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DYNAMAC
CORPORATION

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ATRAZINE SRR

**VOLUME I. DEGRADATION STUDIES
(LABORATORY)**

**METABOLISM STUDIES
(LABORATORY)**

**MOBILITY STUDIES
IN SOIL (LABORATORY)**

**Task 1: Review and Evaluation
of Individual Studies**

**Task 2: Environmental Fate
Assessment**

November 18, 1988

Final Report

Contract No. 68-02-4250

**Submitted to:
Environmental Protection Agency
Arlington, VA 22202**

**Submitted by:
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ATRAZINE

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INTRODUCTION

Atrazine is a selective herbicide developed to control broadleaf weeds on terrestrial food crop, ornamental, terrestrial nonfood, and forestry sites. Agricultural uses include corn, sorghum, sugarcane, pineapple, and macademia nuts. Nonagricultural uses include forest and Christmas tree plantations, turf (warm season only), fence rows, and rights-of-way. Single active ingredient formulations consist of 0.42-8% G, 0.46-8% P/T, 12-90% WP, 22.5-90.1% DF, 2-6 lb/gal and 14.2-43% EC, 1-6.25 lb/gal and 16.3% FLC, and 2-4 lb/gal and 40-48% SC/L. Atrazine may be formulated in multiple active ingredient products which contain other herbicides such as alachlor, cyanazine, metolachlor, and simazine. Atrazine is applied to food crop sites at 0.3-8 lb ai/A and to nonfood sites at 0.11-40 lb ai/A. Applications may be made using ground equipment and/or aircraft. Applications include preplant, preemergence, and postemergence broadcast or band treatments. An estimated 78.4-99 million pounds a.i. were used in the U.S. during 1985-1987. Agricultural uses comprise ≈93% of the annual usage, including field corn (83%), sorghum (10%), sugarcane (1%), sweet corn, popcorn, fallow wheat, macademia nuts, miscellaneous fruits, forage grasses, and noncrop agricultural land; each <1% of the total usage. Turf constitutes the major nonagricultural use, accounting for 1% of the total annual domestic usage. Treated areas should not be entered until sprays have dried.

DEGRADATION STUDIES
(LABORATORY)

DATA EVALUATION RECORD

STUDY 1

CHEM 080803

Atrazine

§161-1

FORMULATION--00--RADIOLABELED ACTIVE INGREDIENT

FICHE/MASTER ID 40431319

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. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

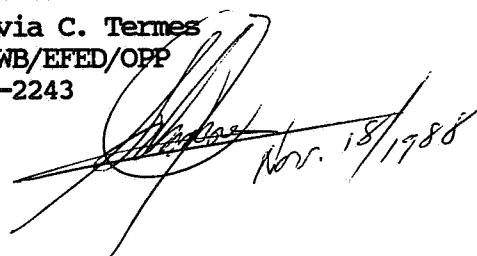
REVIEWED BY: Silvia C. Termes

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CONCLUSIONS:

This study is acceptable and fulfills EPA Data Requirements for Registering Pesticides for hydrolysis studies (§161-1).

It was shown that at the environmentally significant pH 5, 7, and 9, atrazine did not hydrolyze during the 30-day study. Thus, it was concluded that hydrolysis is not an important degradation mechanism for atrazine.

MATERIALS AND METHODS:

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

Buffer solutions:

pH 5, (sodium acetate/acetic acid)
pH 7, ($\text{NaH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$)
pH 9, ($\text{Na}_2\text{B}_4\text{O}_7/\text{acetic acid}$)

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 deg. C. At sampling time (0, 1, 3, 7, 14, 21, and 30 days after dosing), duplicate 20 μL aliquots were removed, radioassayed (LSC to determine volatilization or adsorption losses), and analyzed immediately after sampling by cochromatography (TLC) of the 20 μL aliquots with standard samples. Single-dimension TLC was performed in silica-gel pre-coated 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 value 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.

PERTINENT DATA TABLES AND FIGURES

-1.4-

Atrazine

Page _____ is not included in this copy.

Pages 10 through 13 are not included.

The material not included contains the following type of information:

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

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

DATA EVALUATION RECORD

STUDY 2

CHEM 080803

Atrazine

§161-2

FORMULATION--90--FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00024328

Burkhard, N. and Guth, J.A. 1976. Photodegradation of atrazine, atraton, and ametryne in aqueous solution with acetone as a photosensitizer. Pesti. Sci. 7(1):65-71.

DIRECT REVIEW TIME = 5

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CONCLUSIONS:

Degradation - Photodegradation in Water

This study, which was previously reviewed and found to fulfill data requirements at the time of the (1983) Registration Standard, is unacceptable under current Subdivision N Guidelines because of the following reasons:

- a) the material balances were not provided (the majority of samples were analyzed only for atrazine),
- b) it could not be determined whether the test solutions were sterile or nonsterile,
- c) the artificial light source was incompletely characterized and was not compared to natural sunlight,
- d) degradates were analyzed only in the 6-hour sensitized solution sample,
- e) the test solutions were not buffered,

- f) the purity and specific activity of the test substance were not reported, and
- g) the test solutions were incubated at 15°C instead of 25°C.
- h) One unidentified degradate comprised 10% of the applied dosage.
- i) Electronic absorption spectrum of the test material under experimental conditions was not included in the report.

The reported results indicate, however, that the presence of sensitizers increased the rate of degradation (reportedly a 3- to 11-fold increase).

SUMMARY OF DATA BY REVIEWER:

Ring-labeled [¹⁴C]atrazine (test substance not further characterized), at 10 ppm, degraded with a registrant-calculated half-life of 25 ± 2 hours in unbuffered aqueous solutions (initial pH 6.8) that were irradiated with a 125-W mercury vapor lamp at 15°C; in unbuffered aqueous solutions sensitized with 1% acetone, the half-life decreased to 4.9 ± 0.5 hours. The stated intensity of the light source was 2000 ± 600 J/m²s. In the sensitized solutions after 6 hours of irradiation, atrazine comprised 30% of the applied radioactivity, . . .

2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033) comprised 16%,

2,4-diamino-6-chloro-s-triazine (G-28273) comprised 15%,

2-amino-4-chloro-6-ethylamino-s-triazine (G-28279) comprised 5%, and

one unidentified degradate comprised 10%.

DISCUSSION:

1. Material balances were not provided or were incomplete. The unsensitized solution and the majority of samples from the sensitized solution were analyzed only for atrazine. The 6-hour irradiated sensitized solution was analyzed for atrazine and its degradates, but only 76% of the applied radioactivity was accounted for.
2. It was not stated whether the test solutions were sterile.
3. The characterization of the mercury vapor lamp was incomplete. The spectral energy distribution of the artificial light source was not provided, and the artificial light source was not compared to natural sunlight.
4. The test solutions were not buffered.
5. The purity and specific activity of the test substance were not reported.
6. The test solutions were incubated at 15°C instead of 25°C.

7. Data were reported in terms of "%"; it was not specified if "%" referred to percent of the applied radioactivity, percent of extractable radioactivity, or percent of the radioactivity recovered from the TLC plate. Since the data do not sum to 100%, the reviewer believes the data are most probably percent of the applied and has referred to the data as such in the summary.
8. Data for the degradation of atrazine during irradiation were presented in graph form only and the graph was small and of poor quality; no numerical data were provided. It may be that the irradiated solutions were sampled only three or four times during the study. No data were provided to support the study author's statement that atrazine was stable during 96 hours of incubation in the dark.
9. The method detection limit and recovery efficiencies from fortified samples were not reported.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Ring-labeled [^{14}C]atrazine (test substance not further characterized) was added at 10 ppm to unbuffered (initial pH 6.8) aqueous solutions and to aqueous solutions that had been sensitized with 1% acetone. The solutions were placed inside a Sondex glass "cooler" to filter wavelengths <290 nm and irradiated using a Philips HPK 125-W mercury vapor lamp (intensity $2000 \pm 600 \text{ J/m}^2\text{s}$, spectral energy distribution not provided) at 15°C. As a control, sensitized and unsensitized solutions were incubated in the dark at 15°C. The solutions were sampled at intervals up to 96 hours posttreatment.

A portion of each solution was extracted with ethyl acetate. An aliquot of each ethyl acetate extract was analyzed for atrazine by GC with alkali flame ionization detection. The remainder of the ethyl acetate extract from the sensitized solution sampled after 6 hours of irradiation was concentrated by rotary evaporation, and then [^{14}C]residues were separated by TLC on silica gel plates developed in acetonitrile:water:formic acid (94:5:1). Radioactive areas on the TLC plate were scraped off of the plates, dissolved in acetone, and analyzed by GC.

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Photodegradation of Atrazine, Atraton and Ametryne in Aqueous Solution with Acetone as a Photosensitiser

Niklaus Burhard and Johann A. Guth

Ciba-Geigy Ltd, Agrochemical Division, Basle, Switzerland
(Manuscript received 13 July 1975)

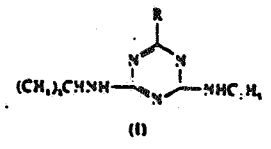
The use of acetone as a photosensitiser on the rate of photodegradation of atrazine, atraton and ametryne in diluted aqueous solutions increased degradation 3- to 11-fold. The mechanism of the sensitised photochemical reaction was studied. The photochemical stability increased in the order methylthio- < chloro- < methoxy-1,3,5-triazines. Sensitised photolysis of atrazine, ametryne and atraton yielded the analogous two de-N-alkyl- and the de-N,N-dialkyl- products as well as the corresponding hydroxy-triazines; irradiation of ametryne also resulted in the formation of demethylthio-1,3,5-triazines. With the exception of demethylthio-triazine formation, sensitised photodecomposition of these triazine herbicides yields no other breakdown products than those obtained by enzymatic and chemical reactions.

1. Introduction

Since symmetrical triazines are among the most widely used herbicides, their behaviour in the environment is vitally important. Photodecomposition is known to be an important factor influencing the performance as well as the fate of pesticides in the field. First observations on changes in the ultraviolet spectra of illuminated 1,3,5-triazine solutions and a decrease in their phytotoxicity were described by Comes and Timmons¹ and Jordan et al.² A first insight into the mechanism of photolytic breakdown of 1,3,5-triazines was provided by Plimmer et al.³ Later, Pope and Zabik⁴ studied the photodegradation of halo-, methylthio-, methoxy- and hydroxy-1,3,5-triazines in various alcohols and water caused by light of wavelengths 254 and 300 nm. Ruzo et al.⁵ reported on the kinetics of photodecomposition of selected 1,3,5-triazines in methanol, butan-1-ol and, to a limited extent, in water on irradiation with light at 300 nm.

The above mentioned investigations on the mechanism of triazine photolysis were carried out without photosensitisers and at relatively high concentrations which are unlikely to occur under environmental conditions. It is well known that many surface waters contain dissolved organic materials, such as humic substances, that strongly absorb ultraviolet and visible light and therefore can act as photosensitisers for other non-absorbing compounds. The influence of photosensitising chemicals on the rate and the route of breakdown of various pesticides has been noted.⁶⁻⁸

The present paper deals with the influence of acetone as a photosensitiser on the rate of photodecomposition and with the mechanism of the sensitised photolysis using atrazine (I, R = Cl), ametryne (I, R = CH₃S) and atraton (I, R = CH₃O) as model compounds. The experiments were carried out in dilute aqueous solutions using a closed photochemical reactor, the usefulness of which has been discussed elsewhere.¹⁰



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2. Experimental

2.1. Photochemical procedure

Aqueous solutions (250 ml) of 10 mg/litre of (ring-¹⁴C)-atrazine, -ametryne and -atraton, respectively, were exposed to artificial light in a photochemical reactor. Photolysis was sensitised by acetone (1 ml/100 ml). Simultaneous "dark-reactions" were carried out to examine if, during the photodegradation study, additional hydrolytic breakdown had occurred. The solution temperature was maintained at approximately 15 C during the experiments. The initial pH value of the aqueous triazine solutions was 5.8.

2.2. Photochemical equipment

The laboratory experiments were carried out in a DEMA photochemical reactor (Hans Mangel, Rorsdorf Bonn, Germany), a magnetically stirred system consisting of a 250 ml reaction vessel, a cooler made from Schott glass, which absorbs the short u.v. light (< 290 nm), and a Philips HPK 125 W mercury vapour lamp (Philips AG, Zurich, Switzerland). The radiation energy level of the u.v. lamp was found to be 2000 = 300 J.m⁻².s⁻¹ (measured with a YSI-Kettering radiometer, Yellow Springs Instrument Co., Ohio, USA).

2.3. Analytical equipment

2.3.1. Thin-layer chromatography

Thin-layer chromatography (t.l.c.) was accomplished on silica gel plates with fluorescent indicator (SL 100, 0.25 mm, ANTEC AG, Birsfelden, Switzerland). The solvent systems were acetonitrile:water:formic acid (4-5-1) and chloroform:methanol:formic acid:water (80-15-4-2), respectively.

2.3.2. Gas-liquid chromatography

Gas-liquid chromatographic (g.l.c.) analyses were carried out with an Aerograph 1400 instrument (Varian Aerograph, Walnut Creek, California, USA) equipped with an alkali flame-ionisation detector (AFID) with rubidium sulphate pellet. The porous-gate glass column (60 cm x 2 mm i.d.) used in all analyses was filled with a 1:1 mixture of 2°, neopentyl glycol succinate and 2° "FFAP" on "Chromosorb G". The column temperatures ranged from 190 to 230 C (isothermal conditions) and the helium carrier gas flow was 50 ml/min.

2.3.3. High pressure liquid chromatography

High pressure liquid chromatography (h.p.l.c.) was accomplished with a Siemens S 200 Liquid Chromatograph (Siemens AG, Karlsruhe, Germany) equipped with a Zeiss PM 4, u.v. and visible spectrophotometric detector (Carl Zeiss, Jena, Germany). The stainless steel column (50 cm x 3.0 mm i.d.) was packed with SIL-X, a superficially porous silica gel, particle size 36-45 μm (Perkin-Elmer, Norwalk, Conn., USA). The mobile phase used was acetonitrile containing distilled water and formic acid (0.75-2%, of each). The flow rate was 1.5-2.5 ml/min.

2.3.4. Measurement of radioactivity

The ¹⁴C activity in solutions was measured with a Packard 2411 liquid scintillation spectrometer (Packard Instrument Company, Downers Grove, Illinois, USA) and the distribution of radioactivity on t.l.c. plates was measured with a Berthold Thin-Layer-Scanner II (Prof. Dr Berthold, Wildbad, Germany).

2.4. Analysis

For kinetic measurements, aliquots of the aqueous solutions were extracted with ethyl acetate after different exposure times and the extracts analysed by g.l.c. For isolation and characterisation of the photolysis products formed, the ethyl acetate extracts were concentrated on a vacuum rotary

Photodegradation

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3.1. Kinetics

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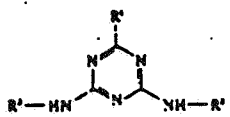
Photodegradation of 1,3,5-triazines

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evaporator and subjected to t.l.c. The radioactive zones were scraped off the plates, the compounds extracted with acetone and further identified by g.l.c. The hydroxytriazines formed during photolysis were determined directly in the water phases using h.p.l.c. R_f values, retention times and chemical structures of the original triazine herbicides and their photoproducts are given in Table 1. Authentic specimens of the compounds listed were obtained by Dr D. Berrer, Pesticides Research Laboratories, Ciba-Geigy Ltd, Agrochemicals Division, Basle, Switzerland.

Table 1. Structures and analytical data for 1,3,5-triazines and their photoproducts



Compound	R ¹	R ²	R ³	Chromatographic data			
				Gas-liquid		Thin-layer	
				Temp. (°C)	Retention time (min)	R_f values	
Atrazine	Cl	Et	Pr ⁱ	230	1.0	—	0.72
	Cl	H	Pr ⁱ	230	1.5	—	0.64
	Cl	Et	H	230	1.8	—	0.60
	Cl	H	H	230	3.0	—	0.53
Ametryne	SMe	Et	Pr ⁱ	230	1.2	—	0.76
	SMe	H	Pr ⁱ	230	1.9	—	0.53
	SMe	Et	H	230	2.3	—	0.49
	SMe	H	H	230	3.7	—	0.45
Atraton	OMe	Et	Pr ⁱ	190	1.0	—	0.50
	OMe	H	Pr ⁱ	190	1.3	—	0.33
	OMe	Et	H	190	1.8	—	0.50
	OMe	H	H	190	3.0	—	0.23
	H	Et	Pr ⁱ	220	1.0	0.41	0.19
	H	H	Pr ⁱ	220	1.7	0.27	0.19
	H	Et	H	220	2.2	0.22	0.17
	H	H	H	220	3.7	0.03	0.15
	OH	Et	Pr ⁱ	—	—	0.24	—
	OH	H	Pr ⁱ	—	—	0.11	—
OH	Et	H	—	—	0.08	—	
OH	H	H	—	—	0.00	—	

Solvent systems: 1. chloroform-methanol-formic acid-water (50-15-4-2).
 2. acetonitrile-water-formic acid (94-3-1).

