering Pesticides by providing information on the metabolism of cyanazine in anaerobic soil.

MATERIALS AND METHODS:

Hanford sandy loam soil (66% sand, 21% silt, 13% clay, organic matter content 1.1%, pH 6.5, CEC 6.0 meq/100 g) was sieved (<2 mm), air-dried,

and treated with triazine ring-labeled [^{14}C]cyanazine (SD 15418, radiochemical purity >99%, specific activity 2.25 µCi/mg, Shell Agricultural Chemical Co.) dissolved in acetone, at 20 ppm. The acetone was allowed to evaporate, and the treated soil was thoroughly mixed, placed in either glass bottles or flasks, and adjusted to 75% of field moisture capacity with deionized water. The bottles and flasks were incubated in the dark at 25°C as described in the aerobic soil metabolism study (Study 2). Aliquots of the trapping solutions were sampled at 0, 17, 48, and 77 days posttreatment and were directly analyzed for total radioactivity using LSC. Soil samples were taken from the bottles at 0, 17, 40, and 77 days posttreatment and were analyzed as described in Study 2.

After 17 days of aerobic incubation, half of the original bottles and half of the original flasks were converted to anaerobic conditions by flooding the soil with deionized water and continuous purging of the soil metabolism chambers with humidified nitrogen.

The trapping solutions and the anaerobic soil from the bottles were sampled at 48 and 77 days posttreatment (31 and 60 days after anaerobic conditions were established), and were analyzed as described in Study 2. The aqueous fraction from the flooded bottles was separated from the soil by filtration and directly analyzed by HPLC and LSC. In addition, day-77 anaerobic soil samples were partitioned with ethyl acetate at pH 7 and 3. The two degradates partitioned into the organic phase at pH 7 along with radiolabeled standards of SD 15418 and SD 20258 were purified on TLC plates as described previously, and the identity of the degradates was confirmed by GC/MS. The degradates partitioned into the organic phase at pH 3 and into the aqueous phase were methylated with diazomethane as were radiolabeled standards of SD 20196 and SD 31223. Purification was done by TLC as described previously, and the identity of the degradates was confirmed by GC/MS. The detection limit was 0.2% of the applied.

REPORTED RESULTS:

Triazine ring-labeled [^{14}C]cyanazine degraded with a half-life of 17-48 days under aerobic conditions (Table 1). Three major degradates, identified as SD 20258 (amide), SD 20196 (chloro acid), and SD 31223 (hydroxy acid), were detected. No volatiles and only trace amounts of $^{14}CO_2$ were detected in the trapping solutions of the aerobic flasks containing treated soil.

Triazine ring-labeled [^{14}C]cyanazine degraded with a half-life of >60 days (calculated half-life ~108 days) under anaerobic conditions (Table 1). The three major degradates identified in the aerobic soil were detected. No volatiles and only trace amounts of $^{14}CO_2$ were detected in the trapping solutions of the anaerobic flasks containing treated soil.

DISCUSSION:

This study fulfills data requirements by providing information on the metabolism of cyanazine in anaerobic soil.

Table 1. Distribution of radioactivity (% of the applied) in sandy loam soil treated with [^{14}C]cyanazine at 20 ppm and incubated in the dark at 25°C.

Sampling interval (days)	Extractable radioactivity[a]							
	Cyanazine	SD 20258[b]	SD 20196[c]	SD-31223[d]	Unidentified compounds[e]	Total extractable radioactivity[b]	Non-extractable radioactivity	Total
				Aerobic				
0	99.1	ND[f]	ND	ND	0.7	99.8	0.2	100.0
17	53.4	26.1	4.8	7.8	2.9	95.0	6.9	101.9
48	11.1	28.0	24.3	16.1	5.5	85.0	9.7	94.7
77	3.6	16.3	37.6	19.7	8.7	85.9	12.2	98.1
				Anaerobic[g]				
48	37.5	26.5	8.0	10.5	2.7	85.2	8.8	94.0
77	36.4	23.0	7.9	14.6	3.6	85.5	12.7	98.2

[a] Includes aqueous methanol and Soxhlet extracts.

[b] 2-([4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide.

[c] N-[4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine.

