

122B
Shaughnessy No.: 080803

Date Out of EAB: APR 12 1988

TO: Robert J. Taylor/Cynthia Giles
Product Manager #25
Registration Division (TS-767C)

FROM: Emil Regelman, Supervisory Chemist
Environmental Chemistry Review Section #3
Exposure Assessment Branch/HED (TS-769C)

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

Attached, please find the EAB review of...

Reg./File #: 100-529

Chemical Name: 2-Chloro-4-ethylamino-6-isopropylamino-s-triazine

Type Product: Herbicide

Product Name: ATRAZINE

Trade Name: AATREX® NINE-O®

Company Name: Ciba-Geigy

Purpose: Review data in response to Standard

Date Received: 12/2/1987

Action Code: 660

Date Completed: 4/9/1988

EAB #(s): 80423

Monitoring Study Requested:

Total Reviewing Time: 5 days

Monitoring Study Volunteered:

Deferrals to:

Ecological Effects Branch

Residue Chemistry Branch

Toxicology Branch

1

1. CHEMICAL:

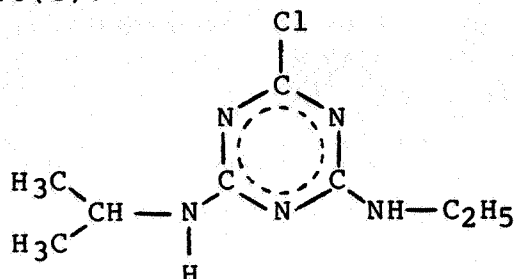
Chemical name: 2-chloro-4-ethylamino-6-isopropylamino-s-triazine

Chemical Abstracts #: 1912-24-9

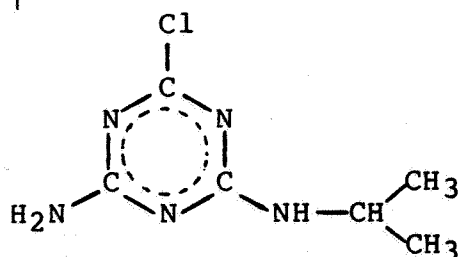
Common name: ATRAZINE

Trade name: AATREX® NINE-O®

Structure(s):

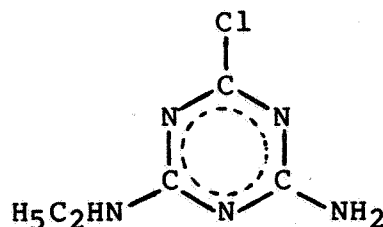


ATRAZINE



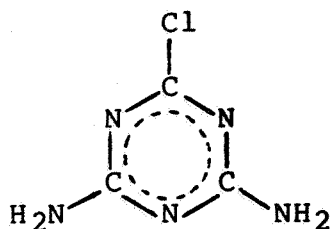
2-amino-4-chloro-6-isopropyl-s-triazine

G-30033



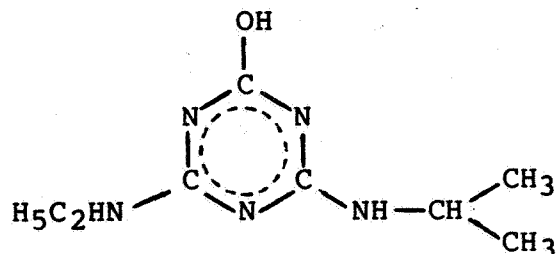
2-amino-4-chloro-6-ethylamino-s-triazine

G-28279



2,4-diamino-6-chloro-triazine

G-28273



2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine

G-34048

DEGRADATES OF ATRAZINE

Physical/Chemical properties of parent atrazine:

Physical state: powder

Color: white

Odor: odorless

Melting point: 175-177°C

Boiling point: not applicable

Vapor pressure: 3.0×10^{-7} mmHg at 20°C

Density: 1.19 gcm³ at 20°C

Solubility at 20°C:

Water.....	33 ppm
Chloroform.....	5.2%
Diethyl ether.....	1.2%
Ethyl acetate.....	2.8%
Methanol.....	1.8%
n-pentane.....	0.04%

Dissociation constant: $pK_a = 1.7$ at 20°C

2. TEST MATERIAL: See specific studies.

3. STUDY/ACTION TYPE: Review of data submitted in response to Standard.

4. STUDY IDENTIFICATION:

The following studies, submitted by Ciba-Geigy Corporation, Agricultural Division, Post Office Box 18300, Greensboro, NC 27419 were reviewed. Atrazine is being evaluated under GWDCI because of groundwater contamination concerns. Therefore, of the submitted studies only those required under GWDCI were reviewed at the present time.

Mobility studies

- Yu, W.C. 1986. Determination of the adsorption/desorption constants of G-30033. Conducted by Cambridge Analytical Associates, Boston, MA. Laboratory study No. 59-6A. Completed February 26, 1986.
MRID No. 404313-28
- Yu, W.C. 1986. Determination of the adsorption/desorption constant of G-28273. Conducted by Cambridge Analytical Associates, Boston, MA. Laboratory study No. 59-5A. Completed February 18, 1986.
MRID No. 404313-27.
- Yu, W.C. 1986. Determination of the adsorption/desorption constant of G-34048. Conducted by Cambridge Analytical Associates, Boston, MA. Laboratory study No. 59-7A. Completed February 26, 1986.
MRID No. 404313-26.