3. Results and discussion

3.1. Kinetics

The results of the kinetic studies on the photolysis of atrazine, ametryne and atraton are graphically presented in Figure 1. The degradation curves demonstrate that the photolysis of the above triazines was strongly sensitised by acetone. With the exception of the sensitised photolysis of atraton, all curves were linear which indicated first order reaction kinetics. The rate constants (k^1) and half-lives ($t_{1/2}$) were calculated using the equations:

$$k^1 = \frac{\ln c_0 - \ln c}{t} \quad (\text{time}^{-1})$$

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N. Burkhard and J. A. Guth

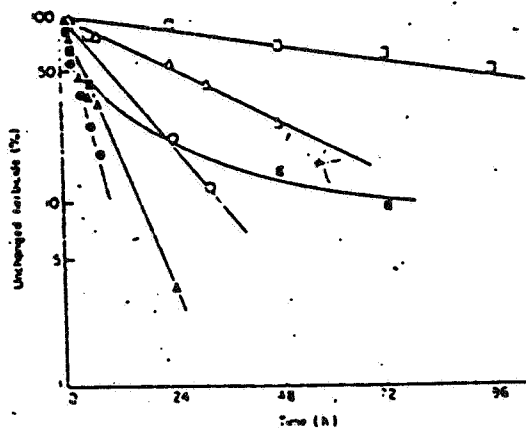


Figure 1. Rate of sensitized and non-sensitized photodecomposition of 1,3,5-triazines in aqueous solutions. O, \circ , Ametryne; Δ , \triangle , atrazine; \square , \square , atraton. Solid symbols with acetone; open symbols without acetone.

where c_0 = initial concentration, and c = concentration at time t

$$t_{0.5}^I = \frac{\ln 2}{k^I}$$

The graphical presentation of $1/c$ as a function of time in the case of sensitized photolysis of atraton (Figure 2) shows a fair linear relationship, consistent with the kinetics of a second order reaction. Rate constants (k^{II}) and half-lives ($t_{0.5}^{II}$) were calculated using the equations:

$$k^{II} = \frac{1/c_2 - 1/c_1}{t_2 - t_1} \quad (\text{concentration}^{-1} \cdot \text{time}^{-1})$$

where c_1, c_2 = concentration at time t_1 and t_2 , respectively

$$t_{0.5}^{II} = \frac{1}{k^{II} \cdot c_0}$$

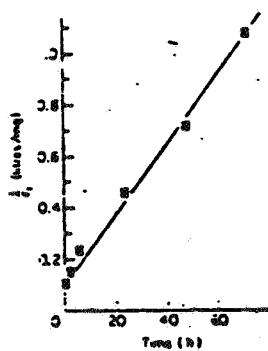


Figure 2. Rate of sensitized photodegradation of atraton plotted as second order reaction.

Photodegradation

A comparison demonstrates the light stability of pounds.

No significant strating that th

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1.2. Photochem

Earlier studies triazines show

Figure 3. Pa containing 1%

and J. A. Guth

Photodegradation of 1,3,5-triazines

A comparison of the calculated half-life values of the three 1,3,5-triazines shown in Table 2 demonstrates that acetone caused a three- to 11 times faster photolytic degradation and that the light stability of 1,3,5-triazines decreased in the sequence methoxy- > chloro- > methylthio-compounds.

No significant breakdown was observed in the "dark reactions" over a period of 96 h demonstrating that the degradation was exclusively due to photolysis.

Table 2. Influence of acetone on the rate of photodecomposition of 1,3,5-triazines in aqueous solution

Compound	Half-lives of aqueous (10 mg/litre) solutions	
	Without acetone (h)	With 1% acetone (h)
Ametryne	10.2 ± 1.3 ^a (1st)	3.3 ± 0.5 (1st)
Atrazine	25 ± 2 (1st)	4.9 ± 0.5 (1st)
Atraton	87 ± 10 (1st)	7.4 ± 0.6 (2nd)

^a 95% confidence limits.

3.2. Photochemical mechanism

Earlier studies of Pipe and Zabik^{3,4} on the non-sensitized photodecomposition of various 1,3,5-triazines showed that halogen-substituted triazine herbicides were photolysed in alcohols and water

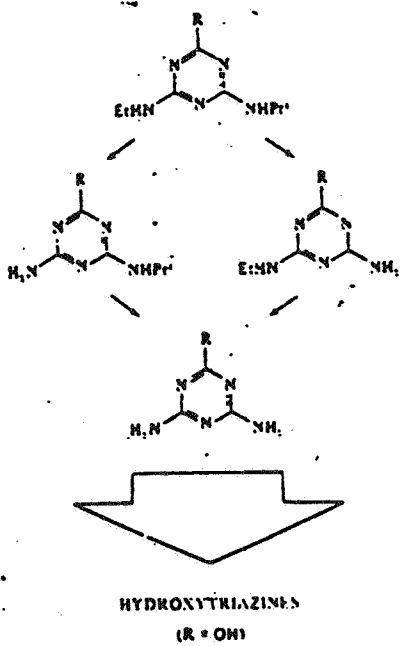


Figure 1. Pathway of photolytic degradation of atrazine (R = Cl) and atraton (R = OMe) in aqueous solution containing 1% of acetone.

(5)
 017

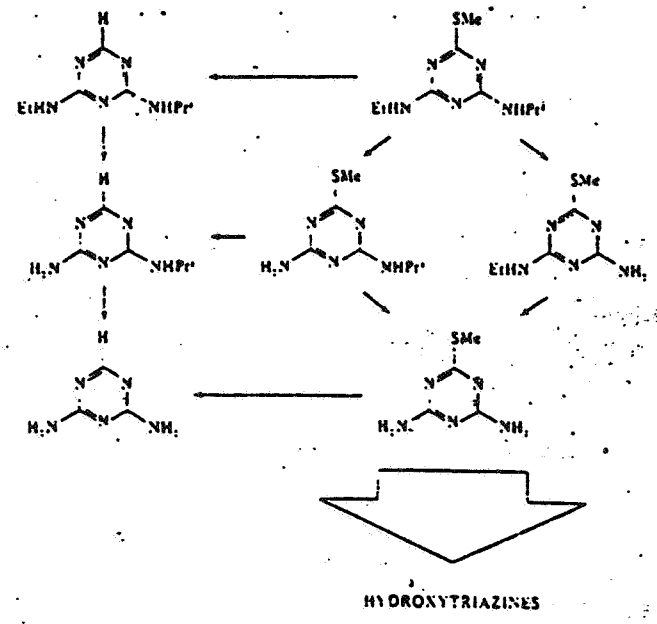


Figure 4. Pathway of sensitized photolysis of ametryne in aqueous solution.

Table 1. Amounts of photoproducts of 1,1,3-triazines formed after exposure to artificial sunlight in the presence of acetone as photosensitizer

$R^1-NH-C_2N_2-NH-R^2$	R ¹	R ³	R ⁴	Photoproducts (in %) determined after an exposure time of:	
				6 h	72 h
Atrazine	Cl	Et	Pr ⁱ	30	Not determined
	Cl	H	Pr ⁱ	16	determined
	Cl	Et	H	3	
	Cl	H	H	15	
	OH	Et or H	Pr ⁱ or H	10	
Ametryne	SMe	Et	Pr ⁱ	39	Not determined
	SMe	H	Pr ⁱ	25	
	SMe	Et	H	2	
	SMe	H	H	3	
	H	Et	Pr ⁱ	5	
	H	H	Pr ⁱ	2	
	H	Et	H	<1	
	H	H	H	10	
Atraton	OH	Et or H	Pr ⁱ or H	4	Not determined
	OMe	Et	Pr ⁱ	9	
	OMe	H	Pr ⁱ	40	
	OMe	Et	H	3	
	OMe	H	H	16	

Photodegradation of

to the corresponding chemically degraded 5-triazine, where
 Our trials on it in Figures 3 and yielded the corresponding hydroxytriazine aqueous ametryne described by us.
 The amounts of artificial sunlight irradiates that the *et al.*¹³ when studies of de-N-methyl of

Acknowledgement
 The authors are

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and J. A. Guth

Photodegradation of 1,3,5-triazines

to the corresponding alkoxy- and hydroxy-compounds, respectively. Alkylthio-triazines were photochemically degraded in the same solvents to a single product, the corresponding de-alkylthio-1,3,5-triazine, whereas alkoxy- and hydroxy-triazines did not react in the same media.

Our trials on the sensitized photolysis of atrazine, ametryne and atraton as graphically summarized in Figures 3 and 4 resulted in the identification of additional photoproducts. Atrazine and atraton yielded the respective two de-V-alkyl and the de-VV'-dialkyl analogues as well as the corresponding hydroxytriazines. In addition to the above mentioned photolysis products, irradiation of an aqueous ametryne solution resulted in the formation of de(methylthio)-1,3,5-triazines as previously described by other authors.¹⁻⁴

The amounts of photoproducts of atrazine, ametryne and atraton formed upon exposure to artificial sunlight are listed in Table 3. The occurrence of two different de-V-alkyl products demonstrates that the de-V-alkylation took place in two steps, which was also postulated by Pimner *et al.*¹³ when studying 1,3,5-triazine dealkylation by free-radical generating systems. Larger amounts of de-V-ethyl compounds were isolated than the corresponding de-V-isopropyl analogues.

Acknowledgement

The authors gratefully acknowledge the skilled technical assistance of Mr. M. Lisibach.

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DATA EVALUATION RECORD

STUDY 3

CHEM 080803

Atrazine

§161-3

FORMULATION—00—RADIOLABELED ACTIVE INGREDIENT

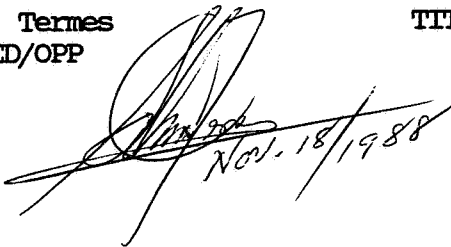
FICHE/MASTER ID 40431320

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. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



Nov. 18/1988

CONCLUSIONS:

This study is not acceptable for the following reasons: 1) significant amounts (19-28%) of radioactivity were left unidentified at the origin of TLC plates (for both natural and artificial sunlight exposures); 2) no other methodology was used to confirm the identity of the photodegradation products; 3) distribution of radioactivity in plates was not expressed as percent of applied dose.

MATERIALS AND METHODS:

Test material: [U-ring ^{14}C]-atrazine, Ciba-Geigy Code No. GAN-1X-48, specific activity 20.6 $\mu\text{Ci}/\text{mg}$ 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 deg. 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 pre-coated TLC plate (silica gel), replaced with a slurry of soil/de-ionized water (1:1 volume), and then dried overnight in an oven at 35 ± 1 deg. 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 deg. C.

Dose preparation and dosing: The atrazine radiolabeled material was dissolved with 10 mL of methanol. An aliquot (425 μL) of this solution was diluted to 3 mL with methanol (dilution contained 620 μg of atrazine). This solution was spotted on the soil strips (two identical 2.1 μg 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 μL of the dosing solution were applied (20- to 30-, 2- to 4- μL 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 $\mu\text{W}/\text{cm}^2$ (natural sunlight on a clear, sunny July day at the test site in Frederick, MD was 1800 to 2300 $\mu\text{W}/\text{cm}^2$). 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 deg. 25' North Latitude and 77 deg. 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 $\mu\text{W}/\text{cm}^2$ during the exposure with a yellow filter and equivalent to 0 to 2300 $\mu\text{W}/\text{cm}^2$ 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 deg. 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 deg. 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 over-spotted with the non-radioactive 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.

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.

PERTINENT DATA TABLES AND FIGURES

-3.5-

Atrazine

Page _____ is not included in this copy.

Pages 31 through 42 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.
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 - 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.

**METABOLISM STUDIES
(LABORATORY)**

DATA EVALUATION RECORD

STUDY 4

CHEM 080803	Atrazine	§162-1
		§162-2

FORMULATION—00—RADIOLABELED ACTIVE INGREDIENT

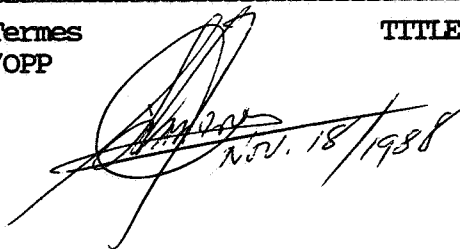
FICHE/MASTER ID 40431321

Rustum, A.M. 1987. Aerobic, aerobic/anaerobic, and sterile soil metabolism of atrazine. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. HLA 6015-185. Completed Nov. 6, 1987. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

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

Based on the 94-day data, the half-life for the aerobic metabolism of atrazine (loam soil) was calculated as 140 days. The main metabolites detected at all sampling times were G-30033 and G-28279, but the metabolite G-34048 was not detected until days 62 and 94.

The calculated half-life for atrazine under anaerobic conditions was about 159 days. The metabolites G-30033 and G-28279 were present at all sampling times in both soil extracts and supernatant water; G-28273 and G-34048 were also present, but not at all sampling times.

MATERIALS AND METHODS:

Test material: ^{14}C -atrazine (U-ring), specific activity 20.6 $\mu\text{Ci}/\text{mg}$ (4.57×10^{10} dpm/g); 95.4% radio purity.

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 μg ^{14}C -atrazine and 100 μg nonlabeled atrazine) to yield 100- μL aliquots containing 4.73×10^6 dpm and a final specific activity of 10.5 $\mu\text{Ci}/\text{mg}$.

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 μL 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 deg. C (50 minutes). The fortification solution was added to 14 of the jars (100 μL 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 deg. 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 deg. 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 radio-activity 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 quantify-

ing 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 radio-activity 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 $^{14}\text{CO}_2$ 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 $^{14}\text{CO}_2$ 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 $^{14}\text{C}\text{O}_2$ 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.

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 50 through 56 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) _____.
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DATA EVALUATION RECORD

STUDY 5

CHEM 080803

Atrazine

§162-1 and 2

FORMULATION--00--ACTIVE INGREDIENT

FICHE/MASTER ID 40629303

Rustum, A.M. 1988. Aerobic, aerobic/anaerobic, and sterile soil metabolism of ¹⁴C-atrazine. Laboratory Project Identification HLA 6015-185. Unpublished study performed by Hazleton Laboratories America, Inc. and submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: M. Coleman

TITLE: Staff Scientist

EDITED BY: K. Patten

TITLE: Task Leader

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD

TEL: 468-2500

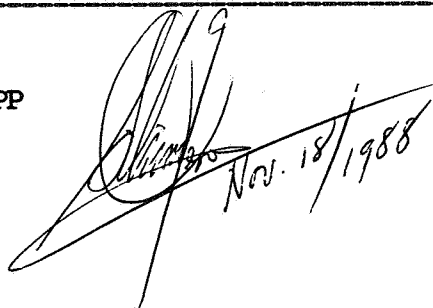
APPROVED BY: S. Termes

TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 557-2243

SIGNATURE:



CONCLUSIONS:

Metabolism - Aerobic Soil

This portion of the study is scientifically sound and provides supplemental information towards the registration of atrazine. This portion of the study does not fulfill EPA Data Requirements for Registering Pesticides because degradates comprising up to 7% of the applied (the water-soluble compounds, and one degradate in the organosoluble fraction) were not identified. The author reported a calculated half-life of 146 days under nonsterile aerobic conditions and to be very slow under sterile conditions.

Metabolism - Anaerobic Soil

This portion of the study is scientifically sound and provides supplemental information towards the registration of atrazine. This portion of the study does not fulfill EPA Data Requirements for Registering Pesti-

cides because degradates comprising up to 6.8% of the applied (the water-soluble compounds in soil and water) were not identified. Note, however, that an acceptable anaerobic aquatic metabolism study (Study 8; MRID 40431323) was submitted. According to Subdivision N Guidelines, an acceptable anaerobic aquatic metabolism study may be used to fulfill data requirements for anaerobic soil metabolism studies.

SUMMARY OF DATA BY REVIEWER:

Metabolism - Aerobic Soil

Uniformly ring-labeled [¹⁴C]atrazine (radiochemical purity ≥95.4%, specific activity 20.6 μCi/mg), at 10.2 ppm, degraded with a half-life of 94-181 days in loam soil incubated aerobically in the dark at 25°C and 75% of 0.33 bar moisture; the registrant-calculated half-life was ≈146 days. [¹⁴C]Atrazine decreased from 90.7% of the applied immediately posttreatment to 56.5% at 94 days, 33.1% at 181 days, and 21.2% at 300 days. The major organosoluble degradate was . . .

2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033), at up to 4.6% of the applied on day 300.

Other degradates were . . .

2-amino-4-chloro-6-ethylamino-s-triazine (G-28279) at up to 2.0% of the applied (maximum on day 244),

2,4-diamino-6-chloro-triazine (G-28273) at up to 0.7% (day 3),
and

2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine (G-34048) at up to 0.7% (days 62 and 94).

