

US EPA ARCHIVE DOCUMENT

Shaughnessy No: 080807

JUL 19 1990

Date Out of EFGWB: _____

TO: Lois Rossi/Jane Talarico
Product Manager #74
Reregistration Branch
Special Review and Reregistration Division (H7508C)

FROM: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #2
Environmental Fate and Ground Water Branch, EFED (H7507C)

THRU: Henry M. Jacoby, Chief
Environmental Fate and Ground Water Branch, EFED (H7507C)

Attached, please find the EFGWB review of:

Reg./File #: 100-541

Common Name: SIMAZINE

Chemical Name: 2-Chloro-4,6-bis(ethylamino)-s-triazine
6-Chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine

Type product: Herbicide

Product Name: Princep; Aquazine

Company Name: Ciba-Geigy Corporation

Purpose: Review of new batch-equilibrium adsorption/desorption studies
submitted to replace previously reviewed studies, which were
invalidated as a result of a laboratory audit conducted by OCM

Date Received: 4/4/90 EFGWB #: 90-0516

Action Code: 660 Total Reviewing Time (decimal days): 2.5

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

1. CHEMICAL:

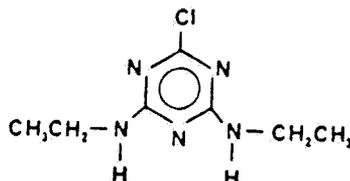
Common name: Simazine

Chemical name: 2-Chloro-4,6-bis(ethylamino)-s-triazine

6-Chloro-N,N'-diethyl-1,3,5-triazine-2,4-diamine

Chemical Abstracts Registry Number: 122-34-9

Structure:



Physical/Chemical properties of active ingredient:

Physical state: powder

Color: white

Vapor pressure: 6.1×10^{-9} Torr

Solubility: 3.5 ppm (at 20 C)

Formulations (Single active ingredient):

Granular (0.63-0.75 and 4-90%)

Pelleted/Tableted (2.5 to 90%)

Wettable Powder (3, 80 and 90%)

Dry Flowable (90%)

Emulsifiable Concentrate (4 lb/gal and 1%)

Flowable Concentrate (4 lb/gal and 0.6%)

Soluble Concentrate/Liquid (4 lb/gal, 0.1 to 80%)

2. STUDY/ACTION TYPE: Review of batch-equilibrium adsorption/desorption studies submitted to replace previously reviewed studies, which were invalidated as a result of a laboratory audit.

3. STUDY IDENTIFICATION:

MRID #41442903

- Spare, W.C. 1989a. Adsorption/desorption of ^{14}C -simazine. Performed by Agrisearch Inc., Frederick, MD; Agrisearch Project No. 12168; Completed on November 28, 1989. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

MRID #41257903

- Spare, W.C. 1989b. Adsorption/desorption of ^{14}C -G-30414. Performed by Agrisearch, Inc., Frederick, MD; Agrisearch ProjectNo. 121172; Completed on July 28, 1989. Submitted by Ciba-Geigy Corporation.

4. REVIEWED BY:

Silvia C. Termes, Chemist
Review Section #2
OPP/EFED/EFGB

Signature: _____

Date: _____

5. APPROVED BY:

Emil Regelman
Supervisory Chemist
Review Section #2
OPP/EFED/EFGB

Signature: _____

Date: _____

6. CONCLUSIONS:

The two studies reviewed (with parent and with the "hydroxysimazine" degradate) are basically acceptable. These two studies, together with the studies conducted with the dealkylated degradates G-28279 and G-28273 (EFGWB review dated 3/6/90), may be used to fulfill data requirements for mobility in soil studies (163-1). All of these studies provide basically acceptable information on the adsorption/desorption behavior of parent simazine, the "hydroxysimazine" (G-30414) and the dealkylated degradates G-28273 and G-28279. The latter two degradates are also degradates of atrazine.

However, EFGWB is requesting the following additional information:

A. Soils used in the studies

- a. For each soil provide a soil classification to the series level, with the name expressed according to the USDA Soil Classification.
- b. For the clay soil (42% clay), indicate which types of clay are present in the soil. This also applies to the sandy loam soil (16.8% clay).

The purpose of requesting the additional information on soils is to identify geographical regions where these soils prevail and relate these regions with those where simazine is used (or has been used). This information was also requested for the studies conducted with atrazine, hydroxyatrazine, and the dealkylated degradates G-28273 and G-28279 (EFGWB review 3/6/90).

