EEB

Shaughnessy No.: 080803

Date Out of EAB: FEB 25 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)

Paul F. Schuda

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: 2/23/1988

EAB #(s): 80269

Monitoring Study Requested: ________

Total Reviewing Time: 15 days

Monitoring Study Volunteered: ________

Deferrals to:

________ Ecological Effects Branch

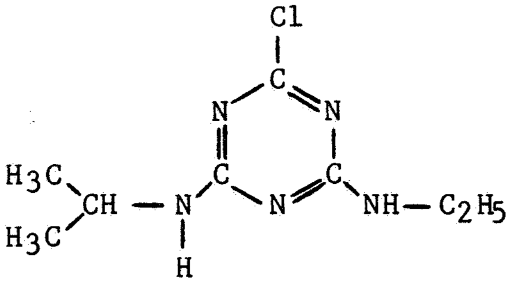
________ Residue Chemistry Branch

________ Toxicology Branch

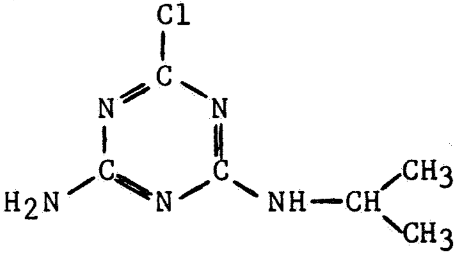
1. CHEMICAL:

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):

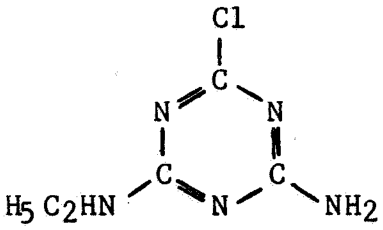


ATRAZINE



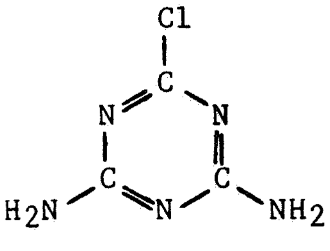
2-amino-4-chloro-6-isopropylamino-s-triazine

G-30033



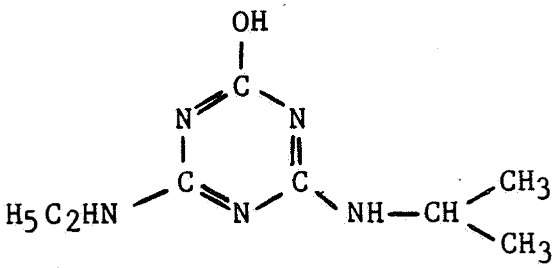
2-amino-4-chloro-6-ethylamino-s-triazine

G-28279



2,4-diamino-6-chloro-triazine

G-28273



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

G-34048

DEGRADATES OF ATRAZINE

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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} mm Hg at 20°C
Density: 1.19 gcm^{-3} at 20°C
Solubility at 20°C:

Water	33 ppm
Chloroform	5.2%
Diethylether	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 submitted data 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.

Laboratory degradation studies

- Spare, W.C. 1986. Determination of the hydrolysis rate constants of atrazine. Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1236. Completed December 31, 1986. EPA Accession No. 404313-19.

- Spare, W.C. 1987. Photodegradation of atrazine on soil surfaces exposed to artificial and natural sunlight. Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1237. Completed April 6, 1987. EPA Accession No. 404313-20.

Laboratory metabolism studies

- Rustum, A.M. 1987. Aerobic, aerobic/anaerobic, and sterile soil metabolism of ^{14}C-atrazine. Conducted by Hazleton Laboratories America, Madison, WI. Laboratory study No. HLA 6015-185. Completed November 6, 1987.
  EPA Accession No. 404313-21.

- Spare, W.C. 1987. Anaerobic aquatic metabolism of atrazine. Conducted by Agrisearch, Inc., Frederick, MD. Laboratory study No. 1231. Completed October 1, 1987.
  EPA Accession No. 404313-23.

- Klaine, S.J. 1987. Biotic and abiotic degradation of atrazine and three of its metabolites in a Western Tennessee soil. Conducted by Department of Biology, Memphis State University, Memphis, TN. Laboratory study No. TX-431. Completed October 22, 1987.
  EPA Accession No. 404313-22.

Mobility studies

- Yu, W.C. 1986. Determination of adsorption/desorption constants of atrazine. Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory study No. 59-1A. Completed February 14, 1986.
  EPA Accession No. 404313-24.

- Yu, W.C. 1986. 1986. Determination of the adsorption/desorption constants of G-28279. Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory study No. 59-4A. Completed February 17, 1986.
  EPA Accession No. 404313-25.

- Blair, J.E. 1986. Determination of the mobility of atrazine in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory study No. 6015-300. Completed March 7, 1986.
  EPA Accession No. 404313-29.

- Blair, J.E. 1986. Determination of the mobility of G-28273 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory study No. 6015-305.
  EPA Accession No. 404313-33.

- Blair, J.E. 1986. Determination of the mobility of G-28279 in selected soils by soil thin layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory study No. 6015-304. Completed February 27, 1986.
  EPA Accession No. 404313-31.

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Degradation studies- field

-White, S.M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on bareground, Hollandale, MN. Prepared by Landis Associates, Inc. Valdosta, GA; Agri-Growth Research, Inc. Hollandale, MN; and Minnesota Valley Testing Labs., Inc., New Ulm, MN. Laboratory study No. 1641-86-71-01-21E-25. Completed October 21, 1987.
EPA Accession No. 404313-37.

-White, S.M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on corn, Hollandale, MN. Prepared by Landis Associates, Inc., Valdosta, GA; Agri-Growth Research, Inc. Hollandale, MN; and Minnesota Valley Testing Labs., Inc., New Ulm, MN. Laboratory study No. 1641-86-71-01-06B-24. Completed October 20, 1987.
EPA Accession No. 404314-39.

-White, S.M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on corn, Ripon, CA. Prepared by Landis Associates, Inc., Valdosta, GA; Research for Hire, Porterville, GA; and Minnesota Valley Testing Labs., Inc., New Ulm, MN. Completed October 23, 1987.
EPA Accession No. 404313-38.

5. REVIEWED BY:

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

Signature:
Date: February 25th, 1988

6. APPROVED BY:

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

Signature:
Date: FEB 25 1988

7. CONCLUSIONS:

Laboratory degradation studies

- Hydrolysis. The hydrolysis study is acceptable. The results indicate that atrazine did not hydrolyse at pH 5, pH 7, or pH 9 during the 30-day study. Therefore, hydrolysis does not appear to be an important degradation mechanism for atrazine.

- Photodegradation on soil. This study, performed with a California sandy loam soil, was not acceptable as presented for the following reasons: (a) significant amounts of radioactivity (ca.

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20% and over) were left unidentified at the origin of TLC plates; (b) the distribution of radioactivity in plates was not expressed in terms of applied dose; and (c) no other methodology was used to confirm the identity of the photodegradation products.

Laboratory metabolism studies

- Aerobic, aerobic/anaerobic, and sterile soil metabolism of ^{14}C-atrazine. This study is only a preliminary report (94-day study instead of the required 12-month study) and is considered a supplemental study only. The study was performed with a California loam soil.

  Based on data collected during 94 days, the half-life for the aerobic metabolism of atrazine was calculated as 140 days. Atrazine decreased from 90.7%(day 0) to 56.5%(day 94). Soil-bound radioactivity continuously increased with time (4.1% at day 0 to 33.3% at day 94). No radioactivity was associated with organic volatile materials. The radioactivity in organic extracts decreased with time, but increased with time in the aqueous extracts. Evolution of $^{14}CO_2$ was low and reached a cumulative total of 0.3% by day 94. The main metabolites present at all sampling times were G-30033 and G-28279. The metabolite G-34048 was not detected until days 62 and 94. In contrast, the aerobic sterile incubation showed that atrazine decreased from 93.7%(day 0) to 77.4%(day 94). Soil-bound radioactivity increased only up to 16.9% by day 94. The decrease in radioactivity in the organic extracts and its increase in aqueous extracts was less marked than in the active aerobic incubation experiments. Therefore, the degradation of atrazine in soil is primarily a microbial process.

  The calculated half-life for atrazine under anaerobic conditions was approximately 159 days. Parent atrazine decreased from 67.0% (day 0 of anaerobic incubation) to 51.2% (day 62 of anaerobic incubation). Soil-bound radioactivity increased from 26.7% (day 0 of anaerobic incubation) to 40.9% (day 62 of anaerobic incubation). No significant amounts of organic volatiles or $^{14}CO_2$ were detected. The metabolites G-30033 and G-28279 were identified at all sampling times in soil extracts and supernatant water; G-28273 and G-34048 were also present, but not at all sampling times.

- Anaerobic aquatic metabolism of atrazine. This study is acceptable. The combined water/sediment half-life calculation gave a half-life for atrazine 608 days (330 days in sediment; 578 days in water alone). Production of volatile materials was minimal. Bound residues increased with time, leveled to about 10% of dose by month 12. About 70% of radioactivity in water and 4% in sediment was still associated with parent atrazine after 12 months; in sterile sample, above 80% of radioactivity remained as atrazine. Metabolites were present at low level (G-30033, 4.7%; G-34048, 5%; and G-28279, 1.4%).

- Biotic and abiotic degradation of atrazine and three of its metabolites in a West Tennessee soil. This study was designed to provide an undisturbed system for studying degradation in situ and is to be considered supplemental to the laboratory studies.

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Several deficiencies were noted in the report (no complete data on soil characteristicts provided; repeated pages; low material balance for total accounted ^{14}C-radioactivity in the atrazine microcosm study; discrepancy between text and Table for the material balance of ^{14}C-deisopropylatrazine microcosm.

It must be pointed out, however, that in contrast with the aerobic (active) and anaerobic laboratory study (short-term preliminary study), the half-lives of atrazine (and of its degradates) were much shorter in the microcosm, in situ studies than in the laboratory studies with the California loam soil. While in the laboratory studies $^{14}CO_2$ evolution was very low, in the microcosm studies $^{14}CO_2$ was a major degradate for atrazine and for its degradates.

Mobility studies

- Determination of adsorption/desorption constants of atrazine and of G-28279 (batch equilibrium studies). These two studies are acceptable. EAB concurs with the study author's results and conclusions. Results are summarized below:

	ATRAZINE			G-28279		
Soil type	Adsorption		Desorption	Adsorption		Desorption
	K_{ads}	K_{oc}	K_{des}	K_{ads}	K_{oc}	K_{des}
Plainfield sand	0.427	90.9	5.948	0.225	1266	12.479
California sandy loam	0.990	55.0	14.90	0.631	828	6.593
Mississippi silt loam	1.455	121	2.261	0.987	188	1.784
Hagerstown clay loam	2.030	135	3.629	1.144	242	2.792

The results indicated that both atrazine and G-28279 are not strongly adsorbed onto the surfaces of soil particles and that both are easily desorbed from these surfaces.