One degradate was isolated at 0.2-0.3% of the applied (0.03 ppm) but not identified. The degradates 2-amino-4-hydroxy-6-isopropylamino-s-triazine (GS-17794) and 2-amino-4-ethylamino-6-hydroxy-s-triazine (GS-17792) were not detected at any sampling interval. At 300 days posttreatment, 21.2% of the applied was [¹⁴C]atrazine, 4.6% was G-30033, 1.8% were other unidentified organosoluble degradates, 6.7% were water-soluble degradates, 6.0% had been evolved as ¹⁴CO₂, and 62.8% was unextractable. The material balance ranged from 95.1 to 102.6% of the applied during the 300-day study.

In sterile soil, [¹⁴C]atrazine was 77.4% of the applied at 94 days posttreatment. G-30033 was the major degradate (1.7% of the applied at 14 days); G-28279, G-28273, G-34038, and one unknown were also detected.

Metabolism - Anaerobic Soil

Uniformly ring-labeled [¹⁴C]atrazine (radiochemical purity ≥95.4%, specific activity 20.6 μCi/mg) decreased from 6.83 to 5.22 ppm (67 to 51.2% of the applied) in anaerobic (flooded plus N₂ atmosphere) loam soil

during 62 days of incubation in the dark at 25°C. The loam soil had been treated with [¹⁴C]atrazine at 10.2 ppm and incubated for 32 days under aerobic conditions (in the dark at 25°C and 75% of 0.33 bar moisture) prior to flooding. Four degradates were isolated from the soil:water system:

2-amino-4-chloro-6-isopropylamino-s-triazine (G-30033) at ≤2.1% of the applied,

2-amino-4-chloro-6-ethylamino-s-triazine (G-28279) at ≤0.7% of the applied,

2,4-diamino-6-chloro-triazine (G-28273) at 0.3% (detected only on day 0 of anaerobic conditions), and

2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine (G-34048) at ≤0.4.

The degradates 2-amino-4-hydroxy-6-isopropylamino-s-triazine (GS-17794) and 2-amino-4-ethylamino-6-hydroxy-s-triazine (GS-17792) were not detected at any sampling interval. At 30 and 62 days postflooding (62 and 94 days posttreatment), 26.8 and 21.6% of the applied radioactivity was in the floodwater rather than the soil phase, respectively. Unextractable [¹⁴C]residues in the soil increased from 26.7 to 40.9% of the applied during the 62 days of anaerobic incubation; no ¹⁴CO₂ evolution was detected (<34 dpm). The material balance ranged from 94.3 to 100.4% of the applied during the 62-day anaerobic study.

DISCUSSION:

1. All degradates present at >0.01 ppm were not identified. The aqueous extracts from the soil, which contained up to 6.7% of the applied radioactivity, were not analyzed to determine composition. In addition, one degrade in the organic extract from the aerobic soil was not identified, although it was present at up to 0.3% of the applied.
2. [¹⁴C]Residues in humic and fulvic acid and humin fractions were determined for samples containing >10% of the total dose as unextractable residues following refluxing in acid/methanol. [¹⁴C]Residues in the humic acid fraction accounted for 1.6-4.5% of total applied activity in soil samples following 64 days of anaerobic incubation or 181 days of aerobic incubation. [¹⁴C]Residues in the fulvic acid fractions from these samples accounted for 3.7-6.5% of total applied activity. The humin fractions accounted for 7.6-13% of the applied radioactivity. [¹⁴C]Residues were not detected in humic/fulvic acid and humin fractions following 94 days of aerobic incubation.
3. A discrepancy is noted in data reporting of the concentration of the parent following 300 days of incubation under aerobic conditions (27.1% in the abstract and 21.2% in the results/tables).

MATERIALS AND METHODS

MATERIALS AND METHODS:

Preliminary studies were conducted for methods development. Mean total recovery from triplicate samples was 99.4% (94.5% organosoluble, 0.7% aqueous, and 4.2% unextractable [¹⁴C]residues). TLC methods were developed for quantification of the parent, chlorotriazine, and hydroxytriazine residues. The following compounds were separated by TLC using chloroform:methanol:formic acid:water (100:20:4:2): parent, 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); 2-amino-4-ethylamino-6-hydroxy-s-triazine (G-17792); and 2-amino-4-hydroxy-6-isopropylamino-s-triazine (G-17794). Separation of the following compounds was achieved using toluene:acetone (75:25): the parent, G-30033, G-28279, and G-28273. The remaining compounds did not migrate from the origin. R_f values are presented in Table 1. The retention characteristics for these compounds separated by HPLC are presented in Table 2.

Metabolism - Aerobic Soil

Nonsterile and sterile (50 minutes at 120°C), sieved (2 mm), California loam soil (51% sand, 37% silt, 12% clay; 1.4% organic matter; pH 7.6; CEC 7 meq/100 g) was treated at 10.2 ppm with a methanolic solution of [¹⁴C]-atrazine (radiopurity >95.4%, specific activity 20.6 μCi/mg, Ciba-Geigy) plus unlabeled technical atrazine (purity 98.8%) in a 1:1 ratio. The solvent was evaporated, and the jars were capped and tumbled for 2 minutes to insure uniform distribution of the pesticide. Water was added to achieve a moisture content of 75% of 0.33 bar, and the mass of the jars was determined. The samples were incubated at 25 ± 1°C in darkness. Traps containing ethylene glycol and 2-ethoxyethanol:ethanolamine (1:1) were connected in series to collect organic volatiles and ¹⁴CO₂, respectively. Water was added to the jars when mass loss was observed to maintain the moisture content at 75% of 0.33 bar. Nonsterile aerobic soils and trapping solvents were sampled at intervals up to 300 days posttreatment. Sterile soils and traps were sampled at intervals up to 94 days posttreatment.

The [¹⁴C]residues in the soil were extracted twice in acetonitrile:water (9:1) for 15 minutes on a magnetic stirrer. The sample was clarified by centrifugation, and the supernatant was decanted. The combined extract was concentrated by rotary evaporation until an aqueous extract remained. Partitioning was carried out with the aqueous solution and methylene chloride. [¹⁴C]Residues were partitioned between aqueous and organic (methylene chloride) phases. [¹⁴C]Residues in the resulting fractions were quantified by LSC.

The distribution of [¹⁴C]residues in the organic extract was determined by autoradiography of one-dimensional TLC using toluene:acetone (75:25) or chloroform:methanol:formic acid:water (100:20:4:2), or by two-dimensional TLC using chloroform:methanol:formic acid:water (100:20:4:2) and toluene:acetic acid:water (50:50:2). Recoveries from LSC of TLC spots were 95-103% from 18 samples fortified at 7535-16,541 dpm/sample.

Unextractable [^{14}C]residues were quantified by total combustion of extracted soils. The recoveries of ^{14}C -atrazine were 96-101% from four samples fortified at 2401-15052 dpm/sample and analyzed by total combustion. Unextractable [^{14}C]residues were released by refluxing the extracted soil for 2 hours with 1 M HCl in methanol in a 10:1 ratio of solvent:soil. The [^{14}C]residues in the extract were quantified by ISC. The extract was concentrated by rotary evaporation, redissolved in 0.01 M potassium phosphate solution at pH 2-3, and centrifuged prior to analysis by HPLC. Humic/fulvic acids were characterized using standard analytical procedures in soil samples which contained >10% of the total applied radioactivity following refluxing.

The [^{14}C]residues in trapping solvents were quantified by ISC.

Metabolism - Anaerobic Soil

A portion of the jars containing treated nonsterile soil were incubated for 32 days as described above, then flooded with 2-3 cm of water. Nitrogen gas was bubbled through the standing water to remove any dissolved oxygen. The samples were incubated at $25 \pm 1^\circ\text{C}$ in darkness under a nitrogen atmosphere. Traps for volatile organics and $^{14}\text{CO}_2$ were installed as described for the aerobic study. Duplicate samples of soil and trapping solvents were analyzed 30-62 days postflooding (62-94 days posttreatment).

The anaerobic soil samples were centrifuged, and the supernatant was decanted. [^{14}C]Residues in the soil and water were partitioned between water and two volumes of chloroform and analyzed as described previously. Unextractable residues in the extracted soil were determined by ISC following combustion.

RESULTS AND/OR CONCLUSIONS OF STUDY AUTHOR(S)

Atrazine

Page _____ is not included in this copy.

Pages 64 through 91 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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DATA EVALUATION RECORD

STUDY 6

CHEM 080803

Atrazine

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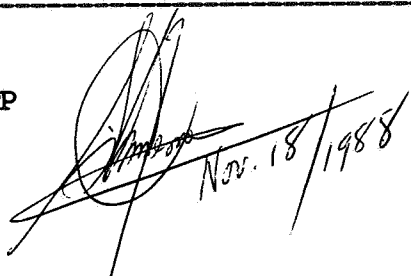
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CONCLUSIONS:



Metabolism - Aerobic Soil

This study was included in the 1983 Registration Standard. This study is unacceptable because material balances were not provided (the soils were analyzed only for atrazine and total extractable triazine residues). In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the pattern of formation and decline of degradates was not addressed, the soils were not completely characterized, and the purity and specific activity of the test substance was not reported. Although the soils may not be typical of those in the continental United States, the soils may be typical of those areas where atrazine is used to control weeds in sugarcane, pineapple, guava, and macadamia nuts.

SUMMARY OF DATA BY REVIEWER:

Ring-labeled [¹⁴C]atrazine (test substance not further characterized), at 10 ppm, degraded with half-lives of ≈10 days in Kapaa humic ferruginous

latosol soil (10% organic matter, pH 4.4) and ≈35 days in Molokai low humic latosol soil (4% organic matter, pH 4.3) that were incubated at 60% of water-holding capacity and 30°C. When the soils were incubated at 50°C, the half-life of atrazine decreased to ≈5 days in both soils. The degradate 2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine (hydroxy-atrazine; G-34048) was isolated from the Kapaa soil.

Total methanol-extractable [¹⁴C]compounds dissipated with half-lives of ≈25 days in Kappa humic ferruginous latosol soil (10% organic matter, pH 4.4) and Kula reddish prairie soil (22% organic matter, pH 5.9), ≈30 days in Kaipoioi latosolic brown forest soil (29% organic matter, pH 5.4), and ≈55 days in Molokai low humic latosol soil (4% organic matter, pH 4.3) that had been treated with ring-labeled [¹⁴C]atrazine at 10 ppm and incubated at 60% of water-holding capacity and 30°C. It was reported that similar data were obtained for soils treated at 5, 50, and 100 ppm and incubated under these conditions (no data for these temperatures were provided).

DISCUSSION:

1. Material balances were not provided. The majority of soil samples were analyzed only for atrazine and total methanol-extractable [¹⁴C]residues. Total radioactivity in the soil prior to extraction and radioactivity remaining in the soil after extraction were not measured.
2. The formation and decline of degradates was not addressed. The study author identified one degradate, hydroxyatrazine, in the Kappa soil at 11 and 34 days posttreatment and in the Molokai soil at 34 days posttreatment, but did not quantify the degradate. Since the concentration of atrazine was considerably lower than the total extractable residues at all sampling intervals and since the detection limit was not reported, other degradates may have been present. In addition, for Experiment 2, only total radioactivity in the methanol extracts was measured; the radioactivity was not characterized.
3. The soils were classified according to the revised 1938 classification system and the 1955 soil survey of Hawaii. Approximate equivalents between the 1938 system and the current taxonomy system are: humic ferruginous latosols are tropohumults; low humic latosols are ustropepts; reddish prairie soils are thermic families of udic subgroups of argiustolls and paleustolls, and latosolic brown forest soils are dystrandpeats. The soils were not completely characterized; the soil textures, textural analyses, and CECs were not reported. In addition, the soils are Hawaiian and contain as much as 29% organic matter; the soils may not be typical of those in the continental United States.
4. The purity and specific activity of the test substance was not reported.
5. It could not be determined how [¹⁴C]compounds on the TLC plates were identified. It was not stated whether reference standards were cochromatographed with the extracts on the TLC plates.

6. Recovery efficiencies from fortified soil samples were not reported.
7. Included in the original document was an experiment designed to determine "the quantities of atrazine and hydroxyatrazine in equilibrium with the soil in aqueous solution". The experiment was not reviewed in this report because it is unacceptable as a batch equilibrium study; it was not demonstrated that atrazine residues reached an equilibrium at any time during this experiment.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Experiment 1

Ring-labeled [¹⁴C]atrazine (test substance not further characterized) was applied at 10 ppm to Kappa humic ferruginous latosol soil (10% organic matter, pH 4.4) and Molokai low humic latosol soil (4% organic matter, pH 4.3) (soils were not further characterized). The soils were incubated at 60% of their water-holding capacity and either 30 or 50°C. The soils were sampled at 0, 4, 11, and 34 days posttreatment.

The soil samples were shaken with methanol on a wrist-action shaker for 2 hours, then filtered. The methanol extracts were analyzed for total radioactivity using ISC and for specific compounds using TLC on silica gel plates developed with chloroform:acetone (9:1). Radioactive compounds on the plates were located and quantified using a radiochromatogram scanner (the method of identification of radioactive areas was not specified).

Experiment 2

Ring-labeled [¹⁴C]atrazine was applied at 1, 5, 10, and 50 ppm to Kappa humic ferruginous latosol soil (10% organic matter, pH 4.4), Kula reddish prairie soil (22% organic matter, pH 5.9), Kaipoi latosolic brown forest soil (29% organic matter, pH 5.4), and Molokai low humic latosol soil (4% organic matter, pH 4.3); the Kapaa soil was also treated at 100 ppm. The soils were incubated at 60% of their water-holding capacity and 30°C. The soils were sampled at 0, 10, 30, and 60 days posttreatment.

The soil samples were shaken with methanol on a wrist-action shaker for two hours; the methanol extracts were analyzed for total radioactivity by ISC.

MATERIALS AND METHODS

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

PERTINENT DATA TABLES AND FIGURES

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WSS 17(11) 509-514 (11/1964)

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Degradation of Atrazine in Four Hawaiian Soils¹

S. R. OBIEN and R. E. GREEN²

Abstract. The degradation of ¹⁴C ring-labeled 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) was studied in the laboratory with four Hawaiian soils selected for their wide range of organic matter contents (4 to 29%), pH values (4.1 to 6.3), and different mineralogies. Atrazine concentrations of 1, 5, 10, 50 and 100 ppmw in soils incubated at 30 C gave similar ¹⁴C recovery curves. Degradation was rapid in all four soils, atrazine recovery at 34 days (30 C) ranged from 15 to 30% of the quantity applied. Degradation was accelerated by a temperature increase from 20 to 30 C, suggesting a chemical rather than a biological process. The loss of atrazine from soils approached a first order reaction rate at 30 C, and deviated from this at 50 C. Hydroxyatrazine was the main degradation product with only a slight amount of an unidentified "Product B". It was concluded that chemical degradation (hydrolysis) was the major pathway of atrazine loss in these soils. This process was more closely related to pH, i.e. faster on low pH soils than with organic matter content or adsorption. The fraction of atrazine adsorbed on soil increased with the decrease in total atrazine caused by degradation. Extraction of soils with both water and methanol and subsequent analysis of extracts by thin-layer chromatography showed that some of the methanol-extractable atrazine was not readily desorbed by water. These results indicate that some of the residual atrazine extracted chemically may not be available for uptake by plants and would be relatively immobile in soil water.

INTRODUCTION

THE triazines are some of the most useful herbicides made available to agriculture since the introduction of (2,4-dichlorophenoxy)acetic acid (2,4-D) in 1945. In

Hawaii, 2-chloro-4,6-bis(ethylamino)-s-triazine (simazine) and 2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine (atrazine) are two of the more important herbicides for sugarcane (*Saccharum officinarum* L.) and pineapple (*Ananas comosus* (L.) Merr.). Another triazine, 2-(ethylamino)-4-(isopropylamino)-6-(methylthio)-s-triazine (ametryne), used extensively in sugarcane and pineapple, recently has been found useful for weed control in bananas (*Musa* spp.) (12). Other newer triazines are being tested for various crops in Hawaii.

Triazine selectivity depends largely on the ability of some plant species to degrade the compound to the biologically inactive hydroxanalogue. In some cases, even a sensitive crop such as bananas may be protected from triazine damage if the soil-applied herbicide is sufficiently adsorbed on the soil to prevent movement to the roots (3). With a given rate of application, the amount in the soil solution is determined to a great extent by the capacity of the soil to adsorb the compound and by the rate of subsequent herbicide release into solution. Results of adsorption-desorption studies with soil-applied herbicides have helped to explain the variable quantities of herbicides required for effective weed control on different Hawaiian soils (18). Herbicidal activities of atrazine and simazine on 10 sugarcane plantations were reduced by the high adsorption associated with high organic matter contents but were increased by high rainfall (16). The period of effective weed control ranged from 40 to 60 days with single applications of these herbicides. This rela-

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tively short period of weed control and the absence of residue accumulation after repeated applications indicate rapid degradation by either biological or chemical means.

The relatively high year-round temperatures and high organic matter contents of many Hawaiian soils suggest that both chemical and microbiological degradations may be more rapid in Hawaii than in temperate-region soils. Measurements of ^{14}C - CO_2 evolution from ^{14}C -labeled triazine applied to a Kapaa soil indicated that microbial degradation was only a small fraction of total degradation (11). These results are consistent with other recently published research on triazine degradation (1, 14).