[d] N-[4-(Ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine.

[e] Includes at least four minor degradates.

[f] Not detected; detection limit <0.2% of the applied.

[g] After 17 days of aerobic incubation, several bottles of soil were made anaerobic by flooding the bottles with water and purging them with nitrogen. Day 48 corresponds to 31 days of anaerobic incubation, and day 77 corresponds to 60 days of anaerobic incubation.

CASE GS -- CYANAZINE STUDY 4 PM --

CHEM 100101 Cyanazine

BRANCH EAB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

McEuen, S.F. and M.D. Woodward. 1986. Mobility of SD 15418 and degradation products in soil measured by soil thin-layer chromatography. RIR-22-007-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265358.

SUBST. CLASS = S.

DIRECT RVW TIME = 4 (MH) START-DATE END DATE

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APPROVED BY: A. Schlosser
TITLE: Chemist
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TEL: 557-7709

SIGNATURE: DATE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.

2. Based on soil TLC tests, [^{14}C]cyanazine was mobile in sandy loam, silty clay loam, and loam (R_f 0.49-0.55) soils, and very mobile in silt loam soil (R_f 0.75). The aged (17 days) [^{14}C]cyanazine residues and the degradates 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide (SD 20258) and N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196) were very mobile in all four soils (R_f 0.65-1.00). The degradate N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223) was mobile in sandy loam soil (R_f = 0.47), and very mobile in silty clay loam, silt loam, and loam (R_f 0.65-0.76) soils.

3. This study contributes toward the fulfillment of EPA Data Requirements for Registering Pesticides by providing information on the the mobility (soil TLC) of aged cyanazine residues in four soils.

MATERIALS AND METHODS:

Hanford sandy loam soil (Table 1) was treated with triazine ring-labeled [^{14}C]cyanazine (SD 15418, radiochemical purity ~99%, specific activity 48.4 µCi/mg, Shell Agricultural Chemical Co.), and the treated soil was incubated under aerobic conditions at 75% of field moisture capacity in the dark at 25°C for 17 days. A portion of the aged soil was extracted with aqueous methanol, and the extract was analyzed by HPLC, freeze-dried, and resolubilized with methanol. Additional soil samples were extracted with methanol, and [^{14}C]cyanazine and its degradates were isolated using HPLC for use in soil TLC tests.

Four soils, ranging in texture from sandy loam to silty clay loam (Table 1), were sieved (<500 µm), mixed with distilled water to form a slurry, spread onto TLC plates (750-µm thickness), and air-dried. Two plates were prepared for each soil type. One plate was spotted with the soil extract obtained after 17 days of aerobic incubation, the [^{14}C]-cyanazine isolated from the aged soil, and radiolabeled standards of DDT, diuron, atrazine, and 2,4-D. The other plate was spotted with the [^{14}C]-degradates isolated from the aged soil, including SD 20258, SD 20196, and SD 31223, along with radiolabeled standards of diuron, atrazine, and 2,4-D. The plates were developed in water to a distance of 10 cm. After development, the plates were air-dried and visualized using autoradiography.

REPORTED RESULTS:

Following the 17 days of incubation, the extractable [^{14}C]residues in the soil consisted of cyanazine (53.4% of the applied), SD 20258 (26.1%), SD 20196 (4.8%), SD 31223 (7.8%), and unidentified compounds (2.9%). [^{14}C]Cyanazine from the aged soil was mobile in sandy loam (R_f = 0.50), silty clay loam (R_f = 0.49), and loam (R_f = 0.55) soils, and very mobile in silt loam soil (R_f = 0.75). The aged soil extract and the degradates SD 20258 and SD 20196 were very mobile in all four soils (R_f values ranged between 0.65 and 1.00). The degradate SD 31223 was mobile in sandy loam soil (R_f = 0.47), and very mobile in silty clay loam (R_f = 0.76), silt loam (R_f = 0.65), and loam (R_f = 0.70) soils.

DISCUSSION:

1. The rate of application of [^{14}C]cyanazine to the soil prior to the aging period was not specified.

2. The purities of the reference pesticides were not specified.

Table 1. Soil characteristics.