- Blair, J.E. 1986. Determination of the mobility of G-34048 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory study No. 6015-302. Completed March 6, 1986.
MRID No. 404313-32.
- Blair, J.E. 1986. Determination of the mobility of G-30033 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory study No. 6016-306. Completed February 27, 1986.
MRID No. 404313-34.
- Saxena, A.M. 1987. Determination of the mobility of soil-aged ¹⁴C-atrazine residues by soil thin-layer chromatography. Conducted by Hazleton Laboratories America, Madison, WI. Laboratory Study No. HLA 6015-186. Completed October 15, 1987.
MRID No. 404313-30.

Degradation studies- field

- Klaine, S.J. 1987. Field dissipation study of atrazine in west Tennessee soil. Conducted by Department of Biology, Memphis State University, Memphis, TN. Laboratory study No. TX-431A. Completed October 22, 1987.
MRID No. 404313-35.

5. REVIEWED BY:

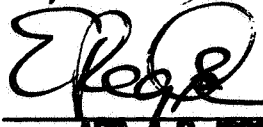
Silvia C. Termes
Chemist, Review Section #3
EAB/HED/OPP

Signature: 

Date: April 12th 1988

6. APPROVED BY:

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

Signature: 

Date: APR 12 1988

7. CONCLUSIONS:

1. Determination of the adsorption/desorption constants for G-30033, G-28273, and G-34048.

These three separate studies are acceptable and fulfill data requirements for adsorption/desorption (batch equilibrium) of these degradates of atrazine on soils.

The Freundlich adsorption/desorption constants for G-30033, G-28273, and G-34048 were determined on four types of soil: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam. Results showed that G-30033 and G-28273

were not strongly adsorbed onto soil particles and that they were easily desorbed. Results for G-34048 indicate that this degradate ("hydroxy atrazine") adsorbed onto the soil particles. Binding of G-34048 onto the soil was attributed to the presence of a polar substituent (-OH).

A summary of sorption constants and of K_{OC} values is presented in Table I. Values for atrazine and for G-28279 were taken from the studies reviewed on 2/25/88.

2a. Determination of the mobility of G-30033 and G-34048 by soil thin-layer chromatography.

These two separate studies may be acceptable if the actual "room temperature" at which the plates were developed can be provided. The reported results indicate that G-30033 was highly mobile in sand (mobility class 5), mobile in the sandy loam and silty loam soils (mobility class 4), and of intermediate mobility in the clay loam soil (mobility class 3). On the other hand, G-34048 was of low mobility in sand and in clay loam soils (mobility class 2) and immobile in the sandy loam and silt loam soils (mobility class 1).

2b. Determination of the mobility of soil-aged ^{14}C -atrazine residues by soil thin-layer chromatography.

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided and if it can be clarified if there were any attempts made to characterize the radioactive zone at the origin of the linear analyzer profiles (attributed to soil-bound radioactivity). If so, indicate which degradates were identified.

The reported results indicate that the most mobile component of soil-aged (32 days) atrazine was unchanged atrazine.

3. Field dissipation of atrazine in West Tennessee soil.

This study can only be considered as supplemental. Several deficiencies were noted, which are indicated in the review of the individual study and in the RECOMMENDATIONS section. The study is unacceptable.

An earlier review (2/25/88) of environmental fate data submitted by the registrant indicated the potential leaching problem of atrazine based on the persistence and mobility data. In that review, the 1/29/88 leaching potential assessment undertaken by the Ground Water Team was also noted. In their assessment, the Ground Water Team concluded that atrazine does have a potential for leaching; levels of atrazine were actually found in groundwaters of 14 of the 18 states for which monitoring data is available. The Ground Water Team has recommended that the registrant conducts a large-scale retrospective monitoring study.

From the data reviewed here and on 2/25/88, it can be concluded that the least mobile of the degradates is the polar G-34048 ("hydroxy atrazine"). The soil thin-layer chromatography study with soil-aged (32 days) atrazine indicated that the most mobile component was unchanged atrazine, but no apparent attempts were made to identify other less mobile radioactive components.

TABLE I

Sorption constants for ATRAZINE and its main degradates

Chemical species	Soil Type					
	sand		sandy loam		silt loam	
	K _{ads}	K _{des}	K _{ads}	K _{des}	K _{ads}	K _{des}
Atrazine	0.427	5.948	0.990	14.90	1.455	2.261
G-28279	0.225	12.479	0.631	6.593	0.987	1.784
G-28273	0.108	5.750	0.209	6.620	0.714	4.340
G-34048	1.643	5.518	6.482	13.08	8.165	16.26
G-30033	0.116	7.900	0.231	10.51	0.798	12.87
					0.963	8.104

Chemical species	K _{oc} Constants					
	Ads	Des	Ads	Des	Ads	Des
Atrazine	90.9	1266	55	828	121	188
G-28279	47.9	2655	35.1	366	82.3	149
G-28273	23.0	1220	11.6	368	59.5	362
G-34048	350	1174	360	727	680	1355
G-30033	24.7	1681	12.8	584	66.5	1073
					64.2	540

10. RECOMMENDATIONS:

163-1: Determination of the mobility of G-34048 and of G-30033 in selected soils by soil thin-layer chromatography

The actual "room temperature" at which the plates were developed should be provided in order to accept these two studies.

163-1: Determination of the mobility of soil-aged ^{14}C -atrazine by soil thin layer chromatography

The actual "room temperature" at which the plates were developed should be provided. The registrant must clarify if attempts were made to identify the less mobile radio-active components.

164-1: Field dissipation study of atrazine in West Tennessee soil

This study is only considered supplemental. The study is unacceptable as presented.