- Determination of the mobility of atrazine, of G-28279, and of G-28273 in soils by soil thin layer chromatography. These three separate studies may be acceptable if the actual "room temperature" at which the plates were developed can be provided. The studies were done by comparing the mobility of atrazine, G-28279, and G-28273 with that of Amiben, Prometon, 2,4-D, and Ethion under the same experimental conditions. The results, in terms of mobilities as defined by EPA's Subdivision N Guidelines are summarized below.

	Mobility class*(value in parenthesis is the R_f value)		
Soil type	Atrazine	G-28279	G-28273
Plainfield sand	5(1)	5(0.98)	5(1.0)
California sandy loam	3(0.57)	2(0.16)	4(0.72)
Mississippi silt loam	4(0.67)	2(0.18)	3(0.39)
Hagerstown silty clay loam	3(0.51)	3(1.78)	3(0.43)

* 1= Immobile (R_f= 0.0-0.09)
2= Low mobility (R_f= 0.1-0.34)
3= Intermediate mobility (R_f= 0.35-0.64)
4= Mobile (R_f= 0.65-0.89)
5= Very mobile (R_f= 0.90-1.0)

Atrazine and its two degradates G-28279 and G-28273 were very mobile in the sand soil. Mobility of atrazine varied from mobile (silt loam soil) to intermediate mobility (sandy loam and silty clay loam soils). The degradate G-28279 showed low mobility in the sandy loam and silt loam soils. G-28273 was mobile in the sandy loam and of intermediate mobility in the silt loam and silty clay soils.

Degradation studies- field

- Bareground (Hollandale, Minnesota; loam soil, 0-3 feet; silt loam soil, 3-4 feet).
  The authors had based their half-life calculation on the average value of atrazine in the 0-6" soil depth at each time interval. The calculated half-life, assuming first-order kinetics, was 369 days (r^2 value 0.379). The authors admit that this reported half-life is not accurate.
  It must be pointed out that, at 14 days post-treatment, the average residue value of atrazine in the 0-6" depth was twice as high as on day 0 (4.23 ppm at day 0 and 10.15 ppm at day 14). Although the authors attributed this variability to factors such as formulation binding and/or equilibration of the residue with the soil, it can

can also bring questions about the validity of the analytical method and/or the actual application rate used. In fact, the range of recoveries of atrazine and degradates (65-174%, atrazine; 32-179%, degradates) was too wide to accurately assess tthe concentration of these materials in soil. The calculated expected concentration of atrazine immediately after treatment (based on 1-acre, $2x10^6$ lb of soil 6"in depth) should have been 10 ppm and not as low as the reported 4.23 ppm value.

If the issue of the validity of the analytical method and/or of the actual application rate is set aside, there is still a general trend that can be observed. Within the 0-6" depth, the amount of atrazine decrease with time while in subsequent soil depths (6-12", 12-18", 18-24", 24-36", 36-48") there is a gradual increase within each soil depth with time, but with a wide variation of residue levels. After 360 days, the reported atrazine levels in the 0-6", 6-12", 12-18", 18-24", 24-36", 36-48" soil depths were 2.90, 0.52, 0.14, 0.14, 0.15, and 0.08 ppm, respectively. Thus, the presence of atrazine (although in low levels) in the 36-48" soil depth after 360 days (no detectable residues were found before 120 days) indicates that atrazine residues have moved through the soil.

- Corn (pre-emergent), Hollandale, Minnesota. Although the study appears to have been conducted according to EPA's Guidelines, there are some concerns about the data presented. The ranges of recoveries of atrazine and degradates from field soils (76-150%, atrazine; 42-183%, degradates) were too wide to accurately assess the concentration of these materials in soil. Incomplete data were presented; for instance, it was stated that the soil was sampled to a depth of 4-feet, but data were only provided to a depth of 3-feet. The r^2 value (0.56) for the calculated half-life of 291 days was poor, and the authors admit that this reported half-life value is not expected to be accurate. It was also noticed in the report that "for unknown reasons", low levels of atrazine residues were detected at the 0-6" and 6-12" depths (0.07-0.09 ppm) prior to treatment. The field did not have a history of atrazine treatment; other pesticides used prior the studies were Banvel, Amiben, and Sencor.

  In the two studies conducted in Minnesota, the ground remained frozen for 30% of the study period and, therefore, the pattern of decline of atrazine will be more typical of cold winter areas.

- Corn (pre-emergent), Ripon, California (sandy loam soil). Although the study appears to have been conducted following EPA's Guildelines, the ranges of recoveries of atrazine and degradates (65-150%, atrazine; 0-195%, degradates) were to wide to accurately assess the concentration of these materials in soil. Data presented were incomplete. It was stated that the soil was sampled to a depth of 4-feet, but data was only provided to a depth of 3-feet. Dates and amounts of irrigation were not provided. There is no indication in the original document if or when the corn was planted. The reported half-life was 58 days (r^2 0.952). As expected, the dissipation of atrazine in the warmer California weather was faster than in the colder Minnesota soil.

Therefore, because it appears to be inaccuracies in the determination of the concentrations of atrazine and degradates in soils, these soil dissipation studies are not acceptable as presented.

(see p. 10)

Summary of groundwater concerns for ATRAZINE (parent)†

	Trigger factors	Reported values
Solubility(H_2O)	>30 ppm	33 ppm *
Hydrolysis half-life	>25 weeks	>30 days at pH 5,7 and 9; no half-lives were estimated*
Soil half-life	2-3 weeeks	aerobic 140 days* anaerobic 159 days* (from preliminary, 94 days study)
K_d	<5, usually <1 or 2	5.9, sand 14.9, sandy loam 2.26, silt loam* 3.63, clay loam*
K_{oc}	5.3 to 300, most values between 15 and 200	90.9, sand* 55.0, sandy loam* 121, silt loam* 135, clay loam*

† From data submitted by registrant and reviewed by EAB
* Denotes potential concern

The Ground Water Team has recently (1/29/1988) assessed the leaching potential and environmental fate of atrazine (based on published scientific literature) to facilitate a decision on whether atrazine should undergo Special Review. Their conclusion was that atrazine, a persistent pesticide, has a potential for leaching and that levels of atrazine have been found in groundwater in 14 of the 18 states for which monitoring data is available. It was recommended that the registrant conducts a large-scale retrospective groundwater monitoring study.

The data summarized above, taken from data submitted by the registrant, also indicates that atrazine present a potential leaching problem.

8. RECOMMENDATIONS:

161-3: Photodegradation on soil (EPA Accession No.404313-20). If the significant amounts of radioactivity left unidentified at the origin of TLC plates cannot be identified and if the radioactivity distribution in plates cannot be expressed in terms of applied dose, then new studies may be required. In new studies, a methodology other than TLC should be used to confirm the identity of the photodegradation products. For photodegradation on soil studies, the Guidelines indicate that one of the soil should be of the type used in aerobic soil metabolism studies (if the latter are required).

163-1 : Determination of the mobility of atrazine, G-28279, and G-28273 in soils by soil thin layer chromatography(EPA Accession Nos. 404313-29; 404313-31; 404313-33).
The actual "room temperature" at which the plates were developed should be provided in order to accept these studies.

164-1 : Field dissipation studies(soil)(EPA Accession Nos.404313-37; 404313-39; 404313-38).
These studies were not acceptable as presented because of inaccuracies in the determination of the concentrations of atrazine and degradates. Incomplete data were supplied for the pre-emergent corn studies in California and in Minnesota, as indicated in the CONCLUSIONS section.

Refer to the recent (1/29/1988) Ground Water Team assessment of the leaching potential of ATRAZINE, where it was recommended that the registrant conducts a large-scale retrospective groundwater monitoring study.

Only those studies required under GWDCI were reviewed. The following studies are being retained in EAB and will be reviewed as part of the ATRAZINE FRSTR, now scheduled for Fiscal Year 1989:

- Forbis, A.D. 1986. Uptake, depuration, and bioconcentration and metabolite characterization of ^{14}C-atrazine by bluegill sunfish (Lepomis macrochirus). Conducted by Analytical Bio-chemistry Laboratories, Inc., Aquatic Toxicology Division, Columbia, MO. Laboratory study No. 34737. Completed December 31, 1986. EPA Accession No. 404313-44

- Simoneaux, B. 1987. Uptake and characterization of Δ-14-C-atrazine metabolites in greenhouse grown corn. Conducted by Ciba-Geigy Corporation, Greensboro, NC. Laboratory study No. ABR-87103. Completed November 17, 1987. EPA Accession No. 404313-42.

- Simoneaux, B. 1987. Uptake and characterization of Δ-14-C-atrazine metabolites in greenhouse grown rotation plants. Conducted by Ciba-Geigy Corporation, Greensboro, NC. Laboratory study No. ABR-87103. Completed November 17, 1987. EPA Accession No. 404313-43.

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- Schofield, M. 1986. Combined field dissipation and aquatic non-target organism accumulation studies on AATRAEX® NINE-O® for forestry use at Oregon City, Oregon. Conducted by Analytical Bio-chemistry Laboratories, Inc., Columbia, MO. Laboratory study No. 32989. Completed November 1986.
  EPA Accession No. 4304313-40.

- Jefferson, D. 1986. Validation of methods for the analysis of hydroxyatrazine (G-34048) in Oregon Olympic silt loam soil. Conducted by Analytical Bio-chemistry Laboratories, Inc., Columbia, MO. Laboratory study No. 32989. Completed October 29, 1986.
  EPA Accession No. 404313-41.

- Huber, M. and Balu, K. 1987. Summary of environmental fate studies for the reregistration of atrazine. [EPA Guidelines not applicable]. Conducted by Agricultural Division, Ciba-Geigy Corporation, Greensboro, NC. Laboratory study No. EIR-87014. Completed November 9, 1987.
  EPA Accession No. 404313-18.

9. BACKGROUND:

a. Introduction

Atrazine is one of the 140 pesticides currently being evaluated under the Ground-Water-Data-Call-In. In a recent review (January 29, 1988), the Ground Water Team assessed the environmental fate and leaching potential of atrazine (based on published scientific literature) to facilitate a decision on whether atrazine should undergo Special Review. It was the Ground Water Team conclusion that atrazine is a persistent pesticide that has a potential for leaching. Levels of atrazine have also been detected in groundwaters of 14 of the 18 states for which monitoring data is available. Their recommendation was that the registrant conducts a large-scale retrospective groundwater monitoring study, with the purpose of assessing the true extent of atrazine contamination throughout the Nation.

b. Directions for use

Atrazine is atriazine herbicide used in the control of broadleaf and grassy weeds in cor, 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

LABORATORY DEGRADATION STUDIES

Spare, William C. 1986. Determination of the hydrolysis rate constants of atrazine. EPA Accession No. 404313-19 Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1236. Completed December 31, 1986.