Soil type	Sand	Silt	Clay	Organic matter	pH	CEC (meq/100 g)
	%					
Hanford sandy loam	64	24	12	1.1	6.7	6.3
Catlin silty clay loam	16	56	28	4.2	5.8	15.2
Walla Walla silt loam	28	56	16	2.1	6.0	11.4
Webster loam	52	30	18	4.2	7.0	14.0

EXECUTIVE SUMMARY

The data summarized here are scientifically valid data that have been reviewed in this report and fulfill or contribute toward the fulfillment of data requirements.

Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at ~10 ppm, was stable for 30 days in the dark at 25°C in sterile aqueous solutions buffered at pH 7 and 9. At pH 5, [^{14}C]cyanazine degraded slowly with a half-life of >30 days (calculated ~148 days). One major degradate, N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223; 13.5% of the applied at day 30), and one minor degradate, tentatively identified as 2-([4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]amino)-2-methylpropanamide (DW 4512), were detected.

Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at 20 ppm, degraded with a half-life of 14-21 days in sandy loam soil maintained at 75% of field moisture capacity under aerobic conditions at 25 ±1°C in the dark. Four major degradates, identified as 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methylpropamide (SD 20258), N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196), N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223), and N-(4-amino-6-chloro-1,3,5-triazin-2-yl)-2-methylalanine (SD 33104), comprised up to 77.6% of the applied (day 90 posttreatment).

Triazine ring-labeled [^{14}C]cyanazine (radiochemical purity >99%), at 20 ppm, ppm, degraded with a half-life of >60 days (calculated half-life ~108 days) in anaerobic sandy loam soil incubated at 25°C in the dark. Three major degradates, identified as 2-([4-chloro-6-(ethylamino-)1,3,5-triazin-2-yl]amino)-2-methylpropanamide (SD 20258), N-[4-chlo-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196), and N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223), were detected.

Based on soil TLC tests, [^{14}C]cyanazine was mobile in sandy loam, silty clay loam, and loam (R_f 0.49-0.55) soils, and very mobile in silt loam soil (R_f 0.75). The aged (17 days) [^{14}C]cyanazine residues and the degradates 2-([4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino)-2-methyl-propamide (SD 20258) and N-[4-chloro-6-(ethylamino)-1,3,5-triazin-2-yl]-2-methylalanine (SD 20196) were very mobile in all four soils (R_f 0.65-1.00). The degradate N-[4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl]-2-methylalanine (SD 31223) was mobile in sandy loam soil (R_f = 0.47), and very mobile in silty clay loam, silt loam, and loam (R_f 0.65-0.76) soils.

RECOMMENDATIONS

Available data are insufficient to fully assess the environmental fate and transport of, and the potential exposure of humans and nontarget organisms to cyanazine. The submission of data relevant to registration requirements (Subdivision N) for terrestrial food crop, terrestrial nonfood, aquatic nonfood crop, domestic outdoor and indoor use sites is summarized below:

Hydrolysis studies: One study (Woodward, 1986; No MRID) was reviewed and is scientifically valid. This study fulfills data requirements by providing information on the hydrolysis of cyanazine at pH 5, 7, and 9.

Photodegradation studies in water: No data were reviewed for this addendum, but all data are required.

Photodegradation studies on soil: No data were reviewed for this addendum, but all data are required.

Photodegradation studies in air: No data were reviewed for this addendum; however, no data are required because cyanazine has a low vapor pressure.

Aerobic soil metabolism studies: One study (Woodward, 1986; No MRID) was reviewed and is scientifically valid. This study partially fulfills data requirements by providing information on the metabolism of cyanazine in aerobic soil for a six month period. Additional data on aerobic metabolism for a period up to one year are required.

Anaerobic soil metabolism studies: One study (Woodward, 1986; No MRID) was reviewed and is scientifically valid. This study fulfills data requirements by providing information on the metabolism of cyanazine in anaerobic soil.

Anaerobic aquatic metabolism studies: No data were reviewed for this addendum; however, no data are required because there are currently no registered aquatic or aquatic impact uses for cyanazine.

Aerobic aquatic metabolism studies: No data were reviewed for this addendum; however, no data are required because there are currently no registered aquatic or aquatic impact uses for cyanazine.