A complete soil analysis (including percentages of sand-clay-silt) should be provided. The registrant must clarify why the 1985 study was conducted for 238 days and while the 1986 was conducted for 43 days only. Also the registrant must clarify why the analyses of all sample depths were not reported.

9. BACKGROUND:

a. Introduction

Atrazine is currently being evaluated under Ground-Water Data-Call-In. A 1/29/88 assessment done by the Ground Water Team of the leaching potential of atrazine (based on published scientific literature) concluded that atrazine is a persistent pesticide that has the potential for leaching. Because atrazine levels have been found in groundwaters of 14 of the 18 states for which monitoring data is available, the Ground Water Team has recommended that registrant conducts a large-scale retrospective groundwater monitoring study with the purpose of assessing the true extent of atrazine contamination throughout the Nation. Environmental fate data on atrazine reviewed by EAB (2/25/88) also indicate that atrazine does present a potential leaching problem. The present review includes data on the mobility of atrazine degradates not reviewed in the 2/25/88 review.

b. Directions for use

Atrazine is a triazine herbicide used in the control of broadleaf and grassy weeds in corn, sorghum, rangeland, sugarcane, macadamia orchards, guava, pineapple, turfgrass farms, conifer reforestation, Christmas tree plantations, proso millet, wheat, grass seed fields, and for nonselective vegetation control in fallow and noncropland. Atrazine is formulated as an emulsifiable concentrate, wettable powder, pellet, granule, tablet, or flow concentrate.

10. DISCUSSION OF INDIVIDUAL STUDIES:

See attached reviews of individual studies.

11. COMPLETION OF ONE LINER:

Not applicable.

12. CONFIDENTIAL BUSINESS INFORMATION:

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

DISCUSSION OF INDIVIDUAL STUDIES

Yu, W.C. 1986. Determination of the adsorption/desorption constants of G-30033. Conducted by Cambridge Analytical Associates, Boston, MA. Laboratory Study No. 59-6A. Completed February 26, 1986. EPA Accession No. 404313-28.

Materials and methods

Soils: Four types of soil were used: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam. Characteristics of these soils are summarized in Table I. The soils were oven-dried at 90°C (24 hr) and autoclaved at 120°C (30 min) prior to use.

Test material: [U-ring-¹⁴C]-30033, specific activity 21.3 uCi/mg and radiochemical purity 99% and G-30033 analytical standard were used.

Test solutions: A stock solution of nominal concentration of 10 ug/mL was prepared by dissolving 2.0 mg ¹⁴C-G-30033 and 4.0 mg of analytical G-30033 in a small quantity of tetrahydrofuran, diluted to 600 mL with a 0.01 N calcium ion solution in deionized, purified water. Dilutions (5 ug/mL, 1 ug/mL, 0.5 ug/mL, and 0.2 ug/mL) of the stock solution were prepared in sterile 0.01 N calcium ion solution. A blank 0.01 N calcium ion solution was also used. The actual concentrations of the stock solution and of the dilutions were determined by HPLC and gave the following values: 11.1 ug/mL (stock solution); 0.22, 0.56, 1.1, and 5.6 ug/mL (dilutions).

Experimental procedure: A preliminary study with the sandy soil was undertaken in order to establish the appropriate soil-to-stock solution ratio and equilibration times.

a) Adsorption phase: Four grams of each of the four soils were placed in 50 mL Pyrex centrifuge tubes (in duplicates) and 20 mL of each of the ¹⁴C-G-30033 dilutions and of the blank calcium ion solution were added. the soil and solution were shaken 24-hr in a shaker bath (200 agitations/min) at 25°C. Then the tubes were centrifuged, the supernatants removed, and the equilibrium concentration (C_e) determined (by LSC).

b) Desorption phase: The soils from the adsorption phase (weighed wet to correct for any residual solution) were treated with 20 mL of 0.01 N calcium ion solution. The samples were shaken for 24-hr in a shaker bath (200 agitations/min), then centrifuged, and the supernatant analyzed by LSC to determine the equilibrium concentration.

Control blanks were included for each set of samples to assess potential interferences from the reagent, soil, and test container.

Analytical methods and calculations: All solutions were analyzed by LSC of ^{14}C -G-30033 in the aqueous phase. Methylene chloride was used to extract ^{14}C -G-30033 from soils; the extracts were analysed by LSC.

The Freundlich equation was used in the calculations,

$$x/m = K_d C_e^{(1/n)}$$

or $\ln(x/m) = \ln K_d + 1/n \ln C_e$

where x/n = soil equilibrium concentration in ug/g
 C_e = aqueous phase equilibrium concentration in ug/mL
 K_d = Freundlich sorption coefficient
 $1/n$ = empirical exponent

Plots of $\ln C_e$ vs $\ln(x/m)$ were obtained for both adsorption and desorption and linear regression analysis of the data yielded n and K_d from the $(1/n)$ slope and the $\ln K_d$ intercept, respectively. The sorption constant was expressed in terms of the soil organic carbon content via

$$K_{oc} = (K_d \times 100) / \% \text{ organic carbon}$$

where the organic carbon content of the soil was calculated by dividing the organic matter content by 1.7.