B. Actual TLC data on samples analyzed after completion of adsorption and desorption phases

The registrant is being requested to provide information showing TLC data in order to determine if the degree of degradation was soil-dependent. If available, data on other degradates that may have been detected should also be provided.

SUMMARY OF RESULTS:

Table I summarizes the results of the studies reviewed here and those of G-28273 and G-28279 reviewed on 3/6/90. The results show that the dealkylated degradates G-28273 and G-28279 adsorb weaker than parent simazine or the "hydroxysimazine" degradate (G-30414). The latter degradate adsorbs stronger than parent simazine in all of the soils. The structures of simazine and its degradates are shown in Figure 1.

Simazine and its dealkylated degradates G-28273 and G-28279 are very mobile in the sand, sandy loam and loam soils as shown by their low (<2) adsorption coefficients (K_{ads}) and the low adsorption K_{oc} values (<500). In the clay soil, the K_{ads} are slightly higher but still below 5. "Hydroxysimazine" (G-30414) adsorbs the strongest, particularly on the the clay soil (K_{ads} ca. 500). Of all the degradates of simazine, "Hydroxysimazine" will be the least mobile.

From Table I it can also be seen that adsorption of parent simazine, the dealkylated degradates, and "Hydroxysimazine" was the strongest in the clay soil. This soil not only had the highest percentage of organic matter content but also the highest clay content. The non-unity value of the slopes of the Freundlich isotherms indicate that adsorption is not solely dependent on the organic matter content.

7. RECOMMENDATIONS:

The registrant should be informed that the batch-equilibrium adsorption/desorption studies conducted with ^{14}C -labeled parent simazine and its degradate "Hydroxysimazine" (G-30414) are basically acceptable. Together with the acceptable studies (EFGWB review of 3/6/90) conducted with the dealkylated degradates G-28273 and G-28279 (MRID #41257904 and 41257905, respectively), these four studies may be used to fulfill data requirements for Mobility in Soil studies (163-1).

The registrant should also be informed that additional information is being requested, as expressed in the CONCLUSIONS section. Copies of the DATA EVALUATION RECORDS of the two studies should be made available to the registrant.

8. BACKGROUND:

a. Introduction

As a result of a laboratory audit conducted by the Office of Compliance Monitoring on 2/14/89, the previously reviewed studies (EFGWB Second Round Review, 7/11/89) were invalidated. The registrant agreed to submit new studies. The new studies were submitted. The studies

conducted with the degradates G-28273 and G-28279 were reviewed on 3/6/90. Those conducted with parent simazine and "Hydroxysimazine" (G-30414) are reviewed here.

b. Directions for use

Simazine is a pesticide registered for uses on terrestrial food crops, terrestrial nonfood crops, noncrop sites, and aquatic nonfood sites. Simazine may be applied preemergence, preplant incorporated, at planting, or post emergence. Its mode of action is inhibition of the Hill reaction of photosynthesis. Application rates vary with use pattern:

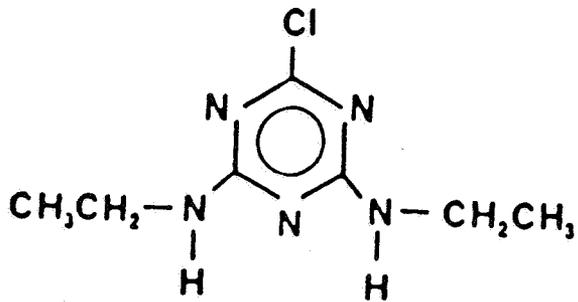
1. Terrestrial food crops (0.8 to 10 lb ai/A)
2. Terrestrial nonfood crops (0.8 to 4.0 lb ai/A)
3. Noncrop sites (4.0 to 40 lb ai/A)
4. Aquatic, water treatment sites (0.8 to 12 lb ai/A)
5. Ponds (1.35 to 6.75 lb ai/A)
6. Swimming pools (0.03 to 0.21 lb ai/ 10,000 gal water)