The objectives of the study reported here were to determine atrazine degradation in some widely different Hawaiian soils and to analyze the extent of chemical hydrolysis of atrazine at two temperatures.

MATERIALS AND METHODS

Soils. The surface soils used vary widely in organic matter content and pH; they are from four different Hawaiian great soil groups sampled on the islands of Kauai, Oahu, and Maui (Table 1). Suehisa (15) reported a positive relationship between organic carbon content and atrazine adsorption coefficient (K_d) for a group of Hawaiian soils including those used in this study. This relationship was confirmed in this study as indicated by a comparison of the K_d values and organic matter contents in Table 1.

Table 1. Characteristics of Hawaiian soils used in atrazine degradation experiments.

Soil	Organic matter (percent)	pH (1:1)	Atrazine K_d
Molokai (LHL) ^a	4 ^b	4.3	2.3
Kapaa (HFL)	10	4.4	2.9
Kula (R.P.)	22	5.3	4.0
Kaipouoi (LBP)	29	5.4	9.3

^aHawaiian great soil groups: Low Humic Latimer (LHL), Humic Ferruginous Latimer (HFL), Reddish Prairie (R.P.), and Latimer Brown Forest (L.B.F.)
^bData by R. H. Suehisa, University of Hawaii.
^cAdsorption coefficient (K_d) was obtained from an equilibrium between 10 ml atrazine solution (10 ppm) and 1-g soil sample.

The soils were screened through a 2-mm sieve and maintained at the original moisture content until used.

Atrazine applications and temperature variables. Atrazine degradation at 30 C was studied on all four soils with applications of 1, 5, 10, and 50 ppmw of atrazine with an additional 100 ppmw treatment for the Kapaa soil. Treatments consisted of 1 ppmw ring-labeled ^{14}C -atrazine with unlabeled atrazine being added for applications greater than 1 ppmw. Treated soils were maintained at 60% water in plastic vials and incubated at 30 C for 0, 10, 30, and 60 days before extraction.

The two soils (Molokai and Kapaa) showing the largest difference in atrazine degradation in the study outlined above were chosen for a subsequent experiment in which two temperature variables were imposed. In this second experiment, 2-g soil samples were treated with 10 ppmw ^{14}C -atrazine, and incubated at 30 and 50 C for 0, 4, 11, and 31 days. The higher temperature (50 C) was expected to enhance chemical hydrolysis of atrazine and to attenuate microbial activity.

Extraction of residual ^{14}C -triazine. In the first experiment, 10-g samples were extracted with 50 ml methanol. The soil-methanol mixture was shaken on a wrist-action shaker for 2 hr and then was filtered through Whatman No. 12 filter paper. A 1-ml aliquot of the clear filtrate was counted by liquid scintillation. Extraction in the second experiment was carried out on 2-g samples with 10 ml methanol or water. The soil-extractant mixture was shaken for 2 hr and then centrifuged for 20 min at 16,000 rpm. Water extraction was used to determine the quantities of atrazine and hydroxyatrazine in equilibrium with the soil in aqueous solution during the measurement period. The solution was centrifuged and a 2-ml aliquot was counted. Before counting, a 15-ml scintillation solution [0.3 g 1,4-bis-2-(1-methyl-5-phenyloxazolyl)-benzene (dimethyl POPOP), 7.0 g 2,5-diphenyloxazole (PPO), and 100 g naphthalene/L of solution with dioxane as solvent] was added to each aliquot. A Packard Model 3101 liquid scintillation spectrometer with a counting efficiency of 60% was used.

Chromatographic analyses of methanol and water extracts. Atrazine and its degradation products in water and methanol extracts were separated by thin-layer chromatography (hereinafter referred to as TLC) and measured with a Packard 7201 radiochromatogram scanner. Known volumes of methanol and water extracts were concentrated by evaporation under low heat, then spotted on precoated silica gel (Eastman Chromatogram Sheet C260, with fluorescent indicator) and developed with a chloroform-acetone mixture (9:1, v/v) for 45 min. The proportion of atrazine and hydroxyatrazine determined by TLC was used to calculate absolute quantities of each from the total extractable ^{14}C activity.

RESULTS AND DISCUSSION

Degradation in relation to soil properties. Atrazine concentrations of 1, 5, 10, and 50 ppmw gave similar recovery curves; thus, curves for only the 10-ppmw application are shown in Figure 1. The order of degradation for all atrazine concentrations in the four soils was Kapaa > Kula > Kaipouoi > Molokai. An examination of soil characteristics such as pH, organic matter content, and atrazine K_d (Table 1) reveals that pH appears to be more closely related to the degree of atrazine degradation than with the other soil properties. A similar observation was made by Weber *et al.* (17) who found that the phytotoxicity of 2-bis(isopropylamino)-6-(methylthio)-s-triazine (prometryne) to wheat (*Triticum aestivum* L. em Thell.) was inversely related to soil acidity, i.e., lower phytotoxicity was obtained at pH 4.5 than at pH 6.5 in the presence of montmorillonite clay or organic matter. They attributed this result to increased adsorption of the protonated prometryne associated with a decrease in pH of the medium. Chemical hydrolysis of the triazines was catalyzed by adsorption on clay and organic matter (2, 13).

In contrast to the above findings of Weber *et al.* (17), Day *et al.* (4) did not observe any relationship between simazine phytotoxicity to oats (*Avena sativum* L., var. Kanota) and the pH and clay content for 65 soils of California. This latter result on pH-phytotoxicity re-

OBIEN AND GREEN : ATRAZINE IN HAWAIIAN SOILS

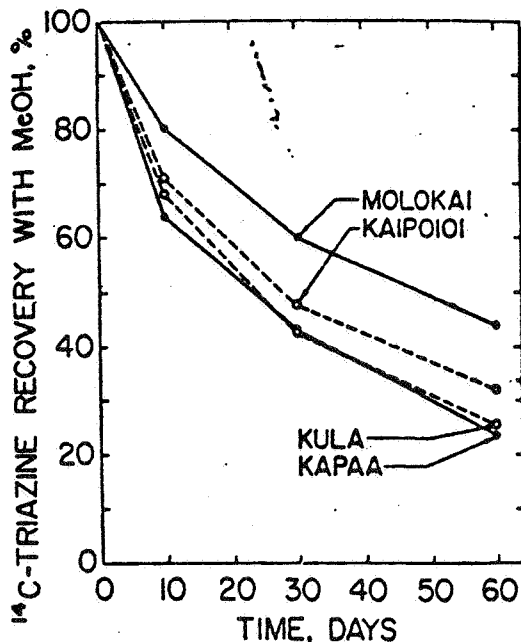


Figure 1. ¹⁴C-atriazine recovery by methanol extractions of four Hawaiian soils treated with 10 ppmw ¹⁴C-atriazine (No correction was made for the presence of ¹⁴C degradation products.)

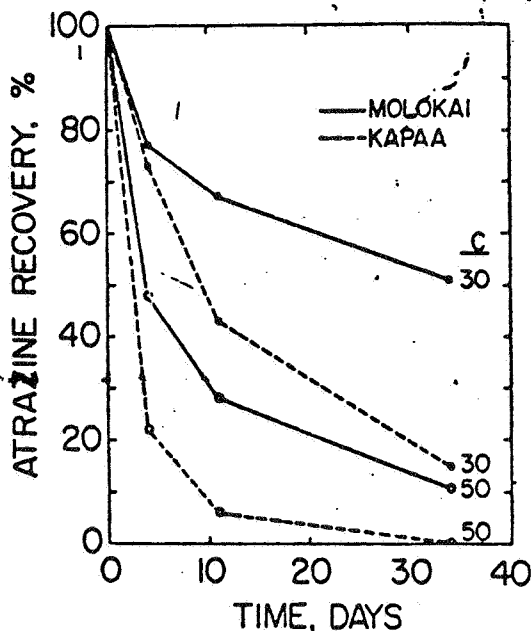


Figure 2. Atrazine recovery by methanol extraction of the Molokai and Kapaa soils treated with 10 ppmw ¹⁴C atrazine and incubated at 30 and 50 C (Corrections were made for the presence of triazine degradation products in the methanol extract.)

relationship might be explained on the basis of the pH of soils used and the pK_a value of simazine ($pK_a = 1.65$). The pK_a value of a compound is an expression of the negative logarithm of the dissociation constant, and provides an estimate of its susceptibility to hydrolysis with changes in acidity. The pH of soils used by Day *et al.* (4) ranged from 5.1 to 7.5, but most were between 6 and 7, much above the pK_a of simazine. Simazine protonation and subsequent hydrolysis would not be closely related to pH in this relatively high pH range.

In the present study, atrazine degradation in the Kaiipoioi soil was less than in the Kula soil, in spite of the lower pH and higher organic matter content and atrazine K_d of the former. It appears that the adsorption sites in these two soils differ in their ability to catalyze chemical hydrolysis. Armstrong and Chesters (2) have shown that some adsorption sites, such as the carboxyl groups on a carboxyl resin, are effective catalysts of atrazine hydrolysis while other sites cause adsorption but have little effect on hydrolysis.

Degradation rates and products in relation to temperature. Measurement of the quantities of degradation products associated with the total ¹⁴C recovery allowed a determination of residual atrazine with time. Figure 2 shows the percent atrazine (total ¹⁴C activity from the extract minus degradation products) recovered from Molokai and Kapaa soils from 0 to 34 days at 30 and 50 C. When the data are plotted on a semi-log scale (figure

not presented here), the loss of atrazine from these soils appeared to approach a first order reaction rate at 30 C. However, deviation from this reaction order occurred at the high temperature. Other workers such as Armstrong *et al.* (1) and Zimdahl² have concluded that degradation of atrazine and other similar herbicides followed the first order reaction. Zimdahl's data reveal a better linear relationship between the log of the recovered herbicides (atrazine, simazine, and ametryne) against time at 13.2 than at 31.2 C. Treated soils were handled in a similar way as in the present work, the moisture at the end of the incubation time being 15 to 30% of field capacity. In contrast, Armstrong *et al.* (1) conducted their studies in perfusion systems in which there was apparently complete mixing of the soil and herbicide, fulfilling a requirement for the occurrence of first order kinetics. In the present study (and that of Zimdahl), atrazine was incubated at 50% moisture, and the possibility exists that adsorption sites were less accessible in these low-water-content systems than in the perfusion system. This soil-herbicide contact is essential for adsorption and subsequent hydrolysis of atrazine to take place (1, 15, 17).

When the methanol and water extracts from Molokai and Kapaa soils were analyzed by TLC, three peaks were observed, namely, atrazine (Rf = 0.92 to 0.94), hydroxy-atrazine (Rf = 0 to 0.05) and a minute amount of an

²Zimdahl, R. I. 1968. A kinetic analysis of herbicide degradation in soil. Ph.D. Thesis, Oregon State University.

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unidentified "Product B" ($R_f = 0.70$). There was almost complete atrazine recovery with meth. for all soils at zero time.

The occurrence and relative amounts of the degradation products obtained by methanol and water extractions are strongly influenced by soil type, temperature, and length of incubation. Atrazine degradation occurred faster in the Kapaa soil than in the Molokai soil (Figure 2). The increased degradation at the higher temperature shown in Figure 2 is evident also in the TLC data which present the relative extent of atrazine hydrolysis with time and temperature (Figures 3, 4, and 5). Sm.

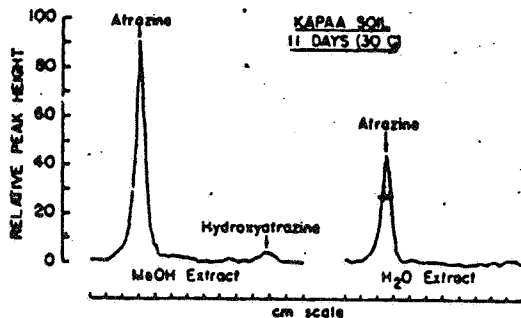


Figure 3. Radiochromatogram of TLC on methanol and water extracts from Kapaa soil 11 days after treatment (30 C).

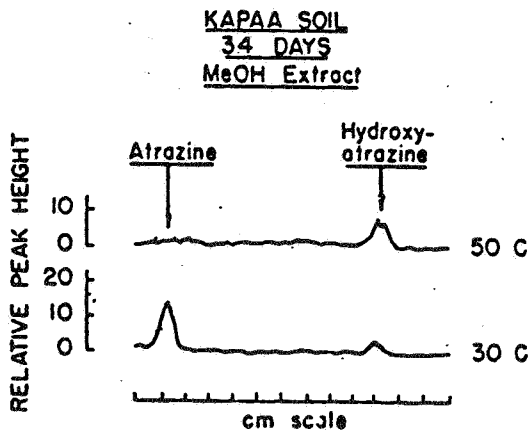


Figure 4. Radiochromatogram of TLC on methanol extracts from Kapaa soil 34 days after treatment (30 and 50 C).

amounts of hydroxyatrazine were detected at 4 days but increased gradually (Figure 3, 11 days) until hydroxyatrazine was the only extracted source of ^{14}C in the Kapaa soil after 34 days at 50 C (Figure 4). The temperature effect on degradation, which is evident in the recovery curves of Figure 2, is seen also in the Kapaa TLC data of Figure 4. The Molokai soil had a lower rate of degradation but a temperature response similar to that

MOLOKAI SOIL 34 DAYS (50 C)

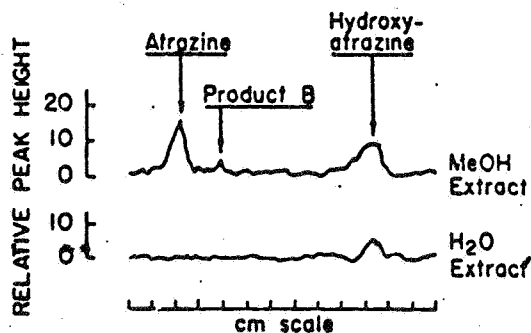


Figure 5. Radiochromatogram of TLC on methanol and water extracts from Molokai soil 34 days after treatment (50 C).

of Kapaa soil (Figure 2). Figure 5 shows the presence of atrazine and hydroxyatrazine in approximately equal quantities and also an unidentified "Product B" in Molokai soil incubated at 50 C. It is particularly significant that no atrazine was detected in the water extract of the Molokai soil after 34 days, showing that some of the methanol-extractable atrazine in this soil was not readily desorbed by water. Such a lack of reversibility in adsorption indicates that not all of the chemically extractable atrazine would be phytotoxic to plants growing in the soil.

A significant aspect of the data in Figure 1 is the high rate of ^{14}C reduction during the first 10 days of the 60-day incubation period. In contrast, data from earlier studies with Kapaa soil showed that $^{14}CO_2$ evolution could account for only about 3% of the loss in ^{14}C -atrazine activity for a period of 9 days (11), the amount being very low compared to data presented in Figure 1. This low ^{14}C loss as measured by $^{14}CO_2$ evolution might suggest other pathways of loss, such as chemical degradation. While biological degradation occurs (9, 11, 14), chemical degradation appeared to be more significant in this study and in those of other workers (1, 7, 14).

Degradation-adsorption relationship. An attempt was made to understand the reduced rate of hydrolysis with time which was reflected in response at 50 C deviating from first order kinetics. Atrazine recovery data were further analyzed by examining the relative quantities of adsorbed and solution atrazine with time. Interest in the relationship between adsorption and degradation has been stimulated by recent evidence obtained by Armstrong and Chesters (2); the first-order rate constants for atrazine hydrolysis in aqueous suspensions of a soil and a carboxyl resin were shown to be linearly related to the percentage of atrazine adsorbed. Thus, changes in adsorption with time could be reflected in degradation rates.

The amount of atrazine adsorbed and apparent adsorption coefficients shown in Table 2 were calculated

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OBIEN AND GREEN : ATRAZINE IN HAWAIIAN SOILS

Table 2. Calculated adsorption of atrazine in relation to atrazine degradation in Molokai and Kapaa soils.*

Soil	C	Days	Total atrazine remaining (Q _t) ^b µg/g	Atrazine conc. in solution (C _s) ^c µg/g	Atrazine adsorbed (C _a) ^d µg/g	Fraction of atrazine adsorbed, % ^e	Apparent adsorption coefficient (K) ^f
Molokai	30	4	7.7	0.54	4.8	62	8.8
		11	6.7	0.35	4.8	72	13.7
		34	5.1	0.21	4.0	79	19.0
	50	4	4.0	0.25	3.4	71	13.6
		11	2.8	0.11	2.2	79	20.0
		34	1.2	0.00	—	—	—
Kapaa	30	4	7.3	0.53	4.4	60	8.3
		11	4.3	0.16	3.4	80	21.3
		34	1.5	0.00	—	—	—
	50	4	2.2	0.17	1.3	57	7.6
		11	0.6	0.00	—	—	—
		34	0.0	0.00	—	—	—

*Calculations of adsorption are based on measured values of methanol and water extractable atrazine to which the partition equation $Q/m = C(W_a + K)$ is applied. Q/m , determined by methanol extraction and corrected for degradation product by T.L.C. at zero time $Q/m = 10 \mu\text{g/g}$ (quantity applied).