Reported results

Logarithmic plots of (x/m) vs C_e (shown in Figures 1 through 2 for the adsorption and desorption phases, respectively) and linear regression analyses yielded the Freundlich constants. Tables II and III present the results for the adsorption and desorption phases, respectively. The adsorption constants (K_{ad}^s) were 0.116(sand), 0.231(sandy loam), 0.798(silty loam), and 1.007(clay loam). The desorption constants (K_{des}) were 7.900(sand), 10.51(sandy loam), 12.87(silty loam), and 8.104(clay loam). The $K_{oc}(\text{ads})$ were 24.7(sand), 12.8(sandy loam), 66.5(silty loam), and 64.2(clay loam). The $K_{oc}(\text{des})$ were 1681(sand), 584(sandy loam), 1073(silty loam), and 540(clay loam). The results indicated that G-30033 was not strongly adsorbed onto soil particles and that it was easily desorbed.

Reviewer's comments

This study is acceptable. EAB concurs with the author's results and conclusions.

Atrazine

Page _____ is not included in this copy.

Pages 12 through 22 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.
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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.

Yu, W.C. 1986. Determination of the adsorption/desorption constants of G-34048. Conducted by Cambridge Analytical Associates, Inc. Boston, MA. Completed February 26, 1986.
EPA Accession No. 404313-26.

Materials and methods

Soils- Four types of soil were used: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam. Characteristics of these soils are summarized in Table I. The soils were oven-dried at 90°C (24 hr) and autoclaved at 120°C (30 min) prior to use.

Test material- [U-ring-¹⁴C]-G-34048, specific activity of 52.2 uCi/mg, 98% radiochemical purity and G-28279 analytical standard were used.

Test solutions- A stock solution of G-34048 of a nominal concentration of 10 ug/mL was prepared by dissolving 2.0 mg of ¹⁴C-G-34048 and 4.0 mg of analytical G-34048 in a small amount of acetic acid and then a small amount of methanol, diluting to 600 mL with a 0.01 N calcium ion solution in deionized, purified water. Dilutions (5 ug/mL, 1 ug/mL, 0.5 ug/mL, and 0.2 ug/mL) of the stock solution were prepared in sterile 0.01 N calcium ion solution. The actual concentrations of the stock solution and the dilutions were determined by HPLC and gave the following values: 10.3 ug/mL (stock solution) and 0.21, 0.52, 1.03, and 5.2 ug/mL (dilutions).

Experimental procedure: A preliminary study with the sandy soil was undertaken in order to establish the appropriate soil-to-stock solution ratio and equilibration times.

- a) Adsorption phase: Four grams of each of the four soils were placed in 50 mL Pyrex centrifuge tubes (in duplicate) and 20 mL of each of the ¹⁴C-G-34048 dilutions and of the blank calcium ion solution were added. The soil-and-solution were shaken for 24-hr in a shaker bath (200 agitations/min) at 25°C. Then the the tubes were centrifuged, the supernatants removed, and the equilibrium concentration (C_e) determined.
- b) Desorption phase: The soils from the adsorption phase (weighed wet to correct for any residual solution) were treated with 20 mL of 0.01 N calcium ion solution. The samples were shaken for 24-hr in a shaker bath (200 agitations/min), then centrifuged, and the supernatants analyzed by LSC to determine the equilibrium concentration.

Control blanks were included for each set of samples to assess any potential interferences from reagents, soils, and test containers.

Analytical methods and calculations: All solutions were analysed by LSC of ^{14}C -G-34048 in the aqueous phase. Methylene chloride was used to extract ^{14}C -G-34048 from the soils; the extracts were analysed by LSC.

The Freundlich equation was used in the calculations,

$$x/m = K_d C_e^{(1/n)}$$

or $\ln(x/m) = \ln K_d + (1/n)\ln C_e$

where (x/m) = soil equilibrium concentration in $\mu\text{g/g}$
 C_e = aqueous phase equilibrium concentration
in $\mu\text{g/mL}$
 K_d = Freundlich sorption coefficient
 $1/n$ = empirical exponent

Plots of $\ln C_e$ vs $\ln(x/m)$ were obtained for both adsorption and desorption; linear regression analysis of the data yielded n and K_d from the $(1/n)$ slope and the $\ln K_d$ intercept, respectively. The sorption constant was also expressed in terms of the organic carbon content via,

$$K_{oc} = (K_d \times 100)/\% \text{ organic carbon}$$

where the organic carbon content of the soil was calculated by dividing the organic matter content by 1.7.

Reported results

Logarithmic plots of (x/m) vs C_e (shown in Figures 1 through 2 for the adsorption and desorption phases, respectively) and linear regression analyses yielded the Freundlich constants. Tables II and III present the results for the adsorption and desorption phases, respectively. The K_{ads} values were 1.643 (sand), 6.482 (sandy loam), 8.165 (silty loam), and 5.867 (clay loam). The K_{des} values were 5.518 (sand), 13.08 (sandy loam), 16.26 (silty loam), and 22.29 (clay loam). The K_{oc} for the adsorption phase were 350 (sand), 360 (sandy loam), 680 (silty loam), and 391 (clay loam). The K_{oc} for the desorption phase were 1,174 (sand), 72 (sandy loam), 1355 (silty loam), and 1486 (clay loam). The results show that G-34048 was adsorbed onto soil particles, indicating that the test material has a polar substituent that binds to the soil.

Reviewer's comments

This study is acceptable. EAB concurs with the author's results and conclusions. G-34048 is "hydroxy atrazine", in which the $-\text{Cl}$ has been replaced by an $-\text{OH}$.

Atrazine

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Pages 25 through 35 are not included.

The material not included contains the following type of information:

- _____ Identity of product inert ingredients.
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Yu, W.C. 1986. Determination of adsorption/desorption constants of G-28273. Conducted by Cambridge Analytical Associates, Boston, MA. Laboratory Study No. 59-5A. Completed February 18, 1986. EPA Accession No. 4043143-27.