Leaching and adsorption/desorption studies: One study (McEuen, 1986; No MRID) was reviewed and is scientifically valid. Based on data submitted for the Cyanazine Standard dated March 17, 1983 and this addendum, all data requirements have been met.

Laboratory volatility studies: No data were reviewed for this addendum; however, no data are required because cyanazine has a low vapor pressure.

Field volatility studies: No data were reviewed for this addendum; however, no data are required because cyanazine has a low vapor pressure.

Terrestrial field dissipation studies: No data were reviewed for this addendum; however, additional data are currently being developed by the registrant.

Aquatic field dissipation studies: No data were reviewed for this addendum; however, no data are required because there are currently no registered aquatic or aquatic impact uses for cyanazine.

Forestry dissipation studies: No data were reviewed for this addendum; however, no data are required because cyanazine currently has no registered forestry uses.

Dissipation studies for combination products and tank mix uses: No data were reviewed for this addendum; however, no data are required because data requirements for combination products and tank mix uses are currently not being imposed.

Long-term field dissipation studies: No data were reviewed for this addendum; however, no data are required because >50% of the application dissipates before another recommended application is applied.

Confined accumulation studies on rotational crops: No data were reviewed for this addendum. A study is needed to determine residues in a representative small grain crop planted 30 days after cyanazine treatment and in representative root and leafy vegetable crops planted 30, 120, and 365 days after cyanazine treatment.

Field accumulation studies on rotational crops: No data were reviewed for this addendum. Based on data submitted for the Cyanazine Standard dated March 17, 1983, data requirements have been partially fulfilled by showing that cyanazine does not accumulate in several rotated crops planted 1 year after cyanazine treatment and that cyanazine does not accumulated in small grain (wheat) planted into clay loam, silty clay loam, and loam soils, 4-5.5 months after cyanazine treatment. Data are required if significant ^{14}C residues of concern are found in the required confined accumulation study.

Accumulation studies on irrigated crops: No data were reviewed for this addendum; however, no data are required because cyanazine has no aquatic food crop or aquatic noncrop uses, is not used in and around holding ponds used for irrigation purposes, and has no uses involving effluents or discharges to water used for crop irrigation.

Laboratory studies of pesticide accumulation in fish: No data were reviewed for this addendum. Based on data submitted for the Cyanazine Standard dated March 17, 1983, no further data are required.

Field accumulation studies on aquatic nontarget organisms: No data were reviewed for this addendum; however, no data are required because cyanazine does not have a forestry, an aquatic noncrop, or an aquatic impact use.

Reentry studies: No data were reviewed for this addendum; however, no data are required because criterion in 40 CFR-158.140 were not met and exposure is expected to be minimal because of use pattern.

Exposure studies: Due to the finding of cyanazine in both surface and groundwater, a monitoring study of surface and ground water is required.

REFERENCES

Woodward, M.D., E.L. Holloway, and S.F. McEuen. 1986. The hydrolytic stability of ^{14}C-SD 15418 in buffered aqueous solution. RIR-22-004-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 263542. Reference 1.

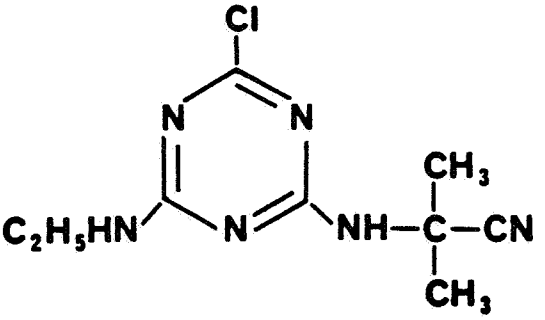
Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under aerobic conditions. RIR-22-019-086. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265358. Reference 2.

Woodward, M.D., S.F. McEuen, and E.L. Holloway. 1986. Degradation of SD 15418 in soil under anaerobic conditions. RIR-22-008-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265359. Reference 3.