Materials and Methods

Test material: [U-ring ^{14}C]-atrazine, Ciba-Geigy Code No. GAN-1X-48, 96.6% purity, specific activity 20.6 uCi/mg.

Buffer solutions:

pH 5, (sodium acetate/acetic acid)
pH 7, (NaH_2PO_4/K_2HPO_4)
pH 9, ($Na_2B_4O_7$/acetic acid)

All glassware and buffer solutions were sterilized.

Stock solutions: The ^{14}C-atrazine (weight unspecified) was dissolved with 10 mL of methanol.

Experimental solutions: 140 mL of the radioactive solution were removed and mixed with 40 mL of the desired buffer solution. The theoretical dose was 5 ppm. Each of these solutions were divided into 20 mL duplicates. The samples were placed in 25 mL screw-capped glass scintillation vials (with teflon lined caps).

Experimental procedure: The vials were covered with foil and placed in an incubator at 25 ± 1 °C. At sampling time (0, 1, 3, 7, 14, 21, and 30 days after dosing), duplicate 20 uL aliquots were removed, radioassayed (LSC to determine volatilization or adsorption losses), and analyzed immediately after sampling by cochromatography (TLC) of the 20 uL aliquots with standard samples. Single-dimension TLC was performed in silica-gel precoated plates, in which the aliquot was spotted (in duplicate plates) at the origin of the plates and then overspotted with nonlabeled atrazine. One of two solvent systems (chloroform/methanol/formic acid/water, 80/15/4/2 by volume; toluene/acetone 75/25, by volume) was used to develop the plates to a solvent front of 15 cm. The air dried plates were visualized under 254 nm-UV light and scanned with a TLC linear analyzer. Standards were confirmed by scanning the developed plate with the analyzer after it had been overspotted with radioactive benzoic acid.

Calculations: A pseudo-first order kinetics was assumed to calculate the hydrolysis half-life of atrazine.

Reported Results and Conclusions

The material balance of total radioactivity is shown in Table I; the average material balance was greater than 96% at all pH levels. Analysis of parent atrazine at each sampling period and at each pH showed that atrazine did not hydrolyze during the 30-day study. Figures 1 through 3 show the observed ppm of atrazine at each pH throughout the 30-day experimental period. Therefore, it was concluded that at environmentally relevant pH and temperature values hydrolysis is not an important degradation mechanism for atrazine.

Reviewer's Comments

The reviewer agrees with the author's conclusion that hydrolysis is not an important degradation mechanism for atrazine.

Atrazine

Page _____ is not included in this copy.

Pages 18 through 21 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.

Spare, William C. 1987. Photodegradation of atrazine on soil surfaces exposed to artificial and natural sunlight. EPA Accession No. 404313-20
Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1237. Completed April 6, 1987.

Materials and Methods

Test material: [U-ring ^{14}C]-atrazine, Ciba-Geigy Code No. GAN-1X-48, specific activity 20.6 uCi/mg and 96% purity.

Soil: California sandy loam soil (58.0% sand, 32% silt, 10% clay, 3.0% organic matter, pH 6.1, 30% field capacity and a cation exchange capacity of 6.0), which was oven dried at 90°C (24 hours) and sieved through a 60-mesh U.S. Standard sieve.

Soil film preparation:

a) soil plates: a 1-cm wide strip of coating was removed from a precoated TLC plate (silica gel), replaced with a slurry of soil/deionized water (1:1 volume), and then dried overnight in an oven at 35 ± 1°C.

b) soil dishes: 2.0 g of prepared soil (soil slurried with 2 mL of water) was spread over the bottom of pyrex glass petri dishes (100 x 15 mm) and then dried overnight in an oven at 35 ± 1°C.

Dose preparation and dosing: The atrazine radiolabeled material was dissolved with 10 mL of methanol. An aliquot (425 uL) of this solution was diluted to 3 mL with methanol (dilution contained 620 ug of atrazine). This dilution was spotted on the soil strips (2 identical 2.1 ug doses, 2 cm apart for each strip; each dose was 10 ppm). The methanol was allowed to evaporate at room temperature. Plates were prepared in duplicate (one of them was covered with foil and used as dark control).

For dosing the petri dishes, 100 uL of the dosing solution were applied (20-to-30, 2-to-4 uL addition each) to each plate. The methanol was allowed to evaporate at room temperature. Dark control dishes were covered with foil.

Light exposure:

a. Artificial sunlight: The soil strips (TLC plates) were placed in an all glass (9" W x 12" L x 4" D) vessels with a pyrex top, with inlet and outlet ports placed in opposite ends of the chamber (which allowed air to pass through the vessel). The artificial light source (450 watt mercury arc lamp) was fitted over the reaction vessel, where the pyrex top served to filter radiation below 290 nm. The emission spectra of the lamp is shown in Table I; the measured (UV meter with a reduction grid) exposure intensity of the lamp ranged from 1800 to 2600 uW/cm^2 (natural sunlight on a clear, sunny July day at the test site in Frederick, MD was 1800 to 2300 uW/cm^2). The artificial light exposure was continuous for 72 hours (equivalent to 6 days of 12 hours of light per day).

b. Natural sunlight: This portion of the study was conducted on the roof of the Laboratory in Frederick, MD (39° 25' North Latitude and 77° 29' West Longitude). The samples were placed on a rack at a 45-degree angle from the surface. Measured natural sunlight intensity ranged from 0 to 6000 + uW/cm^2 during the exposure period with a yellow filter and equivalent to 0 to 2300 uW/cm^2 with the reduction grid. Samples were exposed to natural sunlight for a 45-day period.

Sampling:

a. Artificial sunlight samples (two exposed and two unexposed spots) were removed from the reaction vessel at 0, 1, 4, 22, 30, 48, and 72 hours, covered with aluminum foil, and frozen at -20°C until analyzed.

b. Natural sunlight samples were removed (duplicate exposed-petri dishes and a single dark-control petri dish) at 0, 1/2, 1, 2, 4, 7, 14, 21, 35, and 45 days (except at 35 and 45 days, where only one exposed sample was removed). All dishes were frozen at -20°C until analyzed.

Analyses: Samples exposed to natural sunlight. The soil film was scraped off and transferred into glass scintillation vials. Portions (in duplicate) of soil were combusted to determine total radioactivity. The remaining soil was extracted (acetonitrile/methanol/water, 45/45/10 by volume, 10 mL, shaken and sonicated for 10 minutes). Duplicate aliquots of the extract were removed for LSC (with a scintillation cocktail) and TLC. The extracted soil (in duplicate) was combusted to determined nonextractable radioactive residues.

All soil plates were removed from the freezer, allowed to warm to room temperature, and the origin spots overspotted with the nonradioactive standards [degradates]. Developing solvents were toluene/acetone (75/25 by volume) or chloroform/methanol/formic acid/water (80/15/4/2 by volume). Developed plates were allowed to air dry, then viewed under 254 nm UV light, and scanned for radioactive spots with a linear analyzer fitted with a data acquisition system.

Calculations: Rate constants and half-lives were calculated assuming pseudo-first-order kinetics.

Reported Results and Conclusions

Conditions of exposure to artificial and natural sunlight are shown in Tables II and III, respectively.

Table IV summarizes the results of TLC plates exposed to artificial sunlight, expressed as percents of total radioactivity from the TLC linear analyzer. After 72 hours, the percent of atrazine decreased from 92.9 to 42.2 while the radioactivity at the origin increased from 3.9 to 42.1 percent; this percent radioactivity at the origin includes the degradation products G-34048 and G-28273. Also degradates at the R_f of G-28279 and G-30033 increased from 0.80 percent (at time 0) up to 8 percent (after 72 hours). The calculated half-life was 64 to 88 hours (5 to 7 days) and the rate constant, 0.01086 to 0.00786 (Table V).

A material balance for the samples exposed to natural sunlight is shown in Table VI and Table VII shows the distribution of radioactivity in extracts (as percents from the TLC linear analyzer).

In Table VIII, the photodegradation products under natural sunlight (expressed as percent of dose) are shown. Soil-bound products increased from 10.3 percent (0 hour) to 28 percent after 540 hours; the photoproduct present in the highest amount after 540 hours was G-30033 (18.3%), followed by G-28273 (6.8%) and G-28279 (6.0%). The calculated half-life and rate constant were 143.7 hours (12 days) and 0.00482, respectively (Table IX).

It is the author's conclusion that in both natural and artificial sunlight atrazine degraded rapidly on soil films and that the same photodegradation products were observed from both light sources, but with varying degrees of production.

Figure 1 shows the structures of the main photodegradation products.

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Reviewer's Comments

In Table IV (artificial sunlight) and Tables VII (natural sunlight, toluene/acetone solvent system) and VIII (natural sunlight, percents of photoproducts), it was noticed that significant amounts of radioactivity (ca. 28% Table IV; ca. 19% Table VII; ca. 21% Table VIII) were left unidentified at the origin of TLC plates. Also, in Tables IV and VII, the distribution of radioactivity in plates was not expressed as percent of applied dose.

No other methodology was used to confirm the identity of the photodegradation products.

Atrazine

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LABORATORY METABOLISM STUDIES

Rustum, A.M. 1987. Aerobic, aerobic/anaerobic, and sterile soil metabolism of ^{14}C-atrazine. EPA Accession No. 404313-21 Conducted by Hazleton Laboratories America, Madison, WI. Laboratory Study No. HLA 6015-185. Completed November 6, 1987.

Materials and Methods

Test material: ^{14}C-atrazine (U-ring), specific activity 20.6 uCi/mg (4.57×10^{10} dpm/g); 95.4% radiopurity.

Soil: California loam soil (51.% sand, 37% silt, 12% clay, 1.4% organic matter, pH 7.6, cation exchange capacity 7, field moisture capacity 12 (0.33 bar)). The soil was sieved through a 2-mm mesh screen.

Fortification solution: a ^{14}C-fortified atrazine solution was prepared in methanol (103 ug ^{14}C-atrazine and 100 ug nonlabeled atrazine) to yield 100 uL aliquots containing 4.73×10^{6} dpm and a final specific activity of 10.5 uCi/mg.

Sample preparation and incubation:

a) Biologically active soils. The soil was assayed for microbial activity before initiation of the study. Approximately 20 g soil (dry weight) portions were placed in each of 26 jars. A 100 uL aliquot of the fortified ^{14}C-atrazine solution was added to each jar (10.2 ppm, dry weight basis). The solvent was evaporated, the jars were capped, hand-tumbled (about 2 minutes) to distribute the test material, and water was added as to achieve a moisture content of 75 percent (0.33 bar).

b) Biologically sterile soils. To each of 16 jars, 20 g of soil (dry basis) were added. Then water was added to adjust the soil moisture to 75 percent (0.33 bar). The jars were capped (silicon sponge lids) and autoclaved at 120 °C (50 minutes). The fortification solution was added to 14 of the jars (100 uL aliquots per jar) by injection through the silicon lids and then the jars were tumbled for 2 minutes. The concentration of atrazine per jar was 10.2 ppm (dry weight basis). The other two jars were used to determine the microbial activity at day 0 and 94.