Materials and methods

Soils- Four types of soil were used: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam. Characteristics of these soils are summarized in Table I. The soils were oven-dried at 90°C (24 hr) and autoclaved at 120°C (30 min) prior to use.

Test material: [U-ring-¹⁴C]-G-28273, specific activity 14.1 uCi/mg, radiochemical purity 98% and G-28273 analytical standard.

Test solutions: A stock solution of G-28273 of a nominal concentration of 10 ug/mL was prepared by dissolving 2.0 mg of ¹⁴C-G-28273 and 4.0 mg of analytical G-28273 in a small amount of dimethylsulfoxide, then diluted to 600 mL with a 0.01 N calcium ion solution in deionized, purified water. Dilutions (5 ug/mL, 1 ug/mL, 0.5 ug/mL, and 0.2 ug/mL) of the stock solution were prepared in sterile 0.01 N calcium ion solution. A blank 0.01 N calcium ion solution was also used. The actual concentrations of the stock solution and of the dilutions were determined by HPLC and gave the following values: 8.5 ug/mL (stock solution); 0.17, 0.43, 0.85, and 4.25 ug/mL (dilutions).

Experimental procedure: A preliminary study with the sandy soil was undertaken in order to establish the appropriate soil-to-stock solution ratio and equilibration times.

- a) Adsorption phase: Four grams of each of the four soils were placed in 50 mL Pyrex centrifuge tubes (in duplicate) and 20 mL of each of the ¹⁴C-G-28273 solutions and the blank calcium ion solution were added. The soil-and-solution were shaken for 24-hr in a shaker bath (200 agitations/min) at 25°C. Then the tubes were centrifuged, the supernatants removed, and the equilibrium concentration (C_e) determined.
- b) Desorption phase: The soils from the adsorption phase (weighed wet to correct for any residual solution) were treated with 20 mL of 0.01 N calcium ion solution. The samples were shaken for 24-hrs in the shaker bath (200 agitations/min), then centrifuged, and the supernatants analysed by LSC to determine the equilibrium concentration.

Control blanks were included for each set of samples to assess any potential interferences from reagents, soils, and test containers.

Analytical methods and calculations: All solutions were analysed by LSC of ^{14}C -G-28273 in the aqueous phase. Methylene chloride was used to extract ^{14}C -G-28273 from the soils; the extracts were analysed by LSC.

The Freundlich equation was used in the calculations,

$$x/m = K_d C_e^{(1/n)}$$

or $\ln(x/m) = \ln K_d + (1/n) \ln C_e$

where (x/m) = soil equilibrium concentration in ug/g
 C_e = aqueous phase equilibrium concentration in ug/mL
 K_d = Freundlich sorption coefficient
 $1/n$ = empirical exponent

Plots of $\ln C_e$ vs $\ln(x/m)$ were obtained for both adsorption and desorption phases; linear regression analysis of the data yielded n and K_d from the $(1/n)$ slope and $\ln K_d$ intercept, respectively. The sorption constant was also expressed in terms of the soil organic carbon content via

$$K_{oc} = (K_d \times 100) / \% \text{ organic carbon}$$

where the organic carbon content of the soil was calculated by dividing the organic matter content by 1.7.

Reported results

Logarithmic plots of (x/m) vs C_e (shown in Figures 1 through 2 for the adsorption and desorption phases, respectively) and linear regression analysis yielded the Freundlich constants. Tables II and III present the results for the adsorption and desorption phases, respectively. The K_{ads} values were 0.108 (sand), 0.209 (sandy loam), 0.714 (silty loam), and 0.800 (clay loam). The K_{des} values were 5.750 (sand), 6.620 (sandy loam), 4.340 (silty loam), and 1.172 (clay loam). The K_{oc} (ads) were 23.0 (sand), 11.6 (sandy loam), 59.5 (silty loam), and 53.3 (clay loam). The K_{oc} (des) were 1,220 (sand), 368 (sandy loam), 362 (silty loam), and 78.1 (clay loam). The results showed that G-28273 was not strongly adsorbed onto soil particles and that was easily desorbed.

Reviewer's comments

This study is acceptable. EAB concurs with the author's results and conclusions.

Atrazine

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Pages 38 through 48 are not included.

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Blair, J.E. 1986. Determination of the mobility of G-30033 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-306. Completed February 27, 1986.
EPA Accession No. 404313-34.

Materials and methods

Test material: ^{14}C -G-30033, specific activity 21.3 uCi/mg and 99% radiopurity. ^{14}C -labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion.

Soils- Four different soils were used: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam. Characteristics of these soils are shown in Table I.

Experimental procedures: Soils were sieved through a 1.18-mm screen. The glass plates (20x20 cm) were prepared by placing a tape strip 17 cm away from one edge of the plate. An area of 20x17 cm was uniformly coated with a slurry of soil (one plate for each soil type), dried, and then channels were cut in the soil as to make seven strips 17-cm long and 2.5-cm wide.