9. DISCUSSION OF INDIVIDUAL STUDIES: Please refer to the enclosed Data Evaluation Records.

10. COMPLETION OF ONE-LINER: The information obtained from these studies has been used to update the one-liner.

11. CBI APPENDIX: No CBI.

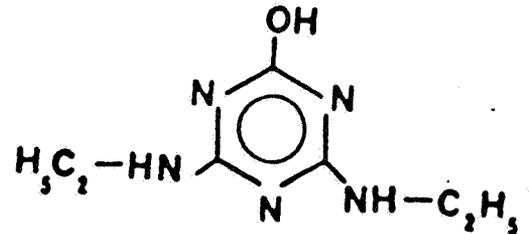
FIGURE 1
SIMAZINE AND ITS MAJOR DEGRADATES/METABOLITES



2-Chloro-4,6-bis(ethylamino)-
s-triazine

Simazine

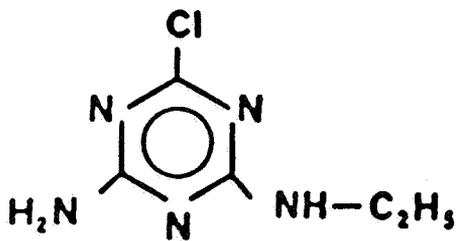
Hydroxylated analog ("hydroxy simazine"):



2-Hydroxy-4,6-
bis(ethylamino)-s-triazine

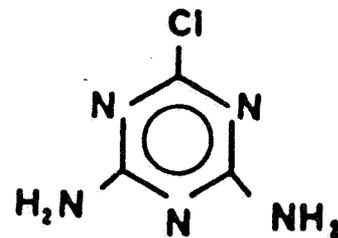
(G-30414)

Dealkylated degradates:



2-Amino-4-chloro-6-
ethylamino-s-triazine

(G-28279)



2,4-Diamino-6-
chloro-s-triazine

(G-28273)

These two degradates are also major degradates of atrazine.

DATA EVALUATION RECORDS

	Page
1. Batch-equilibrium adsorption/desorption study with SIMAZINE	1.1
2. Batch-equilibrium adsorption/desorption study with G-30414	2.1

Batch-equilibrium adsorption/desorption studies with the
dealkylated degradates G-28273 and G-28279 appear in the
ATRAZINE review dated 3/6/90

DATA EVALUATION RECORD

STUDY #1

Shaughnessy No. 080807

Data Requirement 163-1

Chemical: Simazine

2-Chloro-4,6-bis(ethylamino)-s-triazine

Type of chemical: Symmetrical triazine ring herbicide

MRID #41442903

Spare, W.C. 1989. Adsorption/desorption of ¹⁴C-simazine. Performed by Agrisearch Inc., Frederick, MD; Agrisearch Project No. 12168; Completed on November 28, 1989. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

Reviewed by: S.C. Termes, Chemist
OPP/EFED/EFGBW
(703) 557-2243

Date:

July 15, 1990

CONCLUSIONS:

This study is basically acceptable. However, the registrant is requested to provide further information on the soils used in the study. The registrant is also requested to comment and provide information on the actual concentrations of parent simazine in solution after completion of the adsorption and desorption phases. Please refer to REVIEWER'S COMMENTS for further details.

SUMMARY OF DATA

The batch-equilibrium adsorption/desorption studies conducted with four different soils and five different concentrations of simazine indicate that simazine is not strongly adsorbed onto soil. Freundlich adsorption coefficients ranged from 0.48 for the California loam soil to 4.31 for the Maryland clay. The Freundlich desorption coefficients ranged from 0.78 for the California loam to 9.34 for the Maryland clay.

There is, in general, some correlation between K_d values and organic matter content. However, the slope of the Freundlich isotherms were not unity, indicating that the adsorption process was not solely a mere distribution of the organic matter of the soil and the aqueous phase.

The values of the Freundlich adsorption coefficient were below 5 in all of the soils studied, which indicate that simazine is expected to be mobile in those soils.

MATERIALS AND METHODS:

Test Material: Triazine-¹⁴C-labeled simazine, specific activity 9.0 uCi/mg, and radioactive purity 91.7%

Soils: Four soils were used (clay, sand, sandy loam, and loam). The soils were air dried and sieved through a 2-mm mesh sieve prior to use. Soil characteristics are shown in Table I.