^bC_s measured concentration in aqueous solution after treated soil was equilibrated with water at soil water ratio of about 1:5, corrected for degradation product by T.L.C. C_s is expressed in µg atrazine/g solution.

^cC_a calculated as follows: $C_a = Q/m - C_s \times W_a$, where W_a is the effective soil water content, in this case, 5.4 g/g for Molokai soil and 5.3 g/g for Kapaa soil.

^d% adsorbed = $\frac{C_a}{Q/m} \times 100$
^eApparent K = $\frac{C_a}{C_s/C}$

from a partition equation (6) and experimental data. Since the concentrations of atrazine in aqueous solution were measured in a system with about nine times as much water as held by the soil during incubation, the calculated adsorption percentage is probably less than that which actually existed in the incubated samples. Relative values of the various indices of adsorption, however, would correctly represent adsorption changes with time. The calculations show that the decrease in total atrazine with time was accompanied by an increase in the fraction of atrazine adsorbed. Armstrong and Chesters (2) considered the atrazine adsorption percentage to remain essentially constant with time in their systems. The increased percent adsorption measured in the present study may be the result of (a) nonlinear adsorption over the range of solution concentrations encountered as degradation progressed and/or (b) the presence of irreversibly adsorbed atrazine (as indicated by Figure 5) which constituted an increasing percentage of the total atrazine as degradation progressed. Previous studies (5, 8) of atrazine adsorption on Hawaiian soils have shown adsorption isotherms to be logarithmic (Freundlich type) for similar concentrations, i.e., the linear adsorption coefficient or percent adsorption increased with decreasing concentrations. Since the Freundlich equation infers a slope of infinite magnitude as the concentration in solution approaches zero, the increase in the linear adsorption coefficient as degradation progressed is not surprising. However, if adsorption catalyses hydrolysis, one might expect the increase in percent atrazine adsorbed to be accompanied by an increase in the first-order kinetic coefficient rather than the measured decrease. As stated previously, these results may be due in part to the failure of atrazine molecules in unstirred soil to reach those adsorption sites which would catalyze hydrolysis during incubation. If so, deviation from first-order kinetics would be a common occurrence in field soils.

The fraction of atrazine remaining in solution is important in relation to the biological activity of herbicides in the soil. Therefore, a reduction in the amount of atrazine in solution with time due to adsorption and degradation (Table 2) would result in a shorter period of weed control in the field. Since percent adsorption generally increases with lower herbicide concentrations, the level of phytotoxicity predicted by the percent total recovery (Figure 2) actually may be much lower when adsorption is considered. However, if the desorption rate for a given soil is fast enough to replenish the amount adsorbed by plants from the soil solution, a low concentration of atrazine in solution might not critically affect its biological activity. Thus, evaluations of both the kinetics of degradation and the kinetics of desorption are necessary to predict the effectiveness of a herbicide over time.

ACKNOWLEDGMENTS

The authors are grateful to Geigy Agricultural Chemicals, Yonkers, New York, for furnishing the radioactive atrazine used in this study and for the air transportation expenses of the senior author when he presented this paper at the Weed Science Society of America meetings, February 5-9, 1968, New Orleans, Louisiana.

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DATA EVALUATION RECORD

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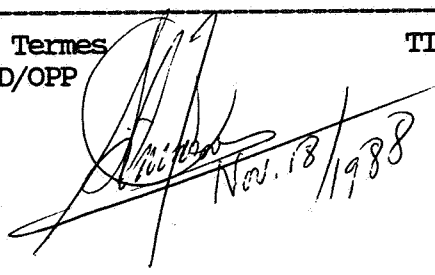
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Klaine, S.J. 1987. Biotic and abiotic degradation of atrazine and three of its metabolites in a West Tennessee soil. Conducted by the Department of Biology, Memphis State University, Memphis, TN. Laboratory Study Nu. TX-431. Completed October 22, 1987. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study was designed to provide an undisturbed system for studying degradation in situ and is to be considered supplemental to the laboratory studies.

However, the study is not acceptable because of the following deficiencies: 1) no complete data on soil characteristics were provided; 2) low material balance for total accounted ¹⁴C-radioactivity in the atrazine microcosms study; 3) discrepancies between text and Table for the material balance of ¹⁴C-deisopropylatrazine microcosms.

MATERIALS AND METHODS:

Test material:

- a. Radioactive materials (atrazine and metabolites)
 1. [U-ring-¹⁴C]-atrazine, 25.6 uCi/mg, 99% purity
 2. [U-ring-¹⁴C]-hydroxyatrazine, 23.5 uCi/mg, 99% purity
 3. [U-ring-¹⁴C]-deisopropylatrazine, 13.7 uCi/mg, 99% purity
 4. [U-ring-¹⁴C]-deethylatrazine, 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 1.35×10^6 RAD over a 12-hr period (Oak Ridge Laboratories). All soil microcosms were brought to 80% field holding capacity and incubated at 25 deg. C.

Dosing: Microcosms were dosed at rates equivalent to field application rates of atrazine (2.20 kg/ha) and those dosed with ¹⁴C 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-¹⁴C]-atrazine microcosm.

Material balances are shown in Table I for days 25, 100, and 180 and in the irradiated microcosm. ¹⁴C₂ and nonextractables increased with time. At 180 days, ¹⁴C₂ accounted for 12.14% of the total added radioactivity and nonextractables for 41.17%. Total ¹⁴C 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 ¹⁴C-activity was associated with nonextractables. Extractables were 1.5-fold greater than in nonirradiated microcosms after 180 days. ¹⁴C₂ 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-¹⁴C]-hydroxyatrazine microcosm.

Table IV shows the material balances for this metabolite. By day 180, evolution of ¹⁴C₂ 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 ¹⁴C-activity accounted for 44.77% (lost during partitioning). Nonextractables were 24.50%. ¹⁴C₂-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-¹⁴C]-deisopropylatrazine microcosm

Table VII shows the material balance for ¹⁴C-deisopropylatrazine. The ¹⁴CO₂ 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 ¹⁴C-activity was 28.45% and was about 3-fold greater than extractable radioactivity in nonirradiated microcosms. Evolution of ¹⁴CO₂ 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 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-¹⁴C]-deethylatrazine microcosms

Table X shows the material balance for ¹⁴C-deethylatrazine determined at 30, 60, and 180 days and 180 days for nonirradiated and irradiated microcosms, respectively. Evolved ¹⁴CO₂ 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 ¹⁴C-activity was found in the nonextractable component (49.16%). Extractables (total) were 46.45% after 180 days. Evolution of ¹⁴CO₂ 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, ¹⁴C-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 ¹⁴CO₂ evolution occurred in irradiated microcosms (thus questioning sterility), it did not exceed 1% except for microcosms dosed with ¹⁴C-deisopropylatrazine (1.8%). The degradation rates of the phytotoxic metabolites deisopropyl- and deethylatrazine were similar to the parent compound and indicate that neither metabolite would persist exceedingly longer than the parent. The nonphytotoxic hydroxyatrazine metabolite exhibited the lowest degradation rate, but total ¹⁴CO₂ 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 ¹⁴C-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 nonirradiated 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; deisopropyl-atrazine, 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 ¹⁴C-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., CO₂ 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).

PERTINENT DATA TABLES AND FIGURES

-7.7-

Atrazine

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Pages 110 through 126 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.
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Atrazine

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FORMULATION—00—RADIOLABELED ACTIVE INGREDIENT

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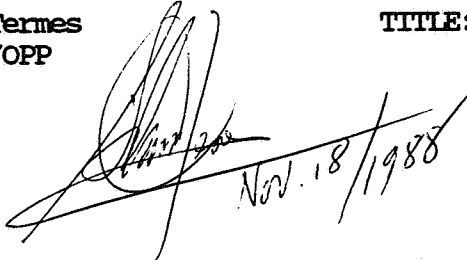
Spare, W.C. 1987. Anaerobic aquatic metabolism of atrazine. Conducted by Agrisearch, Inc., Frederick, MD. Laboratory Study No. 1231. Completed October 1, 1987. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
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CONCLUSIONS:



Nov. 18/1988

This study is acceptable and fulfills data requirements for the anaerobic aquatic metabolism of atrazine (162-3).

The combined water/sediment (sandy clay) half-life was calculated as 608 days (330 days in sediment; 578 days in water). Production of volatile materials was minimal. Bound residues increased with time, but leveled to about 10% of applied 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 samples, above 80% remained as parent atrazine). Metabolites were present at low levels (G-30033, 4.7%; G-34048, 5%; and G-28279, 1.4%).

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 Alkaline	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 $\mu\text{Ci}/\text{mg}$, 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 μL 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 $^{14}\text{CO}_2$ 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 deg. 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 deg. 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 analyzed at 6 and 12 months. Replicate test systems were removed and analyzed at each sampling interval. Analyses consisted of characterization of residual parent and metabolites in water and sediment. Trapping solutions were analyzed for $^{14}\text{CO}_2$ and volatile metabolite production.

Analyses: Carbon-14 radioactivity measurements were done by LSC. Sediment samples were oxidized to $^{14}\text{CO}_2$ 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 $^{14}\text{CO}_2$.

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 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,

$$\ln C = -kt + \ln C_0$$

k = rate constant
C = chemical concentration
t = time (days)
C₀ = 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 shows 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. EFGWB concurs with the study author's conclusions.

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 132 through 136 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.
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MOBILITY STUDIES
IN SOIL (LABORATORY)

DATA EVALUATION RECORD

STUDY 9

CHEM 080803 Atrazine §163-1

FORMULATION—00—ACTIVE INGREDIENT

FICHE/MASTER ID 00027134

Talbert, R.E. and O.H. Fletchall. 1965. The adsorption of some s-triazines in soils. Weeds 13(?):46-52.

DIRECT REVIEW TIME = 8

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study was included in the 1983 Registration Standard. The study is scientifically sound and provides supplemental information towards the registration of atrazine. This study does not fulfill EPA Data Requirements for Registering Pesticides because: Effect of soil characteristics - the test solutions contained a surfactant, the temperature during equilibration was not reported, only one concentration of atrazine instead of at least four concentrations was studied, distribution coefficients (K_d) were calculated instead of Freundlich K values, and desorption was not addressed; Effect of pesticide concentration - the test solutions contained a surfactant, concentrations >30 ppm that were studied exceeded the aqueous solubility of atrazine, the temperature during equilibration was not reported, and desorption was not addressed; Effect of equilibration temperature - the test solutions contained a surfactant, only one concentration of atrazine instead of at least four concentrations was studied, distribution coefficients (K_d) were calculated instead of Freundlich K values, and desorption was not addressed.

SUMMARY OF DATA BY REVIEWER

Based on batch equilibrium experiments, ring-labeled [¹⁴C]atrazine (purity >97%), at 1 ppm, was very mobile in twenty-five soils ranging in texture from sandy loam to clay, with distribution coefficients (K_d = pesticide adsorbed to soil ÷ pesticide in solution) of 0.6-4.8. [¹⁴C]-Atrazine, at 5-70 ppm, was very mobile in silty clay loam soil with a Freundlich K_{ads} value of 4.32 and a n value of 0.87. At temperatures ranging from 3 to 50°C, atrazine was very mobile in silty clay loam soil with distribution coefficients of ≈3.5-5.9; adsorption decreased with increasing temperature.

DISCUSSION:

General

1. The test solutions contained 1 mL X-100 surfactant/L. The study authors stated that "the presence of this small amount surfactant did not affect the adsorption of these triazines"; however, no evidence was provided to support this statement.
2. The soils were not analyzed after adsorption to confirm adsorption and to provide a material balance.
3. Desorption of atrazine was not studied.
4. Two experiments were conducted which were not pertinent to environmental fate data requirements and were therefore not reviewed. One experiment was conducted using clay and peat suspensions. In another experiment, the elution of atrazine from soil that had been treated with atrazine, dried at 50°C, and stored in a desiccator prior to several washings with distilled water was studied.

Effect of soil characteristics

1. The experiment was conducted using only one concentration of atrazine instead of at least four concentrations. Since correct calculation of Freundlich K values require that a range of concentrations be studied, distribution coefficients (K_d ; pesticide adsorbed to soil ÷ pesticide in solution) were calculated instead of Freundlich K values.
2. The temperature during equilibration was not reported.

Effect of pesticide concentration

1. The higher concentrations of atrazine that were studied (5-70 ppm) exceeded the aqueous solubility of atrazine (30 ppm at 20°C). The test substance would not have been completely dissolved in the calcium chloride solutions at the higher atrazine concentrations.
2. The temperature during equilibration was not reported.

Effect of equilibration temperature

The experiment was conducted using only one concentration of atrazine instead of at least four concentrations. Since correct calculation of Freundlich K values require that a range of concentrations be studied, distribution coefficients (K_d ; pesticide adsorbed to soil ÷ pesticide in solution) were calculated instead of Freundlich K values.

MATERIALS AND METHODS

MATERIALS AND METHODS:

A preliminary experiment was conducted in order to determine the amount of time necessary for equilibration. The concentration of atrazine used in this portion of the experiment was 1 ppm, and the temperature was not reported. The data (Figure 1) indicate that equilibrium plateaued by 24 hours posttreatment.

Effect of soil characteristics

Twenty-five soils ranging in texture from sandy loam to clay (Table 1) were mixed with 0.01 M calcium chloride:0.1% X-100 surfactant solutions containing ring-labeled [¹⁴C]atrazine (purity >97%, specific activity 4.84 μCi/mg, source unspecified) at 1 ppm; the soil:solution ratio was 1:10. The soil:solution slurries were shaken for 24 hours and centrifuged, and the supernatants were analyzed for total radioactivity by LSC.

Effect of pesticide concentration

Marshall silty clay loam soil (4% sand, 66% silt, 30% clay, 4.2% organic matter, CEC 21.3, pH 5.4) was mixed with 0.01 M calcium chloride:0.1% X-100 surfactant solutions containing [¹⁴C]atrazine plus nonradiolabeled atrazine (purity 98.5%, source unspecified) at 5-70 ppm; the soil:solution ratio was 1:10. The soil:solution slurries were shaken for 24 hours and centrifuged, and the supernatant was analyzed for total radioactivity by LSC.

Effect of equilibration temperature

Marshall silty clay loam soil was treated with 0.01 M calcium chloride:0.1% X-100 surfactant solutions containing [¹⁴C]atrazine at 1 ppm; the soil:solution ratio was 1:10. The soil:solution slurries were shaken for 24 hours at temperatures of 3, 10, 20, 32, 40, and 50°C. After equilibration, the soil:solution slurries were centrifuged, and the supernatants were analyzed for total radioactivity by LSC.

MATERIALS AND METHODS
STUDY AUTHOR(S) 'S RESULTS AND/OR CONCLUSIONS
PERTINENT DATA TABLES AND FIGURES

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represent the amount of herbicide present because interference may occur from decomposition products. Any decomposition products should be removed and the amount of remaining herbicide determined. This is difficult because of the very small quantities used. The data presented in Figures 4, 5, and 6 represent relative values, especially when an altered spectrum indicates the presence of other compounds. However, the data presented may be used to show relative loss of herbicides under the different conditions.

The losses of all herbicides followed a similar pattern, being most rapid during the initial stages of treatment. The reason for this in the dark is not easily explained. During UV irradiation, the formation of a thin layer of breakdown products probably protects the herbicide beneath from being decomposed. Thus, a steady state is reached in which further decomposition is not possible until the decomposition products are removed. This indicates that very little protection is required to prevent photodecomposition.

The results of these experiments show that the shorter wavelength-higher energy ultraviolet light (far UV)

was most effective in altering the eight herbicides. It should be remembered that the far UV light (253.7 mμ) used here does not occur in sunlight reaching the earth's surface. The ultraviolet radiation in sunlight begins at about 290 mμ. The light source that is most representative of the UV from the sun is the near UV lamp. The far and middle light sources can be used to show, rapidly the effect of UV light on herbicides but are not as representative of field conditions. The most desirable light source for this type of study would be one with the same spectral energy distribution as sunlight.

LITERATURE CITED

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The Adsorption of Some s-Triazines in Soils¹

RONALD E. TALBERT² and O. HALE FLETCHALL³

Abstract and Summary. The extent of adsorption of five C¹⁴-labeled s-triazines, 2-chloro-4,6-bis(ethylamino)-s-triazine (simazine), 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine), 2-chloro-4,6-bis(isopropylamino)-s-triazine (propazine), 2-methoxy-4,6-bis(isopropylamino)-s-triazine (prometon), and 2,4-bis(isopropylamino)-6-methylmercapto-s-triazine (prometryne) from aqueous solutions by soil constituents was expressed as a distribution coefficient (K_d), which is the ratio of the amount of herbicide adsorbed to the amount in the equilibrium solution. The K_d value for a given s-triazine and exchanger remained relatively constant over a range of concentrations. The adsorption reaction was essentially at equilibrium within 1 hour. Increasing the temperature and pH resulted in decreased adsorption of simazine and atrazine. The order of increasing adsorption of these compounds by soils was propazine, atrazine, simazine, prometon and prometryne. Increased amounts of organic matter and/or clay in a soil generally were associated with increased adsorption of these s-triazines. No adsorption of simazine or atrazine was detected with kaolinite, Putnam clay, illite, and montmorillonite were increasingly adsorptive in that order. The organic materials were generally much more adsorptive than the clays. The adsorption reaction was reversible by increasing temperatures, water elution, and elution with various organic solvents. Fifty percent ethanol plus heat was very effective in eluting the chloro-s-triazines from soil.