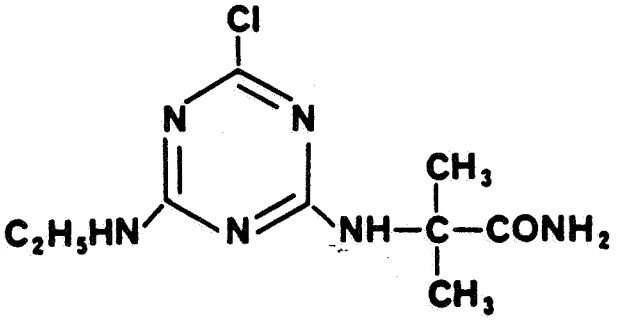
McEuen, S.F. and M.D. Woodward. 1986. Mobility of SD 15418 and degradation products in soil measured by soil thin-layer chromatography. RIR-22-007-86. Submitted by Shell Agricultural Chemical Co., Modesto, CA. Acc. No. 265360. Reference 4.

APPENDIX

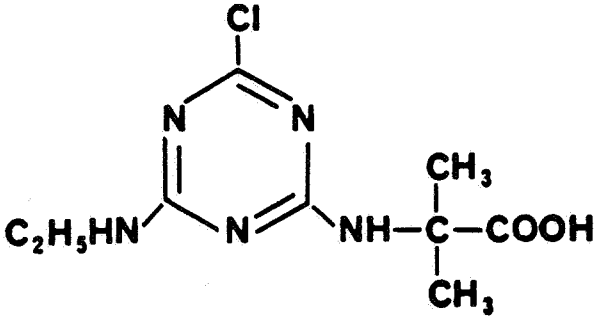
CYANAZINE AND ITS DEGRADATES



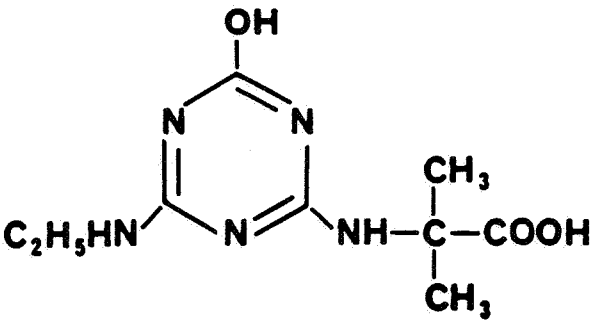
2-[[4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl]amino]-2-methylpropanenitrile
(Cyanazine, SD 15418)



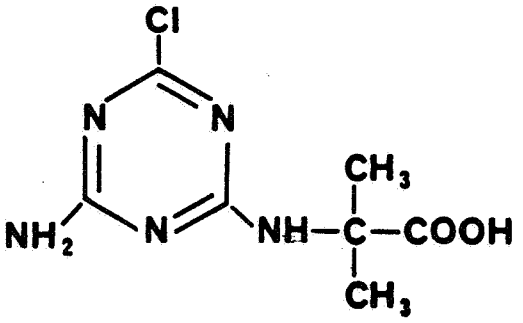
2-((4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl)amino)-2-methylpropanamide
(SD 20258)



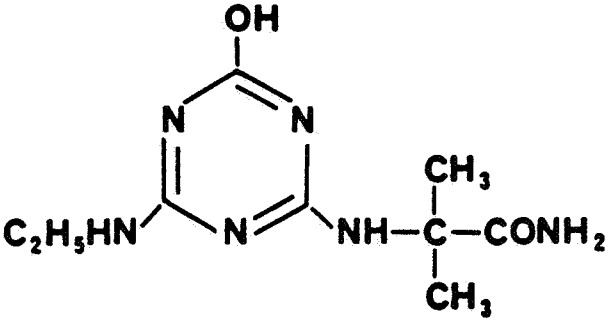
N-(4-Chloro-6-(ethylamino)-1,3,5-triazin-2-yl)-2-methylalanine
(SD 20196)



N-(4-(ethylamino)-6-hydroxy-1,3,5-triazin-2-yl)-2-methylalanine
(SD 31223)



N-(4-amino-6-chloro-1,3,5-triazin-2-yl)-2-methylalanine
(SD 33104)



2-((4-(Ethylamino)-6-hydroxy-1,3,5-triazin-2-yl)amino)-2-methylpropanamide
(DW 4512)