Test solutions:

a) Preliminary study- A stock solution containing 5.04 mg/mL simazine was prepared in a mixture containing methanol/acetone/acetonitrile in a 4.4:3.4:1 (v:v:v). A 0.199 mL aliquot was diluted to 200 mL with 0.01 N calcium ion solution (sterilized, deionized, distilled and boiled water). The nominal concentration of simazine was 5 ug/mL.

b) Final study- A solution of simazine at a nominal concentration of 5 ug/mL was prepared from the stock solution by mixing 0.323 mL volume to a final volume of 325 mL (dilutant: 0.01 N calcium ion solution [as the acetate salt] prepared with sterilized, deionized, distilled and boiled water). From this second stock solution, further solutions were prepared by dilution. The nominal concentrations of these solutions (in addition to the one at 5 ug/mL) were 2.5 ug/mL, 1.2 ug/mL, 0.6 ug/mL, and 0.3 ug/mL. A solution containing no simazine (only calcium ion) was used as control.

Test apparatus: The test system consisted of centrifuge tubes (50 mL) containing soil and simazine solution. Each soil and solution concentration (5-mL solution per 1 g soil) were done in duplicate.

Soil-to-solution ratio and equilibration time were determined in a preliminary experiment. The preliminary experiment was also used to determine if adsorption to glassware and/or caps occurred. A 24-hour equilibration time and a 5-mL solution:1-g soil ratio were established from the preliminary experiment (Tables II-IV).

Adsorption phase: Each complete sample set was shaken for 24-hr in a shaker (200 rpm) for 24-hr at 24 C. After 24-hr, the samples were centrifuged and the equilibrium concentration in solution determined (by ISC). The concentration in soils was determined by difference, except in the CA loam soil, where it was determined by combustion.

Desorption phase: After adsorption, the desorption from soil phase was performed by adding 20 mL of the calcium solution to each of the samples (samples were preweighed to correct for remaining adsorption solution). The samples were then shaken for

24-hr (175-200 rpm), after which the supernatant were analyzed by ISC to determine equilibrium concentration. Soil concentration was determined by difference (except for the CA soil, where it was determined by combustion).

Calculations: The Freundlich equation was used to evaluate batch equilibrium data. The equation can be expressed as

$$x/m = K_d C_e^{1/n} \quad \text{OR} \quad \ln x/m = \ln K_d + 1/n \ln C_e$$

x/m is the soil equilibrium concentration (ug/g)
 C_e is the aqueous phase equilibrium concentration in ug/mL
 K_d is the Freundlich sorption constant and n is a constant

Plots of $\ln C_e$ vs $\ln(x/m)$ were used to determine K_d (from the intercept) and $1/n$ (from the slope).

To express K_d in terms of soil organic carbon content, the following expression was used

$$K_{oc} = (K_d \times 100) / \% \text{ O.C.}, \text{ where } \% \text{ O.C. (organic carbon)} \\ \text{was obtained by dividing the} \\ \% \text{ organic matter by 1.7}$$

Data reduction was performed by mathematical methods of linear regression, means, sums, and logarithm calculations.

REPORTED RESULTS

Equilibrium concentrations (in soil and in aqueous phase) were expressed in terms of total radioactivity as determined by ISC. The mean measured concentration in the solution (C_e) and in soil (x/m) in the adsorption phase of the study are presented in Tables V and VI, respectively. For the desorption phase, this information is presented in Tables VII and VIII. After completion of adsorption and desorption phases, TLC was used to analyze solutions of the highest concentrations, which showed that the concentration of parent simazine ranged from 81 to 100% in all solutions.

The Freundlich adsorption/desorption isotherms are shown in Figures 2-5. Data from linear regression analysis are presented in Tables IX and X for the adsorption and desorption phases, respectively.

The K_d constants for the adsorption phase were below 5 for all soils. Adsorption was strongest in the clay soil (K_{ads} 4.31) and weakest in the California loam soil (K_{ads} 0.48). Desorption constants varied from 0.78 for the loam soil to 9.34 for the clay soil. The sorption constants correlated, in general, with organic matter content. However the slopes of the lines (isotherms) were not unity, indicating that the adsorption process was not solely a mere distribution between organic matter of the soil and the aqueous phase.

REVIEWER'S COMMENTS:

1. It is mentioned that following completion of the adsorption and desorption phases conducted at the highest concentration of simazine, the solutions were analyzed (by TLC) showing parent simazine at 81-100% in all solutions. However, no actual data/results were presented for each soil that may indicate in which soils degradation was more extensive.

Actual parent simazine concentration should have been used in the calculations rather than total radioactivity. This becomes more important for those soils where degradation is more extensive.

The registrant is being requested to provide information showing TLC data in order to determine if the degree of degradation is soil-dependent. If available, data on other degradates present should also be provided.