INTRODUCTION

It is a common observation that soils high in organic matter and clay content require increased rates for

a given herbicidal activity. It is generally accepted that this effect is due to the high adsorptive capacity of these soil constituents for herbicides. Adsorption of herbicides, therefore, is basic to understanding the behavior of herbicides in soil. Adsorption in this case is the process in which the dissolved herbicide becomes physically or chemically bonded to the colloidal surfaces, thereby causing a net decrease in the concentration of the herbicide in the solution phase. As soil-applied herbicides are generally considered to enter-plant roots as solutes with the soil water, the degree of adsorption modifies the availability of the herbicide to plants or the activity of the herbicide (6). In addition, it has been shown that the quantity of organic matter and clay regulates leaching (2, 13) and losses from volatilization (3) of herbicides in soils.

Numerous greenhouse studies have been conducted with various s-triazines and other herbicides comparing their initial toxicity in various soil types (5, 14, 16, 18). These studies have shown the high degree of influence of soil type and more specifically, the relationship of organic matter and clay content, to the initial activity of these herbicides.

Some workers have used the more direct approach of analytically measuring the amount of herbicide adsorption by colloidal constituents (7, 11, 17). Sheets (15) found that 2-chloro-1,6-bis(ethylamino)-s-triazine (simazine) was adsorbed to a cation exchanger and to activated charcoal but not to an anion exchanger. Frisell (7) found that the adsorption of simazine, 2-chloro-4-diethylamino-

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monoethylamino-s-triazine (trietazine) and 2-chloro-4-(diethylamino)-s-triazine (chlorazine) from aqueous solutions was greatest in montmorillonite; illite was intermediate; and kaolinite was least adsorptive. Differences between adsorption of these compounds by montmorillonite were small. Decreasing adsorption occurred with increasing pH of the system and the observed adsorption appeared to be fully reversible.

The investigations reported herein were conducted to (1) develop a simple and rapid testing procedure for determining the extent of herbicide adsorption by soils, (2) determine the effects of various factors on the adsorption of five s-triazines, (3) compare the relative adsorption characteristics of simazine, 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine), 2-chloro-4,6-bis(isopropylamino)-s-triazine (propazine), 2-methoxy-4,6-bis(isopropylamino)-s-triazine (prometone), and 2,4-bis(isopropylamino)-6-methylmercapto-s-triazine (prometryne), and (4) study some characteristics of the adsorption reaction.

MATERIALS AND METHODS

Stock solutions containing 2-20 ppm of ring labeled simazine-C¹⁴ (specific activity 5.07 $\mu\text{C}/\text{mg}$), atrazine-C¹⁴ (4.84 $\mu\text{C}/\text{mg}$), propazine-C¹⁴ (9.2 $\mu\text{C}/\text{mg}$), prometone-C¹⁴ (4.57 $\mu\text{C}/\text{mg}$) and prometryne-C¹⁴ (7.16 $\mu\text{C}/\text{mg}$) were prepared, utilizing a Waring Blendor and 1 ml of 1% X-100 surfactant/L, and stored at 8 C. The presence of this small amount of surfactant did not affect the adsorption of these triazines. The purity of the labeled materials was checked by dissolving in 95 percent alcohol, chromatographing (ascending) on Whatman No. 1 filter paper using n-butanol-acetic acid-water (4:1:1) as a solvent, eluting sections of the filter paper strips in the liquid scintillator and determining the proportion of radioactivity associated with the primary spot of activity (R_f between 0.90 and 0.95 for all five triazines). All the radioactive materials apparently had a purity of 97 percent or more and were used without further purification. Unlabeled technical simazine and atrazine (98.5 percent) were also used in some of the experiments.

Factors affecting adsorption.

The standard procedure used for the determination of adsorption was to weigh 0.5 g of air-dry soil in a 15-ml glass centrifuge tube and add 5 ml of 1 ppmw s-triazine-C¹⁴ (in 0.01 M calcium chloride). The tube was then sealed with an aluminum foil-covered rubber stopper. No adsorption by glass or aluminum foil was observed, whereas rubber stoppers and polypropylene were much more adsorptive.

Each sample was allowed to equilibrate for 24 hours on a shaft which rotated the centrifuge tubes lengthwise at 14 rpm. The samples were then centrifuged and 0.5 ml of the supernatant removed for counting. Samples of the s-triazine-C¹⁴ solution without soil were treated in the same manner and used as a standard. The difference between the amount of s-triazine-C¹⁴ found in the standard solution and in the supernatant of the sample was assumed to have been adsorbed. Each treatment was run in triplicate. Coefficient of variation values for the various experiments ranged from 1 to 5 percent. The results were

expressed as a distribution coefficient (K_d) (12) which is the ratio of the amount of s-triazine-C¹⁴ adsorbed to the amount in the equilibrium solution. K_d values may be calculated directly from the counting data with the following equation:

$$K_d = \frac{\text{cpm standard} - \text{cpm equilibrium solution}}{\text{cpm equilibrium solution}} \times \frac{\text{ml solution}}{\text{g adsorbent}}$$

The latter factor converts the data to equivalent units (ppmw adsorbed/ppmw in solution).

Counting was done on a Packard Tri-Carb automatic liquid scintillation counter. The liquid scintillator consisted of 4 g of 2,5-diphenyloxazole (PPO) plus 0.1 g of 1,4-bis-2-(5-phenyloxazolyl)-benzene (POPOP) in a liter of 30% absolute ethanol and 70% toluene. One-half ml of the aqueous sample was added to 19.5 ml of the liquid scintillator, dissolved by a slight shaking, and counted for two 10-minute periods. The radioactivity was usually quite high and counting errors were less than 2 percent. Standards were used to correct for changes in counting efficiency whenever necessary for comparisons. The counting efficiency was approximately 60%. Differences in quenching between samples were not a problem except when counting the radioactivity in solvents other than water. Standardized toluene-C¹⁴ was added to samples when required to correct for quenching.

All five s-triazine-C¹⁴ herbicides were studied to determine the length of time required for the triazine to become equilibrated between Marshall silty clay loam soil and the aqueous phase of the suspension. The general procedure was modified in that 5 g of soil and 50 ml of the herbicide solutions were equilibrated in 8-oz prescription bottles. A 5-ml sample was removed from each bottle at 1, 6, 12, 24, 36, 48, 72, and 96 hr, centrifuged, a 0.5 ml sample of the supernatant counted, and the remainder of the sample returned to the bottle for further agitation.

Solutions of simazine-C¹⁴ and atrazine-C¹⁴ were equilibrated with Marshall silty clay loam at various temperatures. The same sampling procedure as in the time study was used, except the systems were moved to different temperature environments and allowed to equilibrate at least 1.5 hours before sampling. A laboratory oven was used to obtain the temperatures of 40 and 50 C while temperatures of 5, 10 and 20 C were obtained with refrigeration and 32 C was room temperature.

An experiment was conducted with simazine and atrazine to determine the effect of herbicide concentration on their adsorption by Marshall silty clay loam. Solutions of atrazine containing 5 to 70 ppmw were prepared from unlabeled technical atrazine and atrazine-C¹⁴. Lower concentrations of simazine and atrazine were prepared from the labeled material only. The standard procedure was used to determine the adsorption from the various solutions.

The effect of soil type on the K_d values for the five triazine herbicides was determined. Samples of top soil from twenty-five soil types representing all regions of Missouri (1) were obtained (Table I). Particles greater

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Table 1. The chemical and physical properties of 25 soil types of Missouri as they influence Kd values for five s-triazines.

Soil type	pH	EC	Milliequivalents per 100 g					Percent				Kd values				
			K	Mg	Ca	II	CEC	OM	Loam ^a	Silt	Clay	Propazine	Atrazine	Simazine	Propazine	Propazine
Peoness s.l.	17	3.3	0.1	1.8	7.2	2.7	12.3	1.9	6	74	20	1.1	1.9	2.3	2.8	3.8
Marshall s.l.	20	1.4	0.9	1.5	11.5	4.9	21.3	0.2	4	66	30	1.0	4.5	7.2	8.8	12.3
Grundy s.l.	27	2.8	0.3	1.4	8.0	4.9	15.3	1.6	3	47	50	2.8	4.8	6.5	6.5	9.2
Marion s.l.	27	4.6	0.3	1.7	4.1	3.3	9.9	1.4	9	74	17	2.1	2.2	2.7	1.7	14.2
Kennett s.l.	280	2.4	0.7	1.5	11.0	3.3	18.0	2.9	26	43	31	2.6	2.2	3.1	2.3	8.4
Shelby loam	1	4.3	0.3	2.3	6.9	8.3	28.1	2.8	30	44	26	2.3	2.6	2.6	4.7	7.9
Lambert loam	7	4.7	0.3	1.9	14.3	2.5	48.3	2.3	1	36	63	3.1	3.7	6.8	17.0	17.3
Webster clay	200	3.7	0.8	3.0	15.4	1.3	17.9	2.1	32	50	18	1.9	2.3	2.3	1.5	4.4
Rolla loam	72	7.1	0.3	1.3	17.3	0.8	14.3	1.3	49	30	19	1.2	2.2	2.0	1.3	2.9
Searcy loam	30	4.8	0.4	2.3	17.8	8.3	28.1	4.9	41	19	1.2	1.4	1.4	1.4	1.4	
Sumner s. clay	42	6.4	0.2	1.1	9.9	1.5	9.3	1.0	1	47	20	1.9	2.7	1.9	3.6	3.0
Orange s.l.	17	6.4	0.2	1.1	9.9	1.5	9.3	1.0	1	76	23	1.7	1.9	1.9	1.9	1.9
Ross s.l.	17	6.4	0.2	1.1	9.9	1.5	9.3	1.0	1	76	23	1.7	1.9	1.9	1.9	1.9
Corral s.l.	13	2.7	0.2	1.0	7.1	1.8	8.8	2.7	11	75	14	1.4	1.4	1.4	1.4	1.4
Novocott s.l.	22	2.9	0.4	1.4	12.4	3.0	12.9	1.9	8	72	20	1.8	2.3	2.3	1.7	1.7
Dixon s.l.	15	6.9	0.4	1.8	8.8	2.0	9.1	2.4	4	80	11	1.8	1.7	1.7	1.7	1.7
Rayne s.l.	20	5.3	0.4	1.7	8.8	2.0	9.1	2.4	4	80	11	1.8	1.7	1.7	1.7	1.7
Marion s.l.	20	5.3	0.4	1.7	8.8	2.0	9.1	2.4	4	80	11	1.8	1.7	1.7	1.7	1.7
Union s.l.	5	4.9	0.3	1.3	4.8	3.0	6.8	1.8	2	79	17	2.0	2.2	2.0	2.0	2.0
Lebanon s.l.	5	4.9	0.3	1.3	4.8	3.0	6.8	1.8	2	79	17	2.0	2.2	2.0	2.0	2.0
Clatsop s.l.	4	1.7	0.1	1.1	1.7	1.7	5	1.7	1	79	17	2.1	1.7	1.7	1.7	1.7
Clatsop s.l.	197	6.4	0.4	1.9	6.9	1.8	4.5	1.2	20	63	17	1.7	1.7	1.7	1.7	1.7
Charbon s.l.	133	1.8	0.3	1.9	12.0	1.0	28.2	2.3	23	39	45	1.0	1.1	7.0	38.2	13.4
Shelby clay	230	1.3	0.1	1.1	1.1	2.0	3.2	1.4	84	11	5	1.1	1.1	1.0	1.0	1.0
Linn s.l. med.	4	6.4	0.3	1.2	9.0	1.5	12.8	2.0	10	66	28	2.0	1.0	3.1	3.0	3.0
Waverly s.l.	4	6.4	0.3	1.2	9.0	1.5	12.8	2.0	10	66	28	2.0	1.0	3.1	3.0	3.0
Means	63	5.5	0.5	1.9	8.7	2.9	14.6	2.3	15	61	24	2.0	2.7	1.7	2.8	9.1
C V % (among soils)	122	13	66	64	17	72	62	64	121	37	32	49	64	54	145	99

^aKd = Amount adsorbed (mg/kg) at equilibrium.
 Solvent concentration (mg/L)
 Particle size distribution classes: sand = 2.0 to 0.05 mm, silt = 0.05 to 0.002 mm, clay = <0.002 mm.

than 2 mm diameter were removed by screening and the air-dry samples stored. Organic matter, phosphorus, calcium, magnesium, potassium, hydrogen, and salt pH (in 0.01 M calcium chloride) were determined by standard Missouri soil testing procedures (9), cation exchange capacity by the ammonium distillation method (10), particle distribution by the pipette and sieve method (4), and Kd values by the standard procedure as previously described. Simple correlation coefficients of the various soil properties among themselves, of Kd values of the five triazines among themselves, and between soil properties and Kd values of the five triazines were calculated using the experimental data from the twenty-five soil types.

Four clay materials, Georgia kaolinite, Illinois grunite (illite), Wyoming bentonite (montmorillonite), and Putnam subsoil clay (predominantly biedellite), and two organic materials, Wisconsin peat and peat moss, were included in similar studies. The clays were dispersed and particles of less than 0.002 mm diameter were obtained sedimentation techniques, and prepared as hydrogen systems by passing the suspensions through an IR-123, H-form. The Wisconsin peat was prepared as a sodium system; the inorganic impurities, mostly illite, were removed by sedimentation; and the suspension treated with the IR-120. The clays and Wisconsin peat were adjusted to a pH of 7 with a saturated solution of calcium hydroxide and maintained as suspensions in the following concentrations: kaolinite 0.35 g/ml, illite 0.29 g/ml, montmorillonite 0.05 g/ml, Putnam clay 0.15 g/ml and Wisconsin peat 0.05 g/ml. The peat moss was ground to pass through a 40-mesh screen, moistened, adjusted to a pH of 7 with calcium hydroxide solution, the excess water removed by suction in a Buchner funnel, and the moist residue stored in a refrigerator until used. The cation exchange capacity of these materials was determined from duplicate 0.5-g samples using the ammonium distillation

method (10) employing a micro-steam distillation apparatus.

Kd values for the adsorption of simazine and atrazine by these exchangers were determined by adding 4 ml of the clay or peat suspensions and 1 ml of the labeled s-triazine solution in 15 ml centrifuge tubes. With the peat moss, 0.3 g of the moist material, (0.12 g dry weight), 3.5 ml of distilled water and 1 ml of the triazine solution were equilibrated. All triazine solutions had a concentration of approximately 1 ppmw before equilibration. Samples were taken and counted in the usual manner. In another study, the clay and Wisconsin peat suspensions were adjusted to a pH of 5 with 0.1 N hydrochloric acid and Kd values determined in a similar manner. These values were compared with those obtained at a pH of 7 to indicate the effect of pH on the adsorption equilibrium.

Elution studies.

The soil containing labeled s-triazines was prepared by adding the herbicides in water to bring the soil to 50% moisture, immediately drying under a 50 C air current with intermittent stirring, and stored in a desiccator. Triplicate 1-g samples of Marshall silty clay loam containing simazine and atrazine were washed with successive 5-ml portions of distilled water by allowing the systems to equilibrate for at least 4 hours, centrifuging, sampling for radioassay, discarding supernatant, weighing sample, and adding 5 ml of distilled water. The net amount of herbicide eluted with each successive washing was determined, taking into account the amount of herbicide in the solution remaining with the exchanger after the supernatant was discarded. This procedure was continued until no further radioactivity could be removed. In another study, a 5-g sample of simazine-treated soil was leached with 250 ml of distilled water over a 30-

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... period. The amount of simazine eluted was determined by radio-analysis of the leachate. In another study, 38 organic solvents and mixtures of solvents were compared for their efficiency in extracting simazine from the Marshall soil. In each case, 5 ml of the solvent were added to duplicate 1-g samples of the treated soil and allowed to stand for 6 hours at room temperature. The amount of radioactivity in the solvent at the end of this extraction period was determined. Aqueous ethanol (1:1 v/v) was used in a series of experiments as the eluent to determine the effects of time, temperature, volume, concentration and soil type on the amount simazine eluted. The elution procedure developed was then evaluated for its efficiency in eluting atrazine, propazine, and prometryne from soil.

RESULTS AND DISCUSSION

Factors affecting adsorption.