Aerobic incubation and sample collection:

The jars (biologically active and sterile samples) were placed in the aerobic incubation chamber shown in Figure 1a. Air flowed through at a rate of approximately 100 mL/min and the temperature was kept at 25 ± 1°C, in a dark room (temperature monitored). The traps for organic volatiles and CO_2 contained ethylene glycol (organic volatiles) and 2-ethoxyethanol:ethanolamine (1:1 by volume) for CO_2. The water trap served to protect the vacuum system from corrosive solvent vapors. The moisture content was maintained at 0.33 bar. Biologically active soil was sampled (in duplicate) at 0, 3, 7, 14, 32, 62, and 94 days, and the corresponding CO_2 and organic volatile traps at 3, 7, 14, 21, 32, 47, 62, 84, and 94 days. The sterile soil was sampled (in duplicate) at 0, 7, 14, 21, 32, 47, 62, 80, and 94 days and the corresponding traps at 3, 7, 14, 21, 32, 47, 62, 80, and 94 days.

Anaerobic incubation and sample collection:

After 32 days, four jars from the biologically active aerobic study were removed, covered with nitrogen-purged water (2-to-3 cm) and placed in the incubation chamber (Figure 1b), where nitrogen was continuously circulated. The chamber was kept in the dark at 25 ± 1°C. Traps (connected in series) containing ethylene glycol (to remove organic volatiles; 2-ethoxyethanol:ethanolamine, 1:1 by volume, to remove CO_2) were connected to the chamber; a water trap placed after the other traps served to collect potentially harmful solvent vapors. Samples were assayed (in duplicate) 30 and 62 days after flooding, which corresponded to 62 and 94 days after fortification, respectively. Traps (CO_2 and volatile organics) were sampled at 30, 52, and 62 days after flooding.

Extraction:

a) Aerobic samples: Each soil sample was mixed with solvent (about 30 mL, acetonitrile: water, 9:1) by shaking and then stirring the mixture for approximately 15 minutes (stirring bar), then followed by centrifugation (extraction was performed twice per sample). Decantates were collected in a round-bottom flask and concentrated to the water layer (rotary evaporation).

After quantitatively transferring the water layer to a separatory funnel, the round-bottom flask was rinsed three times with dichloromethane (DMC) and the rinses transferred to the funnel (beginning with Day 80 sterile sampling, the round bottom flask was also rinsed with Multi-Q water after the DMC rinses and the rinses were then combined in the funnel).

The aqueous phase was partitioned twice with DMC (about 30 mL each time). Duplicate aliquots of the resulting organosoluble and aqueous fractions were quantitated by LSC.

b) Anaerobic samples: Soil and aqueous phases were separated by centrifugation. Each decanted water layer was partitioned twice with chloroform (50 mL each time). The organic and aqueous phases were quantified by LSC. Soil samples were extracted as described for the aerobic samples.

Analysis

a) Trapping media: Radioactivity in traps was determined by LSC (duplicate aliquots).

b) Nonextractable residues: Extracted soil samples (in duplicate) were oxidized to CO_2. The CO_2 was trapped and the radioactivity determined by LSC.

c) TLC: Organic phases of aerobic, anaerobic, and sterile samples were concentrated and aliquots applied to TLC plates along with nonradiolabeled atrazine and/or available nonradiolabeled metabolic standards. Two plates were spotted for each sampling time. One plate was developed in toluene:acetone (75:25, Solvent System I) and the other in chloroform:methanol:formic acid:water (100:20:4:2, Solvent System II). Two-dimensional TLC was performed on a selected basis, with chloroform:methanol:formic acid:water (70:25:4:2) in one direction and toluene:HOAc:water (50:50:2) in the second direction, with the purpose of quantifying atrazine and metabolites G-34048, GS-17794, and GS-17792. Solvent System I was superior in separating (and quantifying) parent atrazine from metabolites and was used for half-life determinations. Solvent System II was superior for separating organosoluble metabolites and was used in their quantification. The distribution of radioactivity on each TLC plate was determined with a linear analyzer. Nonradiolabeled standards were located under UV light. Quantitation by LSC was done by scraping the appropriate zone from the plate. The material balance was determined based on the total radioactivity applied to the plates.

Reported Results and Conclusions

a) Aerobic incubation (active, 94 days incubation; final results after approximately 1 year aerobic incubation will be reported later). The overall material balance for the study ranged from 96.6 percent to 101.7 percent. The radioactivity in the organosoluble fraction decreased from a mean value of 96.9 percent (day 0) to 59.1 percent (day 94) while in the aqueous fraction it increased from 0.7 percent (day 0) to 3.9 percent (day 94). Soil-bound radioactivity continuously increased from 4.1 percent (day 0) to 33.3 percent (day 94).

No radioactivity associated with volatile organic material was detected and the amount of $^{14}CO_2$ formed during the experiment reached a cumulative total of 0.3 percent at day 94 (Table I).

Table II shows the decrease of the mean value of atrazine from day 0 (90.7%) to day 94 (56.5%). Assuming first-order kinetics based on a 94-day incubation period the degradation of atrazine was calculated as approximately 140 days (correlation coefficient - 0.952). Table II also shows the distribution of radioactivity through the 94-day incubation period. Metabolites G-30033 and G-28279 were present at all sampling times but G-28273 was absent at days 62 and 94; G-34048, which did not exceed 1.0%, was not detected until days 62 and 94.

b) Aerobic incubation (sterile). Table III shows the material balance (mean values), which ranged from 95.3 to 115.9 percent. The radioactivity in the organosoluble fraction decreased from 98.6 percent (day 0) to 78.5 percent (day 94); however, it increased to 99.6 and 103.3 percent at days 97 and 62, respectively. In the aqueous fraction, the mean value increased from 0.5 (day 0) to 1.1% (day 94). Soil-bound residues increased from 3.6 (day 0) to 16.9 percent (day 94) but no radioactivity was detected in the organic volatiles or $^{14}CO_2$ traps at the end of the 94-day period. Comparison of the decrease of atrazine from day 0 (93.7%) to day 94 (77.4%) under sterile conditions with the amounts under active conditions indicated that degradation of atrazine in soil is primarily a microbial process. The metabolites G-30033, G-28279, G-28273, G-34048, and an unidentified one were detected. In all sample points, G-30033, and G-28279 were detected in amounts less than 2 percent of the total applied radioactivity. Table IV summarizes the distribution of atrazine and its metabolites throughout the 94-day sterile incubation.

c) Anaerobic incubation. Table V shows the distribution of radioactivity in the different fractions and the material balance, which ranged from 99.5 to 100.6 percent. In the organosoluble fraction, the radioactivity decreased from 70.6 percent (mean value, day 0 of anaerobic incubation) to a combined total (water plus soil matrices) after 62 days of anaerobic incubation. Soil-bound residues increased from a mean value of 26.7 percent (day 0 of anaerobic incubation) to 40.9 percent (day 62 anaerobic incubation), which is slightly higher than the soil-bound residues after 94 days aerobic incubation. No significant amounts of organic volatiles of $^{14}CO_2$ were detected in the traps. Parent atrazine decreased from 67.0 percent (day 0 of anaerobic incubation) to a mean value of 51.2 percent at day 62 of anaerobic incubation.

The calculated half-life for atrazine under anaerobic conditions (assuming first-order kinetics) was approximately 159 days. The identified metabolic products were G-30033, G-28279, G-28273, and G-34048. Both G-30033 and G-28279 were identified at all sample points of both the soil-extracted and water-decanted matrices; G-30033 decreased slightly throughout the anaerobic incubation period. Table VI shows the distribution of atrazine and metabolites throughout the anaerobic incubation period.

Reviewer's comments

This study is only a preliminary report (94-day study instead of the 12-month study required by the Subdivision N Guidelines). Therefore, it is to be considered a supplemental study to the final report.

Atrazine

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Spare, William C. 1987. Anaerobic aquatic metabolism of atrazine. EPA Accession No. 404313-23
Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1231. Completed October 1, 1987.

Materials and Methods

Sediment: The sediment was obtained from a farm pond in Georgia. The sediment and pond water were used as received within 24 hours of receipt. The characteristics of the sediment and water were:

Texture	sandy clay
Percent Sand	46.8
Percent Silt	6.4
Percent Clay	46.8
pH	7.2
Cation Exchange Capacity (meq/100 g)	4.1
Percent Organic Matter	0.2
Percent Field Capacity	25.9
Water - Total Alkalinity	43.0
Total Hardness	42.0
Total Suspended Solids (mg/L)	6.0
pH	8.2

Test material: [U-ring ^{14}C-atrazine], specific activity 20.6 uCi/mg, 96% purity and analytical standard.

Test solutions and dosing of samples: The radioactive stock solution was prepared by dissolving ^{14}C-atrazine (1.46 mg/mL) in methanol. The nonradioactive stock solution was prepared at a concentration of 9.69 mg/mL in methanol. For the dosing solution, 5 mL of the radioactive stock solution were combined with 0.7 mL of the nonradioactive stock solution. To sterile pond water (50 mL), 203.6 uL of the dosing solution were added while for anaerobic incubations 1100 mL of pond water were dosed with 4.478 mL of the dosing solution. The calculated dose was 10.1 ppm (zero time analysis performed directly on dosed water).

Metabolism chamber: To each 100 mL-erlenmeyer flask containing 25 g (dry weight) of sediment, 50 mL of the dosed pond water were added. The flasks were covered with foil and stoppered with teflon-coated rubber stoppers. The flasks were connected in series to $^{14}CO_2$ traps, as shown in Figure 1. Aeration was accomplished by bubbling nitrogen (60 mL/min) for 1 hour four times per day. For sterile incubations, the nitrogen was purified by bacterial filters. All systems were maintained at 25 ± 1 °C.

Incubations:

a) Anaerobic chambers: Twenty-four flasks were used (10 for anaerobic and 2 for sterile sampling periods, each in replicate) and connected as indicated above. Anaerobic conditions were monitored with an anaerobic indicator.

b) Sterile chambers: Flasks (four), prepared as for anaerobic incubation, were autoclaved for 1 hour at 15 pounds of pressure at 121 °C. Pond water was autoclaved separately under the same conditions. After autoclaving, the flasks were prepared as described for anaerobic incubation.

Sampling: Zero-time sampling involved analysis of dosed sterile and active water. Active anaerobic test systems were removed from incubation at 1, 3, 7, and 14 days and at 1, 2, 3, 6, 9, and 12 months. Sterile flasks were analysed at 6 and 12 months. Replicate test systems were removed and analysed at each sampling interval. Analyses consisted of characterization of residual parent and metabolites in water and sediment. Trapping solutions were analysed for $^{14}CO_2$ and volatile metabolite production.