A solution containing approximately 0.02 to 0.04 uCi of one of the following: G-30033, Amiben, 2,4-D, Ethion, or Prometon was spotted at the origin (about 3 cm from the bottom) of each channel. The solvent was evaporated and each plate developed in water (room temperature) until the front reached about 14 cm beyond the origin. After the plate dried, radioactivity in the plate was located with a linear analyzer. The frontal R_f values were calculated by measuring the distance from the origin to the leading edge of the radioactivity and dividing by the distance from the origin to the solvent front. For each soil, G-30033 was determined in triplicate and each standard once. Based on frontal R_f value, a mobility class was assigned. A sorption coefficient (K) was calculated from the relative mobility by

$$K = \frac{1/R_f - \phi^{2/3}}{D (1 - \phi^{2/3})}$$

R_f = relative migration of the compound compared to water

ϕ = pore fraction of the soil (assumed to be 0.5)

D= specific gravity of the solids in the soil (assumed to be 2.5)

Reported results

Table II presents the frontal R_f values, mobility classes, and calculated sorption coefficients (K). G-30033 was highly mobile (mobility class 5) in sand, mobile in sandy loam and silt loam soils (mobility class 4), and of intermediate mobility in clay loam soil (mobility class 3).

Reviewer's comments

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided.

Atrazine

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Blair, J.E. 1986. Determination of the mobility of G-34048 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-302. Completed March 7, 1986.
EPA Accession No. 404313-32.

Materials and methods

Test material: ^{14}C -G-34048, specific activity 52.2 uCi/mg and 98% radiopurity. ^{14}C -labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion.

Soils- Four different soils were used: Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown silty clay loam. Characteristics of these soils are shown in Table I.

Experimental procedures: Soils were sieved through a 1.18-mm screen. The glass plates (20x20 cm) were prepared by placing a tape strip 17-cm away from one edge of the plate. An area of 20x17-cm was uniformly coated with a slurry of soil (one plate for each soil type), dried, and then channels were cut in the soil as to make seven strips 17-cm long and 2.5-cm wide.

A solution containing approximately 0.02 to 0.04 uCi of one of the following: G-34048, Amiben, 2,4-D, Ethion, or Prometon was spotted at the origin (about 3-cm away from the bottom) of each channel. The solvent was evaporated and each plate was developed in water (room temperature) until the front reached about 14-cm beyond the origin. After the plate dried, the radioactivity in each strip was located by autoradiography. The frontal R_f values were calculated from each autoradiograph by measuring the distance from the origin to the leading edge of the radioactivity and dividing by the distance from the origin to the solvent front. For each soil, G-34048 was determined in triplicate and each standard once. Based on frontal R_f value, a mobility class was assigned. A sorption coefficient (K) was calculated from the relative mobility by

$$K = \frac{1/R_f - \theta^{2/3}}{D (1 - \theta^{2/3})}$$

R_f = relative migration of the compound compared to water
 θ = pore fraction of the soil (assumed to be 0.5)
 D = specific gravity of the solids in the soil (assumed to be 2.5)

Reported results

Table II presents the frontal R_f values, mobility classes, and calculated sorption coefficients (K). G-34048 was of low mobility in sand and in clay loam soils (mobility class 2), but immobile in sandy loam and silt loam soils (mobility class 1).

Reviewer's comments

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided.

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Saxena, A.M. 1987. Determination of the mobility of soil-aged ^{14}C -atrazine residues by soil thin-layer chromatography.
 Conducted by Hazleton Laboratories America, Madison, WI.
 Laboratory Study No. HLA 6015-186. Completed October 15, 1987.
 EPA Accession No. 404313-30.

Materials and methods

Test material(s)- [U-ring- ^{14}C]atrazine, specific activity 22.0 uCi/mg and 99.4% radiopurity.
 2,4-dichlorophenoxy(2- ^{14}C)acetic acid, specific activity 55 mCi/mmol and 98% radiopurity (reference standard).
 Nonradiolabeled analytical standards of atrazine, and the degradates G-30033, G-28279, and G-28273.

Soil: California loam soil

<u>Physical Characteristics</u>	<u>Value</u>
Sand.....	51%
Silt.....	37%
Clay.....	12%
Organic matter.....	1.4%
pH.....	7.6
Cation exchange capacity.....	7
FMC 0.33 bar.....	12%
<u>Microbial characteristics</u>	<u>Value</u>
Aerobic plate.....	12,000,000 count/g
Anaerobic plate.....	460,000 "
Aerobic spore.....	8,800 "
Anaerobic spore.....	170 "
Yeast.....	200 "
Mold.....	29,000 "

The soil moisture content was determined to be 8.3%. The soil was sieved through a 2-mm mesh screen.

Fortification solution- A solution of ^{14}C - atrazine was prepared in methanol (mean activity 54,890 dpm/uL). The 2,4-D reference standard contained 4,712 dpm per microliter.

Experimental procedures

- Soil fortification: Approximately 21.7 g of sieved soil (20.0 g on a dry basis) were placed in a biometer flask. Then, 200 mL of the ^{14}C -atrazine fortification solution (11.0×10^6 dpm=225 ug; theoretical concentration of 11.3 ppm of ^{14}C -atrazine in dry soil). After the methanol evaporated, the soil was hand-tumbled to homogenize the soil. Water was added to bring the moisture content to 75% of the FMC at 0.33 bar.
- Aerobic incubation: A 10% NaOH solution (10mL) were added to the side arm of the biometer flask. Both the flask and the side arm were sealed (rubber stoppers) and incubated in the darkness at $25 \pm 1^\circ\text{C}$ for 32 days. The NaOH solution

was removed (and replaced with fresh solution) after 1, 7, 14, 21, 28, and 32 days. Radioactivity in duplicate aliquots was determined by LSC; the measured radioactivity in the NaOH trap was indicative of the amount of CO₂ or volatile products (or both) that formed. After 32 days, the aged soil was removed from the biometer flask and ground and homogenized with a mortar and pestle. Five aliquots of the aged soil (about 0.15 g each) were oxidized to determine the amount of ¹⁴C-activity remaining in the soil.