2. The registrant is also being requested to provide soil classification to the series level, with the name expressed according to the USDA Soil Classification.

For the clay soil (42% clay), indicate which types of clay are present in the soil. this also applies to the sandy loam soil (16.8% clay).

The purpose of requesting additional information on the soils is to identify geographical regions where these soils prevail and relate these regions with those where simazine is used (or has been used).

Simazine

RIN: 1646-93

Page ___ is not included in this copy.

Pages 13 through 26 are not included.

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 quality control procedures.
- Identity of the source of product ingredients.
- Sales or other commercial/financial information.
- A draft product label.
- The product confidential statement of formula.
- Information about a pending registration action.
- FIFRA registration data.
- The document is a duplicate of page(s) _____.
- The document is not responsive to the request.

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
STUDY #2

Shaughnessy No.: None (this is a degradate of simazine, Sh.# 080807)

Chemical: "Hydroxysimazine"
2-Hydroxy-4,6-bis(ethylamino)-s-triazine

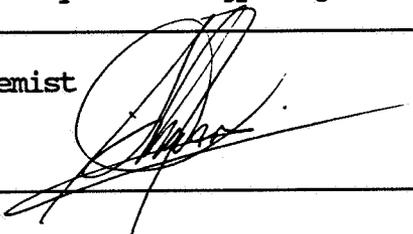
Data Requirement: 163-1

Type of chemical: Symmetrical triazine ring degradate of the herbicide simazine

MRID #41257903

Spare, W.C. 1989. Adsorption/desorption of ¹⁴C-G-30414. Performed by Agrisearch, Inc., Frederick, MD; Agrisearch Project No.12172; Completed on July 28, 1989. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

Reviewed by: S.C. Termes, Chemist
OPP/EFED/EFGWB
(703) 557-2243

Date:  *July 15, 1990*

CONCLUSIONS:

This study is basically acceptable. However, the registrant is requested to provide further information on the soils used in the study. The registrant is also requested to comment and provide information on the actual concentrations of G-30414 in solution/soil after completion of the adsorption and desorption phases. Please refer to REVIEWER'S COMMENTS for further details.

SUMMARY OF DATA

The batch-equilibrium adsorption/desorption studies conducted with four different soils and five different concentrations of the degradate G-30414 ("Hydroxysimazine") indicate that this degradate adsorbs stronger than parent simazine or the dealkylated degradates G-28273 and G-28279.

Freundlich adsorption coefficients for G-30414 ranged from 8.5 in the Maryland sand to 483 in the Maryland clay. The Freundlich desorption coefficients ranged from 25.5 in the Maryland sand to 423 in the Maryland clay. There is, in general, some correlation between K_d values and organic matter content. However the slope of the Freundlich isotherms were not unity, indicating that the adsorption process was not solely a mere distribution of the organic matter of the soil and the aqueous phase.

The values of the Freundlich adsorption coefficients (8.5 and above) indicate that G-30414 is less mobile than parent simazine or the dealkylated degradates and, thus, has the least potential to leach.

MATERIALS AND METHODS:

Test Material: Triazine-¹⁴C-labeled G-30414 (Hydroxysimazine), specific activity 23.9 uCi/mg and radioactive purity 96.3%.

Soils: Four soils were used (clay, sand, sandy loam, and loam). The soils were air dried and sieved through a 2-mm mesh sieve prior to use. Soil characteristics are shown in Table I.

Test solutions:

- a) Preliminary study- A stock solution containing 2.0 mg/mL of G-30414 was prepared in a mixture of chloroform/ acetic acid 6:4 (v:v). A 0.2 mL aliquot was diluted to 200 mL with 0.01 N calcium ion solution (sterilized, deionized, and boiled water). The nominal concentration of G-30414 was 2 ug/mL.
- b) Final study- A solution of G-30414 at a nominal concentration of 2 ug/mL was prepared from the stock solution by mixing 0.4 mL volume to a final volume of 400 mL (dilutant: 0.01 N calcium ion solution [as the acetate salt]; 1.6 mL of acetic acid was added as a cosolvent to aid solubility at the highest concentration). From this second stock solution, other solutions were prepared by dilution with the calcium ion solution. The nominal concentrations of these solutions (in addition to the one at 2 ug/mL) were 1 ug/mL, 0.5 ug/mL, 0.25 ug/mL, and 0.13 ug/mL. A solution containing no G-30414 (only calcium ion) was used as a control.