The effect of time on the adsorption equilibria between soil and water as expressed by distribution coefficients (Kd) for the five s-triazines-C¹⁴ is shown in Figure 1. Al-

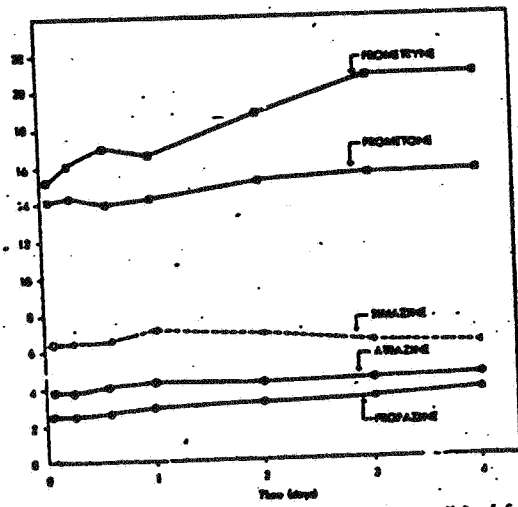


Figure 1. Effect of time on the distribution coefficient (Kd) of five s-triazines between Marshall silty clay loam and the aqueous phase of the suspension.

though the systems approached equilibrium at 1 hour, adsorption slowly increased with time as indicated by Kd values. This effect was most noticeable with prometryne, the herbicide adsorbed to the greatest extent initially. The small increases in adsorption with time after 1 hour, may be due to (1) a delay in the wetting of small interior capillaries, (2) the slow diffusion of the triazine into these interior surfaces, (3) a slow irreversible fixation reaction due to chemical forces, (4) the mechanical breakage of solid particles, or (5) the formation of complexes.

The effect of temperature on Kd values for simazine-C¹⁴ and atrazine-C¹⁴ is shown in Figure 2. The amount

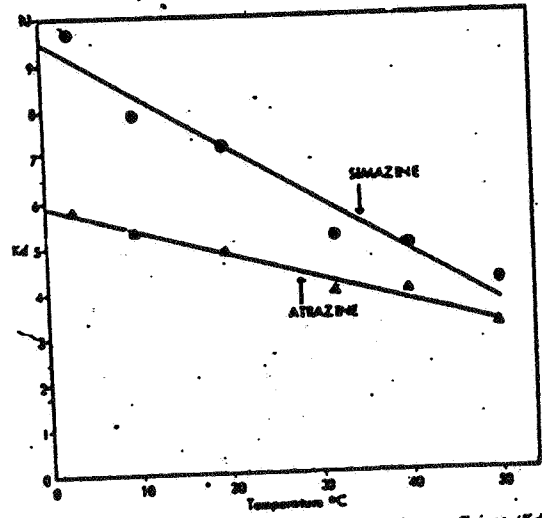


Figure 2. Effect of temperature on the distribution coefficient (Kd) of simazine-C¹⁴ and atrazine-C¹⁴ between Marshall silty clay loam and the aqueous phase of the suspension.

of simazine and atrazine adsorbed decreased with increasing temperature. This is a general phenomenon in adsorption reactions. The adsorption of these compounds was temperature reversible, because when the soil suspensions were removed from 50 to 20, to 10 and to 5 C, adsorption increased proportionally. Also when the temperature was increased from 40 to 50 and from 3 to 32 C, adsorption decreased proportionally. Temperature had a greater effect on the adsorption of simazine than of atrazine.

The amount of simazine-C¹⁴ and atrazine-C¹⁴ adsorbed at various concentrations by Marshall silty clay loam is shown in Figure 3. Adsorption data plotted in this manner are referred to as adsorption isotherms. The slope at each point of this curve, which is the ratio of adsorbed s-triazine to the concentration in the equilibrium solution, is then the Kd value expressing the extent of adsorption at a given concentration. As the concentration of s-triazine was increased, the amount adsorbed increased in an almost linear fashion with these concentrations.

These data were also evaluated in more theoretical terms. The generalized relationship for the adsorption of solutes from solution is given by the empirical Freundlich isotherm of the form

$s = kc^n$

where s is the amount of solute adsorbed by unit mass of adsorbent from a solution of concentration c, and k and n are constants for the given adsorbent and adsorbate (8). By expressing the adsorption data in logarithmic form and plotting log s against log c, a linear plot should result if the data fit the Freundlich equation. Although not shown, the data plotted in Figure 3 were found to follow the generalized form of the above equation. Thus, the adsorption of simazine and atrazine by soil does not

W E E D S

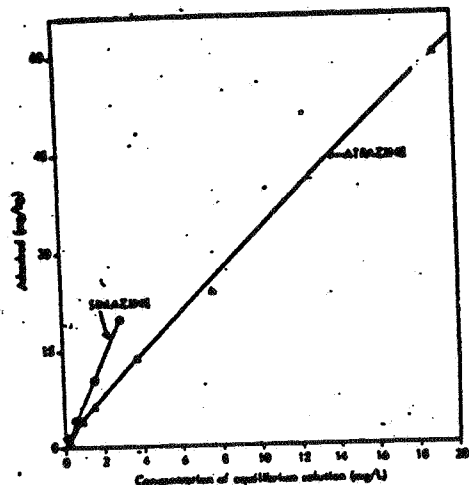


Figure 3. Isotherms for the adsorption of simazine and atrazine by Marshall silty clay loam.

appear to be different from the typical form which is exemplified by the adsorption of acetic acid by charcoal. The values for k and n for the adsorption of simazine and atrazine by Marshall silty clay loam soil were determined as described in Glasstone and Lewis (8). These values for simazine were $k = 7.25$ and $n = 0.88$ and atrazine $k = 4.32$ and $n = 0.87$. The n value indicates the degree of linearity of the adsorption isotherm with a value of 1 being completely linear. As these n values are close to 1, the k values found for the Freundlich equation are very similar to K_d values found for this soil type (Table 1 and Figures 1 and 2) or a is approximately equal to k_c . Over a limited range of concentrations the K_d value changes very slightly, thus justifying its use as a practical single numerical expression of herbicidal adsorption for comparative purposes. However, because of this concentration effect, it is important to have similar concentrations of herbicide present in the equilibrating solutions where comparisons are to be made.

The chemical and physical properties of the various soil types and their effect on adsorption as expressed by K_d values are given in Table 1. In general, the order of increasing adsorption was propazine, atrazine, simazine, prometon, and prometryne. There were few exceptions to this generality within the individual soil types. This order does not follow the inverse relationship between water solubility and adsorption found by Coggins and Crafts (6). The order of decreasing water solubility is prometon, atrazine, prometryne, propazine and simazine. There seems to be little relationship between water solubility and adsorption of these compounds. The adsorption of prometon and prometryne varied more with soil type than the chloro-triazines as indicated by the higher coefficient of variation for K_d values. This agrees with Sheets and Shaw (16) who showed a greater variation in initial effective levels among soil types resulting from the methoxy and methylmercapto derivatives than

those of corresponding chloro derivatives. This effect is evidently due to the greater adsorption of these compounds as compared to the chloro-triazines.

In an attempt to relate the soil characteristics affecting the adsorption of these compounds, correlation coefficients were determined (Table 2). Of the soil charac-

Table 2. Correlation coefficients (r) between soil properties and K_d values of five triazines using the experimental data from 25 soil types of Missouri.

Soil property	K_d values for:				
	Propazine	Atrazine	Simazine	Prometon	Prometryne
OM	.76	.52	.33	.36	.68
PCa	-.11	-.11	-.30	-.16	-.10
pH	-.41	-.39	-.39	-.43	-.40
me K	.38	.43	.43	.38	.44
me Mg	.58	.43	.34	.58	.44
me Ca	.34	.39	.47	.19	.22
me H	.42	.43	.78	.11	.43
CFC	.49	.43	.79	.55	.43
Sand	-.46	-.45	-.34	-.51	-.57
Silt	-.83	-.68	-.17	-.42	-.68
Clay	.71	.65	.77	.68	.68

*Correlation coefficients of .40 at 5 percent level and .50 at 1 percent level required for significance.

teristics determined, adsorption of the triazines was most closely related to organic matter content, clay content, cation exchange capacity and exchangeable magnesium and hydrogen. The relationships between adsorption of these triazines and organic matter and clay content are expected because of the colloidal nature of these constituents. Cation exchange capacity and amounts of exchangeable cations, except potassium, are also, in general, closely associated with organic matter and clay content (Table 3) which may be responsible for the association

Table 3. Correlation coefficients (r) of various soil properties among themselves calculated from experimental data from 25 soil types of Missouri.

Soil property	PCa	pH	Mg	Ca	H	CFC	Sand	Silt	Clay
OM	-.10	-.28	.19	-.26	.07	.72	.43	.46	-.53
PCa		.14	.34	.33	-.34	-.87	.13	.49	-.44
pH			.18	-.13	-.46	-.72	-.87	.85	-.16
me K				.53	-.82	.34	.10	-.34	-.36
me Mg				.46	.45	.77	-.87	-.68	.68
me Ca					.26	.73	-.34	-.15	.17
me H						.68	-.13	-.38	.11
CFC							-.20	-.34	-.72
Sand								-.77	-.34
Silt									-.34

*Correlation coefficients of .40 at 5 percent level and .50 at 1 percent level required for significance.

of the exchangeable cations and triazine adsorption. The adsorption of prometon and prometryne was less closely associated with percent organic matter than the chloro-triazines. Clay content seems to be more related to the adsorption of prometon and prometryne than organic matter. There was a tendency for pH to be negatively correlated with K_d values.

If earlier assumptions are correct concerning the relationships between adsorption and herbicidal activity, leaching, and volatilization, it may be possible to make some predictions as to herbicidal activity, leaching and volatilization in various soils from herbicide adsorption data of the type obtained in these studies. However, any conclusions along these lines are beyond the scope of this study.

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The relationships between adsorption of these s-triazines are shown in Table 4. The chloro derivatives (simazine and atrazine) were apparently adsorbed in a similar manner as indicated by the high correlation coefficients of K_d value between these herbicides. The relationship between the adsorption of prometon and prometryne was much closer than the relationship between the adsorption of the chloro derivatives and prometon or prometryne. Evidently different factors were important in the adsorption of prometon and prometryne than in the adsorption of the chloro-s-triazines.

Table 4. Correlation coefficients (r) of K_d values of five s-triazines among themselves calculated from experimental data from 25 soil types of Missouri.

s-Triazine	Atrazine	Simazine	Prometon	Prometryne
Propazine	.86	.80	.51	.46
Atrazine		.90	.52	.47
Simazine			.60	.72
Prometon				.96

*Correlation coefficient of .40 at 5 percent level and .50 at 1 percent level required for significance.

Studies were conducted to determine the influence of various clay and organic exchangers and their acidity on the adsorption of simazine and atrazine (Table 5). Neither

Table 5. Effect of type of clay or peat and pH on the K_d values for simazine and atrazine.

Exchanger	mg/100g	K _d value, pH 7		K _d value, pH 5	
		Atrazine	Simazine	Atrazine	Simazine
Illite	6	6.0	6.0	6.0	6.0
Illite	20	1.3	2.3	1.3	11.3
Putnam clay	42	1.9	2.7	1.3	6.0
Montmorillonite	106	4.3	12.3	6.0	12.3
Wisconsin peat	118	21.5	21.5	21.5	23.0
Peat moss	106	91.0	82.3	—	—

simazine or atrazine was adsorbed by kaolinite. Illite and montmorillonite were similar in their capacity to adsorb these compounds, although montmorillonite had a cation exchange capacity four times as large as illite. Perhaps the triazines were unable to penetrate into the internal surfaces of the expanding lattice type montmorillonite clay. The Putnam clay, in spite of its relatively high adsorptive capacity for cations adsorbed very little simazine and atrazine. Putnam also has an expanding type lattice. The organic exchangers were generally more adsorptive than the clay exchangers, with the peat, moss having a much greater adsorption capacity than the Wisconsin peat. Cation exchange capacity of these materials was not generally related to the adsorptive capacity for simazine and atrazine. In general, simazine was adsorbed to a greater extent than atrazine by the clay exchangers; but both were adsorbed by the organic exchangers to about the same degree. Increasing the acidity resulted in increased adsorption by the clay systems, but not by Wisconsin peat. It is concluded that the extent of adsorption is highly dependent on the type of organic matter and clay as well as the amounts of these constituents in a soil. This explains to a large extent the imperfection of correlations of amounts of these constituents in soils with their herbicidal adsorption characteristics.

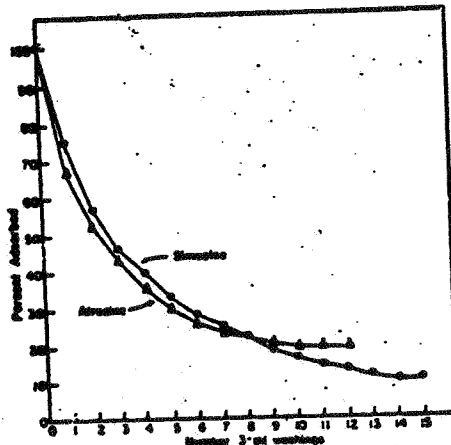


Figure 4. Elution of simazine-C¹⁴ and atrazine-C¹⁴ from Marshall silty clay loam with successive additions of water.

Elution studies.

Water elution of simazine-C¹⁴ and atrazine-C¹⁴ from Marshall silty clay loam is shown in Figure 4. It is apparent that most of these s-triazines could be eluted gradually with water, however, the adsorption reaction was not completely reversible as indicated by the small amounts of simazine (10%) and atrazine (19%) not released during the course of this experiment. When 5 g of treated soil was leached with 280 ml of water, 92% of the original radioactivity added was recovered in the leachate.

Several organic solvents were found to be very effective in eluting simazine from Marshall silty clay loam, including methyl cellosolve, N,N-dimethylformamide, liquefied phenol (88%), pyridine, and mixtures of ethanol and water. Further studies indicated that 90-100% extraction of simazine, atrazine and propazine from various soil types could be obtained with a 50-50 ethanol-water solvent system within 1 hour at a temperature of 66°C with 2 parts solvent to 1 part soil. Longer extraction time was necessary at lower temperatures. Similar procedures were not effective in eluting prometryne from soil. These elution techniques may be useful for the quantitative determination of chloro-triazines in soils.

ACKNOWLEDGMENT

This research was supported in part by a grant from the Ceigy Chemical Corporation, Yonkers, New York, who also furnished the technical and C¹⁴-labeled s-triazines.

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lich K_{ads} values were 1.65 for the sand, 9.13 for the silty clay loam, 9.37 for the sandy loam, and 30.31 for the silt loam soil. The equilibrations were conducted in 2.5 g:10 mL soil:solution slurries at 22-23°C. K_{oc} values were 217 for the sand, 630 for the silty clay loam, 504 for the sandy loam, and 2484 for the silt loam soil. Soil desorption coefficient (K_{des}) values were 6.18, 14.48, 13.52, and 48.97 for the sand, silty clay loam, sandy loam and silt loam soils, respectively.

Following 48 hours of equilibration, Freundlich K_{ads} values were 1.60 for the sand, 8.63 for the silty clay loam, 8.92 for the sandy loam, and 29.12 for the silt loam soil. K_{oc} values were 211, 595, 480, and 2387 for the sand, silty clay loam, sandy loam, and silt loam soils; respective K_{des} values were 12.09, 20.50, 19.19, and 64.00.

DISCUSSION:

1. The soil was too finely sieved (250 or 500 μm ; normal is 2000 μm), so that a significant portion of the sand fraction (0.05-2.00 mm) may have been removed. Since sand content is often correlated with mobility, reducing the sand content may cause the pesticide to appear less mobile.
2. The study was conducted using only one concentration of [^{14}C]atrazine; therefore the Freundlich K values are of limited value. The study should have been conducted using four concentrations of the test substance, which are necessary to accurately calculate Freundlich K values and to demonstrate whether adsorption is concentration-dependent.
3. A preliminary study was not submitted to indicate how long it takes atrazine to reach equilibrium in the test soils; however, data for 24- and 48-hour samples were similar, so apparently equilibrium had been reached by 24 hours. No explanation was provided as to why adsorption was slightly less at 48 hours than at 24 hours.
4. The soil was not analyzed following desorption to determine the material balance and to insure that the atrazine not in solution had been adsorbed to the soil. Only the supernatants were analyzed.
5. The original study was not designed to determine the mobility of atrazine. Rather, atrazine was used as a reference compound to determine the adsorption/desorption properties of the herbicide, FMC 57020.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Sand, sandy loam, silt loam, and silty clay loam soils were air-dried, sieved (250 or 500 μm), and mixed with 0.01 M calcium chloride solutions (2.5-g soil:10-mL solution) containing uniformly ring-labeled [^{14}C]atrazine (radiochemical purity 94.7%, specific activity 8.31 mCi/mMol, Pathfinder Laboratories) at 0.558 $\mu\text{g/mL}$. The soil:solution slurries were shaken for 48 hours at 22-23°C, then centrifuged. Aliquots of the supernatants were removed at 24 and 48 hours and analyzed for total radioactivity by ISC.

To determine desorption, pesticide-free 0.01 M calcium chloride solution was added to the samples to replace the 10 mL of supernatant removed after adsorption. Samples were shaken for 48 hours at 22-23°C and centrifuged, and duplicate aliquots of the supernatant were sampled at 24 and 48 hours and analyzed for total radioactivity using ISC.