Aged soil (4 g) was extracted with acetonitrile:water (9:1). The acetonitrile was evaporated (rotary evaporator) and the aqueous phase was then partitioned with dichloromethane (DCM). The DMC extract was analyzed by TLC (silica gel; toluene/acetone, 75:25) to determine the amount of atrazine remaining. Another plate was spotted with the DMC extract plus solutions of the metabolites (developed in chloroform/MeOH/formic acid/water, in the ratio 100:20:4:2).

The extracted soil (dried and homogenized) was combusted to determine residual radioactivity.

- c) Aged-soil TLC: The soil was sieved (1.18 mesh screen).

A strip of tape was placed approximately 17.5 cm from one edge of a plate (20x20-cm). A slurry of soil and water was applied to a thickness of approximately 1.0mm and allowed to dry. The plate was separated into seven channels (by cutting grooves), each approximately 2.5cm wide.

In three of the seven channels, a zone of soil was scraped from the proposed application site and the scraped zones were replaced with the aged soil (each aged soil contained approximately 0.04 uCi). Two of the remaining channels were spotted with a toluene solution of radio-labeled 2,4-D (0.02 uCi each) and two with an acetone solution of ¹⁴C-atrazine (0.01 uCi each).

- d) Sample analysis: The solvents were allowed to evaporate. The soil plate was developed in an unsaturated tank of water (room temperature) until the water front reached the top of the TLC plate. The plate was allowed to dry overnight. The leading edge of radioactivity in each channel was determined with a linear analyzer to obtain frontal R_f values (calculated by measuring the distance from the origin to the leading edge of the radioactivity and dividing by the distance from the origin to the solvent front). The linear analyzer profiles were verified by autoradiography.

- e) Calculations: The equation below was used to calculate the sorption coefficients from the frontal R_f values:

$$K = \frac{1/R_f - \theta^{2/3}}{D(1-\theta^{2/3})}$$

Where, K= sorption coefficient

R_f= Relative mobility of the compound compared to water

θ= Pore fraction of the soil (assumed to be 0.5)

D= Specific gravity of the solids in soil (2.5)

Reported results and discussion

Aerobic incubation of soil (32 days): Less than 0.1% of the applied radioactivity was trapped in the NaOH solution, which indicated that metabolism of atrazine to volatile products or CO₂ was negligible. The soil was considered to be homogeneous with respect to distribution of radioactivity.

Aged-soil TLC plates: Linear analyzer profiles for soil-aged ¹⁴C-atrazine showed two zones of radioactivity. The zone observed at the origin was attributed to soil-bound radioactivity; the more mobile component observed beyond the origin was attributed to ¹⁴C-atrazine. The leading edge of the more mobile component was used to determine the frontal R_f (mean value 0.52). Unaged ¹⁴C-atrazine showed a frontal value of 0.53. The ¹⁴C-2,4-D showed one component and a mean R_f value of 0.76. The frontal R_f values, mobility class, and sorption coefficient (K) are summarized in Table I. ¹⁴C-atrazine (soil aged and unaged) were classified as having intermediate mobility and 2,4-D as mobile.

Extractions: Acetonitrile:water (9:1) extracted a total of 84.4% of the applied radioactivity from the soil. Combustion analysis of the extracted soil indicated that 17.6% of the applied remained unextractable. Extraction of the aqueous phase with DMC resulted in 82.3% extraction. The TLC analysis of the DMC extract showed a single peak corresponding to atrazine, which indicated that the most mobile component of soil-aged atrazine was unchanged atrazine.

Reviewer's comments

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided and if it can be clarified if there were any attempts to characterize the radioactive zone at the origin of the linear analyzer profiles (attributed to soil-bound radioactivity).

Atrazine

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Klaine, S.J. 1987. Field dissipation study of atrazine in West Tennessee Soil. Conducted by Department of Biology, Memphis State University, Memphis, TN. Laboratory Study No. TX-431A. Completed October 22, 1987. EPA Accession No. 404313-35.

Atrazine was chosen in this study because of its abundant use throughout the USA, physical/chemical properties (summarized in Table I; refer to pertinent references at the end of the study), biological parameters, and availability of analytical methods.

Materials and methods

Site: Located at Agricenter International, Shelby County, SW Tennessee. Altitude 300 ft above sea level. Western 10% of the county is on the Mississippi river flood plain. Average annual temperature in Memphis is 16.7°C. Average annual precipitation is approximately 127 cm (50 in), most of it occurring in winter and early spring, with a second period of heavy precipitation (with showers and thunderstorms) in late spring and early summer. The predominant surface waters (other than the Mississippi) are the Wolf and the Loosahatchie Rivers. However, they are not important sources for municipal, industrial, and agricultural use. Groundwater, because of the abundance, high quality, and relatively low pumping and treatment costs, is used primarily as water source. The county is predominantly industrial, but agriculture provides a large amount of income, with soybeans, cotton, corn, and wheat being the most important crops. The Agricenter is located in the south center of the county, with 1000 acres of fertile farmland. A watershed area approximately 18.21 ha (45 acres) was chosen. Other criteria for choosing the site were the proximity with Memphis State University and to the Wolf River.

Soil: Primary soil type is a Falaya silt loam, which is somewhat poorly drained, very silty. Surface layer is a brown, friable silt loam about 6-inches thick; underlying material is a friable silt loam containing brown and gray mottles, which extends to a depths of several feet. Available water capacity is high. Upon rainwater leaching, the soil becomes strongly acidic. A soil analysis is shown in Table II (P and K content is moderately high). The watershed was divided into several segments (Figure 1) to facilitate sampling.