Analyses: Carbon-14 radioactivity measurements were done by LSC. Sediment samples were oxidized to $^{14}CO_2$ and then counted.

Metabolites in water samples were characterized by first centrifuging the samples to separate the water phase from the sediment, counting directly the aliquots of the water, and then spotting a replicate portion on TLC plates. Sediment samples were extracted with methanol/water, 90/10 (100 mL) by mechanical shaking, removing the sediment by vacuum filtration, and rinsing the sediment several times with dichloromethane. Rinses and extract were evaporated, redissolved in acetone, counted for radioactivity, and spotted for TLC. Bound residues in extracted sediments were quantified by combustion to $^{14}CO_2$.

TLC plates (2 per each sampling interval) were spotted with extract and overspotted with nonradioactive parent. Nonradioactive metabolite standards were chromatographed in a separate column. Two solvent systems were used: chloroform/methanol/formic acid/water (80/15/4/2 by volume) and toluene/acetone (75/25 by volume), developed

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to a 15 cm solvent front. Radioactive zones were scanned with a linear analyzer and visualized under 254 nm light.

Calculations: The metabolic rate constant was calculated assuming pseudo-first order degradation,

$$\ln C = -kt + \ln C_o$$

k = rate constant
C = chemical concentration
t = time (days)
C_o = initial concentration

$$\text{where } t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Reported Results and Conclusions

The radiocarbon balance is shown in Table I. For the active aerobic incubations, it ranged from 83.8 to 108.1 percent of the original dose. Table II shows the TLC results. Production of volatile products was minimal (< 1%) through 6 months of anaerobic aquatic incubation, with some increase noted in the amount of bound residues, which leveled at about 10 percent of dose by 12 months. By 12 months most of the radioactivity was associated with parent atrazine (about 70% in the water and 4% in the sediment). Metabolites were present at low levels: G-30033 (4.7%, 0.48 ppm), G-34048 (5%, 0.52 ppm), and G-28279 (1.4%, 0.14 ppm).

Table III show the half-life and rate constant calculations. The anaerobic aquatic metabolism of atrazine is depicted in Figures 2 and 3. The half-lives of atrazine in water and sediment were different (330 days sediment and 578 days water). A combined water/sediment calculation showed a half-life of 608 days.

In sterile samples, above 80% of the radioactivity remained as atrazine (Table IV).

Reviewer's comments

This study was found acceptable. EAB concurs with the study author's conclusions.

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Atrazine

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Klaine, S.J. 1987. Biotic and abiotic degradation of atrazine and three of its metabolites in a West Tennessee Soil. Conducted by Department of Biology, Memphis State University, Memphis, TN 38152. Laboratory Study No. TX-431. Completed October 22, 1987.

Materials and Methods

Test material:

a. Radioactive materials (atrazine and metabolites)
   1. [U-ring-^{14}C]-atrazine, 25.6 uCi/mg, 99% purity
   2. [U-ring-^{14}C]-hydroxyatrazine, 23.5 uCi/mg, 99% purity
   3. [U-ring-^{14}C]-deisopropylatrazine, 13.7 uCi/mg, 99% purity
   4. [U-ring-^{14}C]-deethyltatrazine, 21.3 uCi/mg, 99% purity

b. Reference standards (atrazine and metabolites) (1), (2), (3), and (4), corresponding purities of 98.2%, 98%, > 90%, approximately 99%, and approximately 95%.

All solvents were of HPLC grade

Soil: The soil used was obtained from three sites within an 18 ha field at the Agricenter International in Shelby County, TN. The primary soil is a Falaya silt loam, with organic matter content 0.9% and pH ranging from 5.0 to 5.5. Soils were characterized according to ASTM procedures [but no actual results of the analyses were presented in the report]. The operations that had occurred in the experimental field prior to the tests are summarized in Figure 1. Note that there is a history of atrazine use in the experimental field.

Analysis of atrazine and metabolites in soils: Prior to the start of each assay, background atrazine and metabolite concentrations were determined in the soil samples from each of the three sites. Soil samples were also analyzed at each sampling date. The extraction procedure used is outlined in Figure 2.

Soil microcosms: Intact soil cores were obtained using 125 mL serum bottles, which had the bottoms cut off. This "coring device" provided a microcosm when sealed at the bottom, which could provide an undisturbed system for study in situ degradation. Abiotic degradation rates were determined with irradiated soil samples, in which the soil was added to 125 mL serum sample (intact), then sealed, and exposed to 1.35 x 10^6 RAD over a 12-hr period (Oak Ridge Laboratories). All soil microcosms were brought to 80% field holding capacity and incubated at 25 °C.

Dosing: Microcosms were dosed at rates equivalent to field application rates of atrazine (2.20 kg/ha) and those dosed with ^{14}C metabolites at 0.5 kg/ha each. The incubation system is shown in Figure 3. The activities in the various components of the microcosms were determined by oxidation of aliquots in a biological oxidizer and LSC of aliquots of the trapping solution used in the oxidizer.

Reported Results

a) [U-ring-^{14}C]-atrazine microcosm.

Material balances are shown in Table I for days 25, 100, and 180 and in the irradiated microcosm. $^{14}CO_2$ and nonextractables increased with time. At 180 days, $^{14}CO_2$ accounted for 12.14% of the total added radioactivity and nonextractables for 41.17%. Total ^{14}C extractables (organic and aqueous) decreased from 72.6% (25 days) to 28.76 (180 days). The organic extracts decreased from 50.34% (day 25) to 5.43% (day 180); this fraction contains parent atrazine and the metabolites deethylatrazine and deisopropylatrazine. The aqueous soluble fraction increased to 15.28% on day 100, but then decreased to 7.52% on day 180; this fraction would include hydroxylated metabolites of atrazine. One of these, hydroxyatrazine, increased in concentration by day 100.

In the irradiated microcosms (determinations only after 180 days) the maximum ^{14}C-activity was associated with nonextractables. Extractables were 1.5-fold greater than in nonirradiated microcosms after 180 days. $^{14}CO_2$ evolution was 0.06% compared to 12.14% for nonirradiated microcosms, which represents a difference of 200-fold between the two systems and thus, indicate the importance of the biological contribution.

Table II shows the atrazine and metabolite concentrations at 25, 100, and 180 days after application on a soil dry weight basis; total concentrations of atrazine and metabolites are shown in Table III. Atrazine decreased from 5.36 ug/g of soil (day 0) to 0.04 ug/g soil after 180 days, with a subsequent increase in concentration of the three metabolites as shown in Figure 4. The concentration of hydroxyatrazine was the highest at the conclusion of the study (0.41 ug/g soil). The half-lives for atrazine at 25, 100, and 180 days were 18, 19, and 26 days, respectively, with an average half-life value of 21 days. In irradiated microcosms, atrazine concentration decreased from 7.72 ug/g soil (day of application) to 0.11 ug/g soil (180 days), with concentrations of metabolites at day 180 about 2-fold greater than in nonirradiated microcosms.

b) [U-ring-^{14}C]-hydroxyatrazine microcosm.

Table IV shows the material balances for this metabolite. By day 180, evolution of $^{14}CO_2$ in nonirradiated microcosms was 20.99% of the total label added and nonextractables accounted for 32.90%. Total extractables (organic and aqueous phases) were 77.25% after 25 days and 35.61% (day 180), the aqueous soluble fraction (which contain the parent hydroxyatrazine) decreased from 58.03% (day 25) to 19.73% (day 180), but the dealkylated metabolites were not analyzed.

In the irradiated microcosm (determined only after 180 days), extracted ^{14}C-activity accounted for 44.77% (lost during partitioning). Nonextractables were 24.50%. $^{14}CO_2$-activity was 0.87%, compared to the 20.99% found in nonirradiated microcosms and which is a 24-fold difference.

The concentrations of hydroxyatrazine in soil microcosms (on a soil dry weight basis) at sampling days 25, 100, and 180 after application are shown in TAble V and the total concentrations of hydroxyatrazine appear on Table VI. Concentration of hydroxyatrazine in soil decreased from 1.24 ug/g soil (day 0) to 0.41 ug/g soil (180 days, Figure 5). The half-lives on the three sampling days 25, 100, and 180 were 128, 116, and 117 days, respectively, with an average half-life value of 120 days.

In irradiated microcosms, the concentration of hydroxyatrazine decreased from 1.75 ug/g soil (day of application) to 0.76 ug/g soil (day 180), which is a 2-fold greater than in nonirradiated microcosms.

c) [U-ring-^{14}C]-deisopropylatrazine microcosm

Table VII shows the material balance for ^{14}C-deisopropylatrazine. The $^{14}CO_2$ evolved increased and reached 16.38% at day 180; nonextractables increased and reached 60.33% of the label after 180 days. The total extractables decreased from 56.57% (after 30 days) to 10.91% (day 180); the organic soluble fraction decreased from 6.59% (day 30) to 0.62% (day 180). The organic fraction contains the parent deisopropylatrazine and soluble residues.

In irradiated microcosms (determined only after 180 days), the greatest percentage of activity (59.91%) was associated with nonextractables. Extractable ^{14}C-activity was 28.45% and was about 3-fold greater than extractable radioactivity in nonirradiated microcosms. Evolution of $^{14}CO_2$ was 1.76%, compared to 16.38% in nonirradiated microcosms (9-fold difference).

Concentrations of deisopropylatrazine on a soil dry weight basis are presented in Table VIII and total concentrations are shown in Table IX. Deisopropylatrazine decreased from 1.20 ug/g

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soil on day 0 to 0.02 ug/g soil (180 days). The half-lives at sampling dates 30, 60, and 180 were 14, 20, and 32, respectively; the average half-life value is 22 days. In irradiated soils, deisopropylatrazine concentration decreased from 1.75 ug/g soil (day of application) to 0.04 ug/g soil (day 180), which is 2-fold greater than in nonirradiated microcosms.

d) [U-ring-^{14}C]-deethylatrazine microcosms

Table X shows the material balance for ^{14}C-deethylatrazine determined at 30, 60, and 180 days and 180 days for nonirradiated and irradiated microcosms, respectively. Evolved $^{14}CO_2$ in nonirradiated microcosms reached 24.72% at day 180 (the highest observed) and nonextractables reached 66.92%. Extractables decreased from 54.99% (day 30) to 6.30% (day 180). The organic soluble fraction, which contains the parent deethylatrazine and soluble residues, decreased from 19.34% (day 30) to 0.43% (day 180).

In irradiated soils, the highest percentage of ^{14}C-activity was found in the nonextractable component (49.16%). Extractables (total) were 46.45% after 180 days. Evolution of $^{14}CO_2$ was only 0.63%, compared to 24.72% in nonirradiated microcosms, which is a 39-fold difference between nonirradiated and irradiated microcosms.