Test apparatus: The test system consisted of centrifuge tubes (50 mL) containing soil and G-30414 solution. Each soil and solution concentration were done in duplicate.

Soil-to-solution ratio and equilibration time were determined in a preliminary experiment. The preliminary experiment was also used to determine if adsorption to glassware and/or caps occurred. A 4-hr equilibration time and a 125-solution to 1 g of soil ratio were determined from the preliminary experiment (Tables II-IV).

Adsorption phase: Each complete sample set was shaken for 4-hrs in a shaker (200 rpm) at 24 C. After 4 hrs., the samples were centrifuged and the equilibrium concentration in solution determined by ISC. The concentration of G-30414 adsorbed onto soil was determined by difference.

Desorption phase: After adsorption, the desorption phase was performed by adding 25-mL of the calcium solution to each of the samples (samples were preweighed to correct for any remaining adsorption solution). The samples were then shaken for

4-hr (175-200 rpm), after which the supernatants were analyzed by LSC to determine equilibrium concentration; soil concentration was determined by difference.

Calculations: The Freundlich equation was used to evaluate batch equilibrium data. the equation can be expressed as

$$x/m = K_d C_e^{1/n} \quad \text{OR} \quad \ln x/m = \ln K_d + 1/n \ln C_e$$

x/m is the soil equilibrium concentration (ug/g)
 C_e is the aqueous phase equilibrium concentration in ug/mL
 K_d is the Freundlich sorption constant and n is a constant

Plots of $\ln C_e$ vs $\ln(x/m)$ were used to determine K_d (from the intercept) and $1/n$ (from the slope).

To express K_d in terms of soil organic carbon content, the following expression was used

$$K_{oc} = (K_d \times 100)/\% \text{ O.C.}, \text{ where } \% \text{ O.C. (organic carbon)}$$

was obtained by dividing the
% organic matter by 1.7

Data reduction was performed by mathematical methods of linear regression, means, sums, and logarithm calculations.

REPORTED RESULTS

Equilibrium concentrations (in soil and in aqueous phase) were expressed in terms of total radioactivity as determined by LSC. The mean measured concentration in the solution (C_e) and in soil (x/m) in the adsorption phase of the study are presented in Tables V and VI, respectively. For the desorption phase, this information is presented in Tables VII and VIII. After completion of adsorption and desorption phases, TLC was used to analyze solutions of studies conducted at the highest concentration, which showed G-30414 at 85.9 to 100% of the radioactivity in all solutions.

The Freundlich adsorption/desorption isotherms are shown in Figures 2-5. Data from linear regression analyses are presented in Tables IX and X for the adsorption and desorption phases, respectively.

The K_d constants for the adsorption phase ranged from 8.5 for the Maryland sand to 483 in the Maryland clay. Desorption constants varied from 26 for the Maryland sand to 423 for the Maryland clay. The sorption constants correlated, in general, with organic matter content. However, the slopes of the lines (isotherms) were not unity, indicating that the adsorption process was not solely a mere distribution between organic matter of the soil and the aqueous phase.

Note: G-30414 adsorbs stronger than parent simazine or any of the dealkylated degradates.

REVIEWER'S COMMENTS:

1. It is mentioned that following completion of the adsorption and desorption phases conducted with the highest concentration of G-30414, the solutions were analyzed (by TLC) showing G-30414 at 85.9 to 100% in all solutions. However, no actual data/results were presented for each soil that may indicate in which soils degradation may be more extensive.

Actual G-30414 concentration should have been used in the calculations rather than total radioactivity. This becomes important for those soils where degradation is more extensive.

The registrant is being requested to provide information showing TLC data in order to determine if the degree of degradation is soil-dependent. If available, data on other degradates present should also be provided.

2. The registrant is also being requested to provide soil classification to the series level, with the name expressed according to the USDA Soil Classification.

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The purpose of requesting additional information on the soils is to identify geographical regions where these soils prevail and relate these regions with those where simazine is used (or has been used).

Simazine

RIN: 1646-93

Page ___ is not included in this copy.

Pages 31 through 43 are not included.

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 quality control procedures.
 - Identity of the source of product ingredients.
 - Sales or other commercial/financial information.
 - A draft product label.
 - The product confidential statement of formula.
 - Information about a pending registration action.
 - FIFRA registration data.
 - The document is a duplicate of page(s) _____.
 - The document is not responsive to the request.
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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.