Agronomic practices: Agronomic activities are summarized in Table III. Ten ha (24 acres) of the north watershed were planted in corn; 8 ha (21 acres) were set aside (in accordance with a federal program) during 1985 and 1986. Fertilizers: nitrogen was supplied in the form of urea, phosphorus as diammonium polyphosphate, and potassium as potash (first application of first year); second application consisted of ammonium nitrate.

Atrazine application: Atrazine was applied with a 12-row boom; the boom contained 25 nozzles, 61 cm (24 in) above the soil surface.

Application rates- 1985: 1.27 kg/ha (1.14 lb/acre)

1986: 1.67 kg/ha (1.5 lb/acre).

Atrazine was used as the emulsifiable concentrate and following

label requirements. Spray operations were conducted during periods of low temperature and wind velocities.

Soil sampling: North watershed was divided into 4-subareas and each subarea sampled at five depths: 0-20 cm; 20-40 cm; 40-60 cm; 60-80 cm; 80-100 cm. Sampling was done with a split-tube core sampler (approximately 2-cm diameter). Background atrazine was measured at each depth interval. Analyses were performed immediately after sampling. Sampling times after atrazine application were 0, 1, 3, 7, 14, 28, 56, 84, and 238 days (in 1985) and 0, 1, 3, 7, 22, and 43 days (in 1986).

Determination of atrazine application rate: This was determined by two methods. One method consisted of randomly placing glass-fiber filter pads (1.2 μ m) through the watershed. The pads were collected after application, combined, and sent for analysis. The other method consisted in timing the nozzles and calculating the spray volumes discharged by the 12-row boom used to apply the atrazine (this was done immediately preceding application on May 17, 1985 and on May 7, 1986). Soil sampling at day 0 also serve to confirm the application rate.

Soil sampling: Soil samples were analyzed for pH, organic content, and water content. Analyses were performed in accordance to standard ASTM methods.

Analysis of atrazine in soils: Each core was divided into subsamples representing the different depths: 0-10 cm, 10-20-cm, 20-30 cm, 30-40 cm, 40-50 cm, 60-70 cm, and 90-100 cm. Atrazine analyses were performed in triplicate. For 1985, values are reported through 238 days after application. The extraction procedure used is shown in Figure 2. Atrazine standards were prepared from samples obtained from Ciba-Geigy.

Reported results and discussion

Atrazine levels

- a) Prior application: 0.0011 ug/g (1985); 0.0077 ug/g (1986), based on soil cores in planted area. The 1986 value was higher because it was taken in Jan. and not before atrazine application in May. Top 20-cm of soil.
- b) Day 0: Average of 0.69 ug/g or 9.2 ug/cm² at the surface; this represents 94% of the atrazine (9.7 ug/cm²) as measured on the filter pads; top 10-cm, 1985.
Average of 1.29 ug/g or 16.9 ug/cm² at the soil surface; this represents 108% of the applied atrazine (15.6 ug/cm²) as measured by the filter pad technique; top 10-cm, 1986.

Atrazine concentrations with time

Following atrazine application in 1985, 36% of the applied atrazine remained in the soil after 28 days, 6% after 84 days, and 2% after 238 days. Results are shown in Table IV. Figures 3 and 4 show atrazine

levels at different depths. On day 7, following first runoff event after application, levels in the 10-20 cm depth were 0.0091 ug/g. Levels at this depth increased approximately 400% during next 3-weeks and decreased to 0.0080 ug/g on day 84. This migration was attributed to runoff events (5/23; 6/10). Atrazine concentrations never exceeded 0.01 ug/g in the 20-30 cm depth.

Table V show the atrazine levels at different depths for 1986 application (also Figures 5 and 6). Between days 7 and 22, atrazine levels in the 10-20 cm depth decreased, which was attributed to the lack of rain. After 7 days of application, approximately 50% of the atrazine remained in the soil 0-10 cm depth, 41% after 22 days, and 23% after 43 days. Between days 22 and 43, levels increased about 300% in the 10-20 cm depth (caused by several rainfalls).

Atrazine half-life

A first-order kinetics was assumed in the calculation of the decay of atrazine. Using data from the field soil for the 1985 application, a half-life of atrazine of approximately 20 days was calculated. For 1986, the data from the field soil indicate that two distinct exponential periods exist: an initial period exhibiting higher reduction constants (ending between 7 and 22 days, with several small rainfall events with little runoff) and a second exponential period exhibiting lower reduction constants (significant rainfall after 28 days of application may be responsible). The "half-life" for the initial period was about 7-days; for the second period it was about 20-days.

Nutrient concentrations and physical conditions of soils

These are summarized in Tables VI-XI.

Crop performance

Excellent development of the corn was observed due to the sufficient and well-distributed rainfall from the second planting date through the end of June 1985. The growth of Johnson grass was heavy during early summer; there was also problem with smartweed and cocklebur; insects were not a problem. Corn yield was only 38 bushels/A in 1985 (attributed to maize dwarf mosaic virus carried by the Johnson grass). Corn development was slower in 1986. Rainfall was not well-distributed and the problems with the Johnson grass and the virus were more severe.

Reviewer's comments

This study can only be considered as supplementary. Although a complete elemental analysis of the soil was provided, no information on the percentages of sand-clay-silt was given. While the 1985 application was sampled through a 238-day period, the 1986 application was only sampled through a 43-day period. Not all of the results of the soil-depth samples said to have been analyzed were shown. The 1986 application shows only analyses down to the 20-30 cm depth.

Atrazine

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