The concentrations of deethylatrazine (on a soil dry weight basis) at 30, 60, and 180 days for nonirradiated microcosms, and 180 days for irradiated microcosms, are shown in Table XI and the total concentrations in Table XII. In nonirradiated microcosms, ^{14}C-deethylatrazine decreased from 1.22 ug/g soil (day 0) to 0.02 ug/g soil after 180 days. The half-lives at 30, 60, and 180 days were 26, 26 and 31 days, respectively; the average half-life is 28 days.

In irradiated soil microcosms, the concentration of deethylatrazine decreased from 1.75 ug/g soil (day 0) to 0.08 ug/g soil on day 180, which was 4-fold greater than in nonirradiated microcosms.

Author's Conclusions

Biotic degradation rates of atrazine and the three metabolites were significantly greater in nonirradiated microcosms than in irradiated ones. Although some $^{14}CO_2$ evolution occurred in irradiated microcosms (thus questioning sterility), it did not exceed 1% except for microcosms dosed with ^{14}C-deisopropylatrazine (1.8%). The degradation rates of the phytoxic metabolites deisopropyl- and deethylatrazine were similar to the parent compound and indicate that neither metabolite would persist exceedingly longer than the parent. The nonphytoxic hydroxyatrazine

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metabolite exhibited the lowest degradation rate, but total $^{14}CO_2$ evolved was high, indicating that the microbial degradation of this metabolite is comparable to the rate of the chlorinated dealkylatrazines despite its apparent persistence in the environment.

For ^{14}C-atrazine, the concentration decreased from 5.36 to 0.04 ug/g soil during the 180-day experimental period. After 100 days, concentration of hydroxyatrazine had increased to 0.50 ug/g soil, with the dealkylated metabolites increasing to 0.02 and 0.11 ug/g soil (deisopropyl and deethylatrazine metabolites, respectively), but decreased afterwards. At the termination of the experimental period, the concentration of hydroxyatrazine was the highest (0.41 ug/g soil). The half-life of atrazine in non-irradiated microcosms was 21 days.

The concentration of metabolite in soil microcosms decreased during the 180-day incubation study (hydroxyatrazine 1.24 to 0.41 ug/g soil; deisopropylatrazine, 1.20 to 0.02 ug/g soil; deethylatrazine, 1.22 to 0.02 ug/g soil) and half-lives of 120, 22, and 28 days for hydroxyatrazine, deisopropylatrazine, and deethylatrazine, respectively.

Nonextractable ^{14}C-activity in nonirradiated soils increased with time and ranged from 33% (hydroxyatrazine) to 67% (deethylatrazine), but high levels of nonextractable activity was also observed in irradiated soil microcosms. Total extractables decreased during the incubation period.

Mineralization (i.e., CO_2 evolution) of atrazine and its metabolites was a significant degradation path.

It is the author's conclusion that biotic processes can significantly reduce atrazine and metabolite concentrations.

Reviewer's comments

No actual results of the soil analysis were shown in the report. It was noted that pages 11 and 13 of the report are identical.
The mass balance for the atrazine microcosm study was somewhat low (81-94%) for total accounted ^{14}C activity and high for unaccounted ^{14}C activity (6.5-19%).
For the ^{14}C-deisopropylatrazine microcosm there is a discrepancy between the text and table (Table 11 of the report) with respect to the days when material balances were determined (30, 60, and 180 days in text; 25, 100, and 180 days in the Table).

Atrazine

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LABORATORY MOBILITY STUDIES

Yu, W.C. 1986. Determination of adsorption/desorption constants of atrazine. EPA Accession No. 404313-24
Conducted by Cambridge Analytical Associates, Inc., Boston, MA.
Laboratory Study No. 59-1A. Completed February 14, 1986.

Materials and Methods

Soils: Four soil types were used (Plainfield sand, California sandy loam, Mississippi silt loam, and Hagerstown clay loam) were used. Characteristics of these soils were shown in Table 1. The soils were oven-dried at 90 °C (24 hr) and autoclaved at 120 °C (30 min) prior to use.

Test material: [U-ring-^{14}C]-atrazine, specific activity 30.4 uCi/mg, purity >90% and analytical standard (non-radioactive) atrazine.

Test solution: A sterilized stock solution containing 10 ug/mL of atrazine, prepared by dissolving 0.5 mg of the ^{14}C-atrazine and 3.5 mg of the nonlabeled atrazine in 400 mL of 0.01 N calcium ion solution in deionized water was used for the preliminary experiments. The 10 ug/mL radioactive stock solution for the definitive study was prepared as before. From this solution, aqueous dilutions (5 ug/mL, 1 ug/mL, 0.5 ug/mL, 0.2 ug/mL) were made with sterile 0.01 N calcium ion solution as the diluent. This calcium ion solution was also used as a blank solution.

Experimental Method

In order to establish the appropriate ratio of soil to stock solution and the equilibration time, preliminary studies were conducted with the sandy soil (< 1% organic matter), since it was anticipated that the measured adsorption constants would be smaller with this soil than with those of higher organic matter content.

Definitive Study

a) Adsorption: Four grams of each of the four different soils were placed (in duplicate) in 50 mL Pyrex centrifuge tubes for each test solution concentration. Twenty mL of test solution (0.00, 0.20, 0.50, 1.0 and 5.0 ug/mL of atrazine) were transferred to the appropriate container, capped and shaken for 24-hrs in a shaker bath (200 agitations/min; 25 °C). Then the tubes were centrifuged and the equilibrium concentration (C_e) of atrazine determined in all the solutions.

b) Desorption: The desorption phase of the study was performed on the atrazine-adsorbed soil samples. The wet soil samples were weighed (to correct final calculations for any water still remaining with the soil) prior to the addition of the blank 0.01 N calcium ion solution (20 mL per tube). The samples were shaken for 24-hr as in the adsorption phase. Then the samples were centrifuged and the supernatant was analyzed by LSC to determine the equilibrium concentration (C_e).

Control samples (^{14}C-atrazine solution without soil; 0.01 N calcium ion solution with and without soil) were included to assess any possible interferences.

Analytical Methods

Actual concentration of ^{14}C-atrazine in stock solutions was determined by HPLC. All solutions from the adsorption/desorption experiments were analyzed by LSC (i.e., ^{14}C-atrazine in the aqueous phase). Soils were extracted with methylene chloride and the extracts analyzed for ^{14}C-atrazine by LSC.

Calculations: All calculations were based on the Freundlich equation,

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

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

where, x/m is the soil equilibrium concentration, ug/g
C_e, aqueous phase equilibrium concentration, ug/mL
K_d, Freundlich sorption constant
$1/n$ empirical exponent

Plots of ln C_e versus ln x/m were done for adsorption and desorption and the values n and K_d were determined by linear regression analysis.

K_d can also be expressed in terms of the soil organic matter content:

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

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

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Reported Results

The actual atrazine concentration in the stock solution (as determined by HPLC) was 9.70 ug/mL and, thus, the actual test concentration for the adsorption study were 0.19, 0.49, 0.97 and 4.85 ug/mL of atrazine.

Logarithmic plots of x/m vs C_e yielded a straight line for all four soils, for both adsorption and desorption, as shown in Figures 1 and 2. The results of linear regression analysis for the adsorption and desorption phases are shown in Tables II and III, respectively. The K_{ads} constants ranged from 0.427 (sand) to 2.030 (loam soil). The K_{des} constants ranged from 2.261 (silty loam) to 14.90(sandy loam), which indicated that atrazine 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

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Yu, W.C. 1986. Determination of adsorption/desorption constants of G-28279. EPA Accession No. 404313-25
Conducted by Cambridge Analytical Associates, Inc., Boston, MA.
Laboratory Study No. 59-4A. Completed February 17, 1986.

Materials and Methods

Soils: The following 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-^{14}C]-G-28279, specific activity 13.7 uCi/mg and radiochemical purity 99% and analytical G-28279 standard were used.

Test solution: A stock solution of G-28279 of a nominal concentration of 10 ug/mL was prepared by dissolving 1.9 mg ^{14}C-G-28279 and 4.1 mg of analytical G-28279 in a small amount 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 this 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 the dilutions were determined by HPLC and gave the following values: 9.9 ug/mL (stock solution); 0.02, 0.50, 0.99, and 4.95 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 ^{14}C-G-28279 solutions and blank 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 and the equilibrium concentration (C_e),the supernatants removed, and the equilibrium concentration (C_e) determined.

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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 a shaker bath (200 agitations/min), then centrifuged, and the supernatant analyzed by LSC to determine the equilibrium concentration.

Analytical Methods

All solutions were analyzed by LSC of ^{14}C-G-28279 in the aqueous phase. Methylene chloride was used to extract ^{14}C-G-28279 for analysis by LSC.

Calculations: 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 and 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 $K_{oc} = (K_d \times 100)/\%$ 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 2 and 3 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. For the adsorption phase K_{ads} varied between 0.225 (sand) and 1.144 (loam soil). For the desorption phase, K_{des} varied between 1.784 (silty loam) and 12.479 (sand). Thus, these results indicated that G-28279 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.

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Atrazine

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Blair, J.E. 1986. Determination of the mobility of atrazine in selected soils by soil thin layer chromatography. EPA Accession No. 404313-29
Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-300. Completed March 7, 1986.

Materials and Methods

Test material: ^{14}C-atrazine, specific activity 30.4 uCi/mg and > 99% radiopurity. ^{14}C-labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion (the structures of these reference compounds are shown in Figure 1).

Soil: 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 (20 x 20 cm) were prepared by placing a tape strip 17 cm away from one edge of the plate. An area of 20 x 17 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 0.01 to 0.03 uCi of one of the following: Atrazine, 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 each strip 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, atrazine 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). Atrazine was of high mobility class (5) in Plainfield sand, intermediate mobility (3) in California sandy loam and Hagerstown silty clay loam and mobile (4) in Mississippi silt loam. Atrazine was in the same or a lower mobility class than any of the reference standards, except Ethion.

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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Pages 112 through 114 are not included.

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Blair, J.E. 1986. Determination of the mobility of G-28273 in selected soils by soil thin layer chromatography. EPA Accession No. 404313-33

Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-305. Completed February 27, 1986.

Materials and Methods

Test material: ^{14}C-G-28273, specific activity 14.1 uCi/mg, radiopurity of 98%. ^{14}C-labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion (the structures of these reference compounds are shown in Figure 1).

Soil: 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 (20 x 20 cm) were prepared by placing a tape strip 17 cm away from one edge of the plate. An area of 20 x 17 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 0.11 uCi of one of the following: G-28273, 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 each strip was determined by autoradiography. 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 type, G-28273 was determined in triplicate, but each standard was determined once. Based on the frontal R_f values, a mobility class was assigned. A sorption coefficient (K) was determined by

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

R_f = relative migration of the compound relative to water
O = 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 2 presents the frontal R_f values, mobility classes, and calculated sorption coefficients (K) for G-28273 and reference pesticides. G-28273 was classified of the highest mobility class (5) in the Plainfield sand, intermediate mobility (3) in Hagerstown silty clay loam and Mississippi silt loam, and mobile (4) in the California sandy loam soil.

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-28279 in selected soils by soil thin layer chromatography. EPA Accession No. 404313-31
Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-304. Completed February 27, 1986.

Materials and Methods

Test material: ^{14}C-G-28279, specific activity 13.7 uCi/mg and radiopurity of 99%. ^{14}C-labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion (the structures of these compounds are shown in Figure 1).

Soil: 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 (20 x 20 cm) were prepared by placing a tape strip 17 cm away from one edge of the plate. An area of 20 x 17 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-28279, 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 each strip was determined by autoradiography. 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 type, G-28279 was determined in triplicate, but each standard was determined once. Based on the frontal R_f values, a mobility class was assigned. A sorption coefficient (K) was determined,

$$K = \frac{1/R_f - 0^{2/3}}{D\,(1 - 0^{2/3})}$$

R_f = relative migration of the compound relative to water
0 = 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 2 presents the frontal R_f values, mobility classes, and calculated sorption coefficients (K) for G-28279 and reference pesticides. G-28279 was of the highest mobility (5) in Plainfield sand, of intermediate mobility (3) in Hagerstown silty clay loam, and a low mobility (2) in California sandy loam and Mississippi silt loam.

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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DISSIPATION STUDIES (SOIL)- FIELD

DATA EVALUATION RECORD

CASE -- ATRAZINE STUDY 1 PM --

CHEM 080803 Atrazine

BRANCH EAB

FORMULATION--XX--DRY FLOWABLE

FICHE/MASTER ID 40431337 CONTENT CAT 01

White, S. M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on bareground, Hollandale, MN. Laboratory Study No. 1641-86-71-01-21E-25. Prepared by Landis Associates, Inc., Valdosta, GA; Agri-Growth Research, Inc., Hollandale, MN; and Minnesota Valley Testing Labs., Inc., New Ulm, MN; and submitted by Ciba-Geigy Corporation, Greensboro, NC.

SUBST. CLASS = S

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

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Feb. 25/88

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

This study is unacceptable because the analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil (recovery of atrazine from fortified samples ranged from 65 to 147%, and recovery of its degradates ranged from 32 to 179%). Howerer, this study appears to have been conducted according to EPA Data Requirements for Registering Pesticides.

Ancillary Study - Freezer Storage Stability

This study is unacceptable because details of the methodology were incomplete, so that it could not be determined if atrazine and its degradates were stable in frozen soil.

SUMMARY OF DATA BY REVIEWER:

Field Dissipation - Terrestrial

Atrazine (90% dry flowable) was applied at a nominal concentration of 20 lb ai/A to a field plot of unvegetated loam soil located in Minnesota in July, 1986. In the 0- to 6-inch depth, atrazine was 4.23 ppm (5.06 ppm total residues) immediately after treatment, increased to 10.15 ppm (11.66 ppm total) at 14 days, decreased to 5.34 ppm (6.75 ppm total) at 28 days, and was 2.90 ppm (4.88 ppm total) at 360 days posttreatment. The major degradate was 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (hydroxy-atrazine; G-34048) at up to 1.21 ppm. 2-Amino-4-chloro-6-isopropylamino-s-triazine (G-30033) and 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279) were <1 ppm in the 0- to 6-inch depth throughout the study. In deeper soil, total atrazine residues (atrazine plus the degradates G-34048, G-30033, and G-28279) were most concentrated at 360 days posttreatment; residues were detected in the 6- to 12-inch depth at up to 1.14 ppm, in the 12- to 18-inch depth at up to 0.24 ppm, in the 18- to 24-inch depth at up to 0.14 ppm, in the 24- to 36-inch depth at up to 0.15 ppm, and in the 36- to 48-inch depth at up to 0.08 ppm.

Ancillary Study - Freezer Storage Stability

Atrazine ranged from 0.985 to 1.188 ppm, G-28279 ranged from 0.930 to 1.400 ppm, and G-30033 ranged from 0.988 to 1.996 ppm in soil fortified at approximately 1 ppm and stored frozen for up to 145 days. Concentrations did not appear to be related to length of storage.

DISCUSSION:

Field Dissipation - Terrestrial

1. The analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil. Recovery from fortified soil samples ranged from 65 to 147% for atrazine (average 100.4%), 60 to 165% for 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279; average 107.3%), 60 to 179% for 2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033; average 106.8%), and 32 to 147% for 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (G-34048; average 81.9%).

2. Data for soil samples taken immediately after treatment appear to be inaccurate, either because of uneven application to the bare soil in the field or analytical errors. Atrazine was applied to the test plots at a nominal concentration of 20 lb ai/A; measurements during spraying ranged from 13.93 to 20.50 lb ai/A (average 16.28 + 2.65 lb ai/A). Assuming that 1 acre, 6-inch depth equals 2,000,000 pounds of soil, the expected concentration of atrazine in the soil immediately after treatment would be approximately 10 ppm (7-10 ppm based on spray drift data). However, the measured concentration at time 0 was 4.23 ppm of atrazine (5.06 ppm total residues) which was much lower than expected. Also, subsequent samples are much more concentrated than day 0; at 14 and 28 days, the measured concentration of atrazine was 10.15 and 5.34 ppm, respectively.

3. The study author calculated a half-life of 369 days with an r^2 value of 0.379. Because of the poor correlation, the study author stated that the calculated half-life was inaccurate.

4. The ground was frozen for 30% of the study period. The pattern of decline of atrazine would be typical of cold winter areas; atrazine would be expected to dissipate faster in warmer areas.

5. During the first 14 days following treatment, 2.95 inches of rain were received, air temperatures ranged from 56 to 90°F, and soil temperatures (4-inch depth) ranged from 64 to 91°F. Between 14 and 28 days posttreatment, 0.93 inches of rain were received, air temperatures ranged from 56 to 92°F, and soil temperatures ranged from 67 to 100°F. During the entire test period, total precipitation was approximately 28.36 inches, and high and low air temperatures ranged from -1 to 97°F and -17 to 75°F, respectively.

Ancillary Study - Freezer Storage Stability

1. Insufficient details about the methodology were provided to review. The soil was described only as being obtained in New Ulm, Minnesota. It was not stated whether each soil sample represents a separate treatment, or if soil was treated, homogenized, and then subsampled. It was not stated if the soils were frozen moist or dry. The freezer temperature was not reported.

2. No freezer storage stability data were provided for G-34048.

3. Apparently the soil was not analyzed immediately after treatment to confirm the application rate.

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STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

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Atrazine

Page_____ is not included in this copy.

Pages 130 through 141 are not included.

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_____ 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.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Field Dissipatation - Terrestrial

Atrazine (90% dry flowable, Ciba-Geigy Corporation) was applied at 20 lb ai/A to an unvegetated field plot (50 x 50 feet) of loam soil (47.5% sand, 37.5% silt, 25% clay, 6.2% organic matter, pH 7.9, CEC 23.9 meq/100 g) that was located in Hollandale, Minnesota, on July 2, 1986. One untreated control plot was located approximately 150 feet from the test plot. Soil (three cores per plot; 0- to 6-, 6- to 12-, 12- to 18-, 18- to 24-, 24- to 36-, and 36- to 48-inch depths) from the treated and control plots was sampled prior to treatment, immediately after treatment, and at intervals up to 360 days posttreatment using a combination of excavation and hydraulic probe techniques. The samples from each depth were air-dried, then mixed to yield one composite sample for analysis. The samples were frozen until analysis.

A portion of each soil sample was extracted by refluxing for 2 hours with methanol:water (90:10). The extracts were concentrated and analyzed for atrazine, G-30033, and G-28279 by GC with nitrogen-phosphorous detection. In order to extract G-34048 from the soil, additional soil was Soxhlet-extracted overnight in methanol:water (80:20). The extract was evaporated to remove methanol and filtered through a XAD-4 column. Aliquots of the extracts were analyzed by HPLC. The detection limits were 0.05 ppm for atrazine and its degradates.

Ancillary Study - Freezer Storage Stability

Soil from New Ulm, Minnesota, was treated with either atrazine, G-28279, or G-30033 at approximately 1 ppm. The soil was stored frozen (temperature and moisture content unspecified) for up to 145 days. Samples were analyzed on days 1, 7, and 145 using methods described in the field dissipation portion of this study.

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Atrazine

Page______ is not included in this copy.

Pages 144 through 155 are not included.

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_____ 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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DATA EVALUATION RECORD

CASE -- ATRAZINE STUDY 2 PM --

CHEM 080803 Atrazine

BRANCH EAB

FORMULATION--XX--DRY FLOWABLE

FICHE/MASTER ID 40431339 CONTENT CAT 01

White, S. M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on corn, Hollandale, MN. Laboratory Study No. 1641-86-71-01-06B-24. Prepared by Landis Associates, Inc., Valdosta, GA; Agri-Growth Research, Inc., Hollandale, MN; and Minnesota Valley Testing Labs., Inc., New Ulm, MN; and submitted by Ciba-Geigy Corporation, Greensboro, NC.

SUBST. CLASS = S

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

REVIEWED BY: R.Tamma
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: S. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

(S. Termes)
Feb. 26/1988

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

This study is unacceptable because the analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil (recovery of atrazine from fortified samples ranged from 76 to 150%, and recovery of its degradates ranged from 42 to 183%). However, this study appears to have been conducted according to EPA Data Requirements for Registering Pesticides.

SUMMARY OF DATA BY REVIEWER:

Atrazine (90% dry flowable) was applied at a nominal concentration of 4.4 lb ai/A to a field plot of loam soil planted to corn located in Minnesota in June, 1986. In the 0- to 6-inch depth, atrazine was 1.20 ppm (1.37 ppm total residues) immediately after treatment, increased to 1.40 ppm (1.59 ppm total) at 2 days, ranged from 0.48 to 1.00 ppm (0.90-1.17 ppm total) with no discernable pattern between 7 and 290 days, and was 0.37 ppm (0.91 ppm total)

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at 360 days posttreatment. The major degradates were 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (hydroxy-atrazine; G-34048) at up to 0.20 ppm and 2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033) at up to 0.30 ppm. 2-Amino-4-chloro-6-ethylamino-s-triazine (G-28279) was 0.1 ppm in the 0- to 6-inch depth throughout the study. Atrazine residues (atrazine plus the degradates G-34048, G-30033, and G-28279) were detected in the 6- to 12-inch depth at up to 0.29 ppm (days 0 and 95), but were not detected (<0.05 ppm) in the 12- to 18-, 18- to 24-, and 24- to 36-inch depths at any sampling interval.

DISCUSSION:

1. The analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil. Recovery from fortified soil samples ranged from 76 to 150% for atrazine (average 111.7%), 76 to 183% for 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279; average 108.5%), 56 to 143% for 2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033; average 107.6%), and 42 to 142% for 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (G-34048; average 83.3%).

2. The study author calculated a half-life of 291 days with an r^2 value of 0.56.

3. The ground was frozen for 30% of the study period. The pattern of decline of atrazine would be typical of cold winter areas; atrazine would be expected to dissipate faster in warmer areas.

4. During the first 2 days following treatment, 1.15 inches of rain were received, air temperatures ranged from 68 to 92°F, and soil temperatures (4-inch depth) ranged from 72 to 93°F. Between 2 and 7 days posttreatment, 0.80 inches of rain were received, air temperatures ranged from 52 to 90°F, and soil temperatures ranged from 62 to 85°F. Between 7 and 13 days posttreatment, 0.42 inches of rain were received, air temperatures ranged from 55 to 86°F, and soil temperatures ranged from 64 to 93°F. During the entire test period, total precipitation was approximately 28.36 inches, and air temperatures ranged from -17 to 97°F.

5. The freezer storage stability study included with this document was reviewed in Study 1 of this addendum.

6. Although the registrant stated that soil was sampled to a depth of 4 feet, data were provided only to a depth of 3 feet.

7. Based on concentrations measured during spraying, the actual application of atrazine was 2.63-3.36 lb ai/A (2.95 ± 0.27 lb ai/A).

STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

Atrazine

Page_____ is not included in this copy.

Pages 159 through 169 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.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Atrazine (90% dry flowable, Ciba-Geigy Corporation) was applied at 4.4 lb ai/A to a field plot (50 x 50 feet) of loam soil (47.5% sand, 37.5% silt, 25% clay, 6.2% organic matter, pH 7.9, CEC 23.9 meq/100 g) that was located in Hollandale, Minnesota, on June 20, 1986. The plot had been planted to field corn on June 17, 1986. One untreated control plot was located approximately 150 feet from the test plot. Soil (three cores per plot; 0- to 6-, 6- to 12-, 12- to 18-, 18- to 24-, and 24- to 36-inch depths) from the treated and control plots was sampled prior to treatment, immediately after treatment, and at intervals up to 360 days posttreatment using a combination of excavation and hydraulic probe techniques. The samples from each depth were air-dried, then mixed to yield one composite sample for analysis. The samples were frozen until analysis.

A portion of each soil sample was extracted by refluxing for 2 hours with methanol:water (90:10). The extracts were concentrated and analyzed for atrazine, G-30033, and G-28279 by GC with nitrogen-phosphorous detection. In order to extract G-34048 from the soil, additional soil was Soxhlet-extracted overnight in methanol:water (80:20). The extract was evaporated to remove methanol and filtered through a XAD-4 column. Aliquots of the extracts were analyzed by HPLC. The detection limits were 0.05 ppm for atrazine and its degradates.

Atrazine

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____ 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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DATA EVALUATION RECORD

CASE -- ATRAZINE STUDY 3 PM --

CHEM 080803 Atrazine

BRANCH EAB

FORMULATION--XX--DRY FLOWABLE

FICHE/MASTER ID 40431338 CONTENT CAT 01
White, S. M. 1987. Field dissipation study on Aatrex Nine-O for terrestrial uses on corn, Ripon, CA. Laboratory Study No. 1641-86-71-01-06B-22. Prepared by Landis Associates, Inc., Valdosta, GA; Research for Hire, Porterville, CA; and Minnesota Valley Testing Labs., Inc., New Ulm, MN; and submitted by Ciba-Geigy Corporation, Greensboro, NC.

SUBST. CLASS = S

DIRECT RVW TIME = 12 (MH) START-DATE END DATE

REVIEWED BY: R.Tamma
TITLE: Staff Scientist
ORG: Dynamac Corp., Rockville, MD
TEL: 468-2500

APPROVED BY: S. Termes
TITLE: Chemist
ORG: EAB/HED/OPP
TEL: 557-1981

STermes
Feb 25/1988

SIGNATURE:

CONCLUSIONS:

Field Dissipation - Terrestrial

This study is unacceptable because the analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil (recovery of atrazine from fortified samples ranged from 65 to 150%, and recovery of its degradates ranged from 0 to 195%). However, this study appears to have been conducted according to EPA Data Requirements for Registering Pesticides.

SUMMARY OF DATA BY REVIEWER:

Atrazine (90% dry flowable), applied at a nominal concentration of 3.96 lb ai/A to a field plot of sandy loam soil located in California in July, 1986, dissipated with a registrant-calculated half-life of 58 days (r^2 0.952). In the 0- to 6-inch depth, atrazine was 1.15 ppm (1.15 ppm total residues) immediately after treatment, increased to 2.82 ppm (2.82 ppm total) at 7 days, decreased to 1.18 ppm (1.18 ppm total) at 14 days, decreased to 0.50 ppm (0.74

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ppm total) at 60 days, and was 0.02 ppm (0.53 ppm total) at 358 days posttreatment. The major degradates were 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (hydroxy-atrazine; G-34048) at up to 0.49 ppm. 2-Amino-4-chloro-6-isopropylamino-s-triazine (G-30033) and 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279) were 0.08 ppm in the 0- to 6-inch depth throughout the study. Atrazine residues (atrazine plus the degradates G-34048, G-30033, and G-28279) were detected in the 6- to 12-inch depth at up to 0.31 ppm (day 267), but were not detected (<0.05 ppm) in the 12- to 18-, 18- to 24-, and 24- to 36-inch depths at any sampling interval.

DISCUSSION:

1. The analytical method was inadequate to accurately assess the concentration of atrazine and its degradates in field soil. Recovery from fortified soil samples ranged from 65 to 150% for atrazine (average 100.7%), 51 to 195% for 2-amino-4-chloro-6-ethylamino-s-triazine (G-28279; average 96.0%), 56 to 164% for 2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033; average 107.7%), and 0 to 114% for 2-hydroxy-4-ethylamino-6-isopropylamino-s-triazine (G-34048; average 24.8%).

2. During the first 7 days following treatment, 0.03 inches of rain were received and air temperatures ranged from 51 to 99°F. Between 7 and 14 days posttreatment, no rain was received and air temperatures ranged from 54 to 100°F. Between 14 and 60 days posttreatment, 0.15 inches of rain were received and air temperatures ranged from 46 to 99°F. During the entire test period, total precipitation was approximately 9.02 inches, and air temperatures ranged from 22 to 104°F.

3. The freezer storage stability study included with this document was reviewed in Study 1 of this addendum.

4. Field records provided in the original document indicate that the plots were irrigated. The dates and amounts of irrigation were not reported.

5. Although the registrant stated that the atrazine was applied as a preemergent to corn, there in no indication in the original document if or when the corn was planted.

6. Although the registrant stated that soil was sampled to a depth of 4 feet, data were provided only to a depth of 3 feet.

7. Based on concentrations measured during spraying, the actual application of atrazine was 1.06-4.53 lb ai/A (2.94 ± 1.40 lb ai/A).

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STUDY AUTHOR(S)'S RESULTS AND/OR CONCLUSIONS

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Atrazine

Page_____ is not included in this copy.

Pages 187 through 197 are not included.

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_____ Identity of product inert ingredients.

_____ Identity of product impurities.

_____ Description of the product manufacturing process.

_____ Description of quality control procedures.

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_____ 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) __________.

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MATERIALS AND METHODS

MATERIALS AND METHODS:

Atrazine (90% dry flowable, Ciba-Geigy Corporation) was applied at 3.96 lb ai/A to a field plot (50 x 50 feet) of sandy loam soil (55.0% sand, 32.5% silt, 12.5% clay, 1.3% organic matter, pH 7.3, CEC 12.2 meq/100 g) that was located in Ripon, California, on July 23, 1986. One untreated control plot was located approximately 150 feet from the test plot. Soil (three cores per plot; 0- to 6-, 6- to 12-, 12- to 18-, 18- to 24-, and 24- to 36-inch depths) from the treated and control plots was sampled prior to treatment, immediately after treatment, and at intervals up to 358 days posttreatment using a combination of excavation and hydraulic probe techniques. The samples from each depth were air-dried, then mixed to yield one composite sample for analysis. The samples were frozen until analysis.

A portion of each soil sample was extracted by refluxing for 2 hours with methanol:water (90:10). The extracts were concentrated and analyzed for atrazine, G-30033, and G-28279 by GC with nitrogen-phosphorous detection. In order to extract G-34048 from the soil, additional soil was Soxhlet-extracted overnight in methanol:water (80:20). The extract was evaporated to remove methanol and filtered through a XAD-4 column. Aliquots of the extracts were analyzed by HPLC. The detection limits were 0.05 ppm for atrazine and its degradates.

Atrazine

Page_____ is not included in this copy.

Pages 200 through 210 are not included.

The material not included contains the following type of information:

_____ Identity of product inert ingredients.

_____ Identity of product impurities.

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_____ The product confidential statement of formula.

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__✓__ FIFRA registration data.

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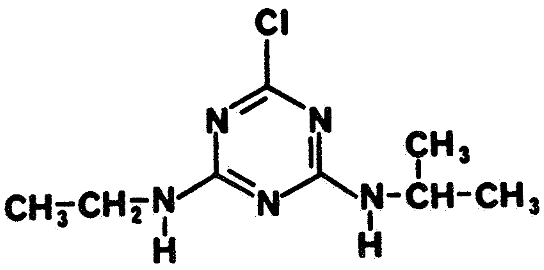
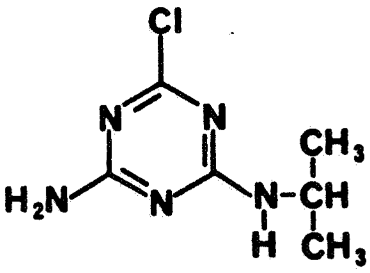
ATRAZINE AND ITS DEGRADATES



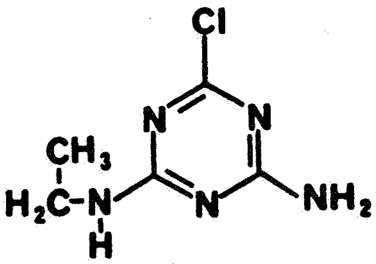
2-Chloro-4-ethylamino-6-isopropylamino-s-triazine

(Atrazine)



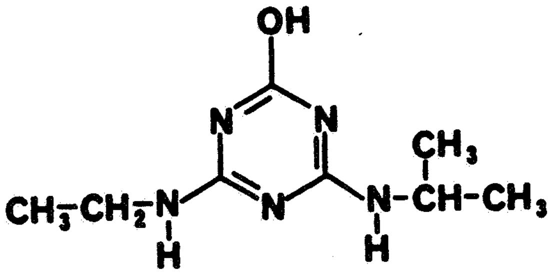
2-Amino-4-chloro-6-isopropylamino-s-triazine

(G-30033)



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

(G-28279)



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

(G-34048)