Atrazine

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DATA EVALUATION RECORD

STUDY 11

CHEM 080803

Atrazine

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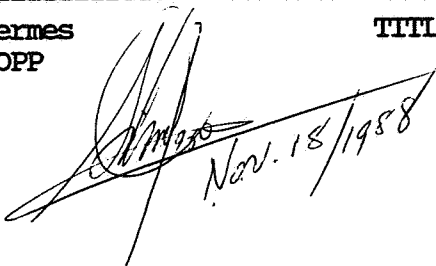
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Yu, W.C. 1986. Determination of adsorption/desorption constants of atrazine. Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory Study No. 59-1A. Completed Feb. 14, 1986. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
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TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study is acceptable and partially contributes to fulfill data requirements for the mobility of atrazine and its degradates on soils (163-1).

A batch-equilibrium adsorption/desorption study was conducted with four different soils and four different concentrations of ¹⁴C-labeled atrazine. Freundlich sorption constants (K_{ads} and K_{des}) were calculated for each of the four different soils.

The K_{ads} constants ranged from 0.427 (sand) to 2.030 (loam soil). The K_{des} constants ranged from 2.261 (silty loam soil) to 14.90 (sandy loam soil). K_{oc} ranged from 55.0 (sandy loam soil) to 135 (loam soil) for the adsorption phase.

These results indicate that atrazine was not strongly adsorbed onto soil particles and that desorption occurred readily.

MATERIALS AND METHODS:

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

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

Test solution: A sterilized stock solution containing 10 ug/mL of atrazine, prepared by dissolving 0.5 mg of the ¹⁴C-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 deg. 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 ISC 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 ISC (i.e., ^{14}C -atrazine in the aqueous phase). Soils were extracted with methylene chloride and the extracts analyzed for ^{14}C -atrazine by ISC.

Calculations: All calculations were based on the Freundlich equation,

$$x/m = K_d C_e (1/n)$$

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

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.

REPORTED RESULTS

The actual atrazine concentration in the stock solution (as determined by HPLC) was 9.70 ug/mL and, thus, the actual test concentrations 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. EFGWB concurs with the author's results and conclusions.

PERTINENT DATA TABLES AND FIGURES

Atrazine

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MATERIALS AND METHODS:

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

Test material: [U-ring-¹⁴C]-G-28273, specific activity 14.1 $\mu\text{Ci}/\text{mg}$, radiochemical purity 98% and G-28273 analytical standard.

Test solution: A stock solution of G-28273 of a nominal concentration of 10 $\mu\text{g}/\text{mL}$ was prepared by dissolving 2.0 mg of ¹⁴C-G-28273 and 4.0 mg of analytical G-28273 in a small amount of dimethylsulfide, then diluted to 600 mL with a 0.01 N calcium ion solution in deionized, purified water. Dilutions (5 $\mu\text{g}/\text{mL}$, 10.5 $\mu\text{g}/\text{mL}$, and 0.2 $\mu\text{g}/\text{mL}$) of the stock solution were prepared in sterile 0.01 N calcium ion solution. A blank 0.01 N calcium ion solution was also used. The actual concentrations of the stock solution and of the dilutions were determined by HPLC and gave the following values: 8.5 $\mu\text{g}/\text{mL}$ (stock solution); 0.17, 0.43, 0.85, and 4.25 $\mu\text{g}/\text{mL}$ (dilutions).

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

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

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

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

The Freundlich equation was used in the calculations,

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

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

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

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

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

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

REPORTED RESULTS

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

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

-12.4-

Atrazine

Page _____ is not included in this copy.

Pages 180 through 190 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.
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DATA EVALUATION RECORD

STUDY 13

CHEM 080803

G-28279 (degradate of ATRAZINE)
2-amino-4-chloro-6-ethylamino-s-triazine

§163-1

FORMULATION—RADIOLABELED MATERIAL

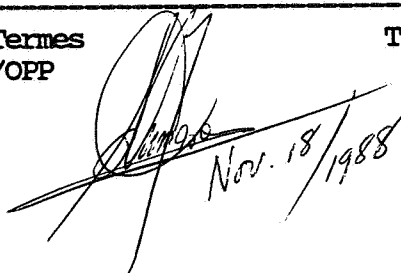
FICHE/MASTER ID 40431325

Yu, W.C. 1986. Determination of adsorption/desorption constants of G-28279.
Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory
Study No. 59-6A. Completed Feb. 17, 1986. Submitted by Ciba-Geigy Corpora-
tion, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study is acceptable and partially contributes to fulfill data requirements for the mobility of atrazine and its degradates on soils (163-1).

A batch-equilibrium adsorption/desorption study was conducted with four different soils and four different concentrations of ^{14}C -labeled G-28279. Freundlich sorption constants (K_{ads} and K_{des}) were calculated for each of the four different soils.

The K_{ads} constants ranged from 0.225 (sand) to 1.144 (loam soil). The K_{des} constants ranged from 1.784 (silty loam) to 12.479 (sand). The K_{OC} for the adsorption phase ranged from 35.1 to 82.3.

The results indicate that G-28279 was not strongly adsorbed onto soil particles and that desorption occurred readily.

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 deg. C (24 hrs) and autoclaved at 120 deg. C (30 min.) prior to use.

Test material: [U-ring-¹⁴C]-G-28279, specific activity 13.7 $\mu\text{Ci}/\text{mg}$ and radio-chemical purity 99% and analytical G-28279 standard were used.

Test solution: A stock solution of G-28279 of a nominal concentration of 10 $\mu\text{g}/\text{mL}$ was prepared by dissolving 1.9 mg ¹⁴C-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 $\mu\text{g}/\text{mL}$, 1 $\mu\text{g}/\text{mL}$, 0.5 $\mu\text{g}/\text{mL}$, and 0.2 $\mu\text{g}/\text{mL}$) 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 $\mu\text{g}/\text{mL}$ (stock solution); 0.02, 0.50, 0.99, and 4.95 $\mu\text{g}/\text{mL}$ (dilutions).

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

- a) Adsorption phase: Four grams of each of the four soils were placed in 50 mL Pyrex centrifuge tubes (in duplicates) and 20 mL of each of the ¹⁴C-G-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 deg. C. Then the tubes were centrifuged and the equilibrium concentration (C_e), the supernatants removed, and the equilibrium concentration (C_e) determined.
- b) Desorption phase: The soils from the adsorption phase (weighed wet to correct for any residual solution) were treated with 20 mL of 0.01 N calcium ion solution. The samples were shaken for 24-hrs in 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 ¹⁴C-G-28279 in the aqueous phase. Methylene chloride was used to extract ¹⁴C-G-28279 for analysis by LSC.

Calculations: The Freundlich equation was used in the calculations,

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

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

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 analysis yielded the Freundlich constants. Tables II and III present the results for the adsorption and desorption phases, respectively. 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. EFGWB concurs with the author's results and conclusions.

PERTINENT DATA TABLES AND FIGURES

-13.4-

Atrazine

Page _____ is not included in this copy.

Pages 195 through 205 are not included.

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DATA EVALUATION RECORD

STUDY 14

CHEM 080803

G-30033 (degrade of ATRAZINE)
2-amino-4-chloro-6-isopropyl-s-triazine

\$163-1

FORMULATION—RADIOLABELED MATERIAL

FICHE/MASTER ID 40431328

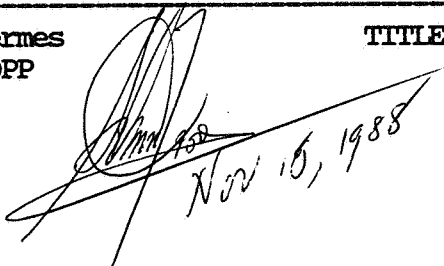
Yu, W.C. 1986. Determination of adsorption/desorption constants of G-30033.
Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory
Study No. 59-6A. Completed Feb. 26, 1986. Submitted by Ciba-Geigy Corpora-
tion, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:

CONCLUSIONS:

 Nov 10, 1988

This study is acceptable and partially contributes to fulfill data requirements for the mobility of atrazine and its degradates on soils (163-1).

A batch-equilibrium adsorption/desorption study was conducted with four different soils and four different concentrations of ^{14}C -labeled G-30033. Freundlich sorption constants (K_{ads} and K_{des}) were calculated for each of the four different soils.

The K_{ads} constants ranged from 0.116 (sand) to 0.963 (silty clay loam). The K_{des} constants ranged from 8.104 (silty clay loam) to 12.87 (silt loam). The K_{oc} for the adsorption phase ranged from 12.8 (sandy loam) to 66.5 (silt loam).

The results indicate that G-30033 was not strongly adsorbed onto soil particles and that desorption occurred readily.

MATERIALS AND METHODS:

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

Test material: [U-ring- ^{14}C]-G-30033, specific activity 21.3 $\mu\text{Ci}/\text{mg}$ and radiochemical purity 99% and analytical G-30033 standard were used.

Test solution: A stock solution of nominal concentration of 10 $\mu\text{g}/\text{mL}$ was prepared by dissolving 2.0 mg ^{14}C -G-30033 and 4.0 mg of analytical G-30033 in a small amount of tetrahydrofuran, diluted to 600 mL with a 0.01 N calcium ion solution in deionized, purified water. Dilutions (5 $\mu\text{g}/\text{mL}$, 1 $\mu\text{g}/\text{mL}$, 0.5 $\mu\text{g}/\text{mL}$, and 0.2 $\mu\text{g}/\text{mL}$) 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: 11.1 $\mu\text{g}/\text{mL}$ (stock solution); 0.02, 0.56, 1.1, and 5.6 $\mu\text{g}/\text{mL}$ (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-30033 solutions and of the blank solution were added. The soil and solution were shaken for 24-hrs in a shaker bath (200 agitations/min) at 25 deg. C. Then the tubes were centrifuged, the supernatants removed, and the equilibrium concentration (C_e), determined (by ISC).
- 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 ISC to determine the equilibrium concentration.

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

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

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 expressed in terms of the soil organic carbon content via

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

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

REPORTED RESULTS

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

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 210 through 220 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.
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DATA EVALUATION RECORD

STUDY 15

CHEM 080803

G-34048 (degradate of ATRAZINE)
2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine

§163-1

FORMULATION—RADIOLABELED MATERIAL

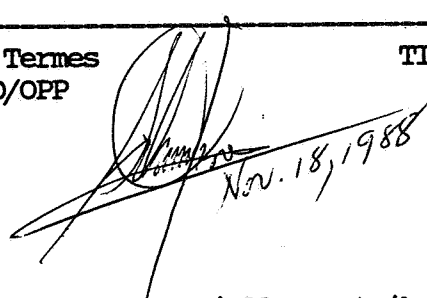
FICHE/MASTER ID 40431326

Yu, W.C. 1986. Determination of adsorption/desorption constants of G-34048. Conducted by Cambridge Analytical Associates, Inc., Boston, MA. Laboratory Study No. 59-7A. Completed Feb. 26, 1986. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study is acceptable and partially contributes to fulfill data requirements for the mobility of atrazine and its degradates on soils (163-1).

A batch-equilibrium adsorption/desorption study was conducted with four different soils and four different concentrations of ^{14}C -labeled G-34048. Freundlich sorption constants (K_{ads} and K_{des}) were calculated for each of the four different soils.

The K_{ads} constants ranged from 1.643 (sand) to 8.165 (silt clay loam). The K_{des} constants ranged from 5.518 (sand) to 22.26 (silty clay loam). The K_{oc} for the adsorption phase ranged from 350 (sand) to 680 (silt loam).

The results indicate that of all of the atrazine degradates, G-34048 was the strongest adsorbed.

221

MATERIALS AND METHODS:

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

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

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

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

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

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

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

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; linear regression analysis of the data yielded n and K_d from the $(1/n)$ slope and the $\ln K_d$ intercept, respectively. The sorption constant was expressed in terms of the soil organic carbon content via,

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

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

REPORTED RESULTS

Logarithmic plots of (x/m) vs C_e (shown in Figures 1 through 2 for the adsorption and desorption phases, respectively) and linear regression analysis yielded the Freundlich constants. Tables II and III present the results for the adsorption and desorption phases, respectively. The K_{ads} values were 1.643 (sand), 6.482 (sandy loam), 8.165 (silty loam), and 5.867 (clay loam). The K_{des} values were 5.518 (sand), 13.08 (sandy loam), 16.26 (silty loam), and 22.294 (clay loam). The K_{oc} for the adsorption phase were 350 (sand), 360 (sandy loam), 680 (silty loam), and 391 (clay loam). The K_{oc} for the desorption phase were 1,174 (sand), 72 (sandy loam), 1355 (silty loam), and 1486 (clay loam). The results show that G-34048 was adsorbed onto soil particles, indicating that the test material has a polar substituent that binds to the soil.

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 225 through 235 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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 - Sales or other commercial/financial information.
 - A draft product label.
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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.

SUMMARY OF DATA BY REVIEWER:

Using soil TLC methods, radiolabeled atrazine (test substance uncharacterized) was determined to be intermediately mobile (Class 3) to mobile (Class 4) with R_f values of 0.34-0.74 in thirteen soils ranging in texture from sandy loam to clay (CECs ranging from 0.2-33.7 meq/100 g).

DISCUSSION:

1. These papers are summaries of numerous experiments. The study author combined the experiments in order to make general conclusions and to compare and contrast the behavior of different pesticides. The most useful document, in terms of the needs of the environmental fate data requirement, is part III. Most information that was provided was too general to permit an accurate critique. For example, the analytical methods include allusions to radiochromatogram scanning, autoradiography, and bioassay methods.
2. The atrazine was not adequately characterized. The test substance was stated to be radioactive. The label position, radiochemical purity, specific activity, and source were not reported.
4. Much of the data are marginally legible; some data are illegible.
5. The sand and silt content of the soils were not reported, so the classification according to the USDA Soil Textural Classification System could not be confirmed.

MATERIALS AND METHODS

STUDY AUTHOR'S RESULTS AND/OR CONCLUSIONS

PERTINENT DATA TABLES AND FIGURES

1. Boland / Raven Sup. / 12-23-82

BEST DOCUMENT AVAILABLE

HELLING: PESTICIDE MOBILITY IN SOILS: II. APPLICATIONS OF SOIL THIN-LAYER CHROMATOGRAPHY 737

is also suitable for nonlabeled compounds; for it is rather tedious, however. In summary, the three methods gave essentially identical pictures of fenac movement on Hagerstown silt soil plates. Autoradiography is considered the most convenient method.

ACKNOWLEDGEMENT

I thank C. T. Dieter and B. C. Turner for assistance during most of this and succeeding (4, 5) research. Appreciation is expressed to these companies for supplying many radio-labeled pesticides used herein: Amchem, Chemagro, CIBA, DuPont, Elanco, Fisons, Geigy, PPG Industries, Rohm &amp; Thompson-Hayward, Upjohn, and Velsicol. Montmorillonite and kaolinite clays (4) were furnished, respectively, by American Colloid Co. and Georgia Kaolin Co.

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Pesticide Mobility in Soils II. Applications of Soil Thin-Layer Chromatography¹

CHARLES S. HELLING²

ABSTRACT

Herbicides were grouped into five categories based on their mobilities on Hagerstown silty clay loam plates, using thin-layer chromatography. Diffusion was also examined in air-dry soils. Methyl esterification greatly reduced mobility of herbicides while increasing diffusion and volatility. Surfactant Tween 20 (1% in solution) increased 2,4-D mobility, but 0.5% solutions of five surfactants were relatively ineffective with several herbicides. Metabolites of 2,4-D, propachlor, and 2,4-D were less mobile than their parent compounds. Two chlorinated dibenzo-p-dioxins, potent herbicides, were immobile. Movement of compounds in chlorpropham/propham/p-chlorophenyl methylcarbamate and atrazine/propachlor combinations were mutually exclusive.

Dicamba and fenac R_f values were directly related to soil pH in the range of pH 5.0 to 6.5-6.7. Other soil modifications included *in situ* oxidation of soil organic matter and the use of model clays. Chlorpropham and propham mobilities were increased by removal of organic matter. Diphenamid was less mobile in oxidized soil, immobile in Ca-montmorillonite, and moderately mobile in kaolinite.

Additional Key Words for Indexing: herbicide, insecticide, leaching, diffusion, clays, adsorption, surfactants, dioxins.

THIS paper, the second in a tripartite series, deals with the use of soil thin-layer chromatography (soil TLC) to determine pesticide mobility and the influence of some edaphic and other factors on this movement. Parameters of the soil TLC technique *per se* were discussed earlier (20). The third paper describes the influence of soil parameters on pesticide movement, using statistical analyses of soil TLC data (21). Since its introduction (22), soil TLC has been used to compare movement of several triazines (10), urea, and uracil herbicides (33) and to study factors influencing 2,4-D³ movement (15). Many nonradioactive herbicides and fungicides may now be investigated using soil TLC as algae,⁴ grass (10), and fungal⁵ bioassay techniques are reported.

Soil TLC is an inherently versatile technique, partly

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³Other chemical names mentioned in this text are those in the preceding publication (20).

⁴C. S., D. D. Kaufman, and C. T. Dieter. 1971. A simple method for the detection of pesticide mobility in soils. Weed Res. 11:1-4.

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⁶R. J., and D. R. Oderwald. 1970. Soil thin-layer chromatography of fungicides. Phytopathology 60:1018 (Abstr.).

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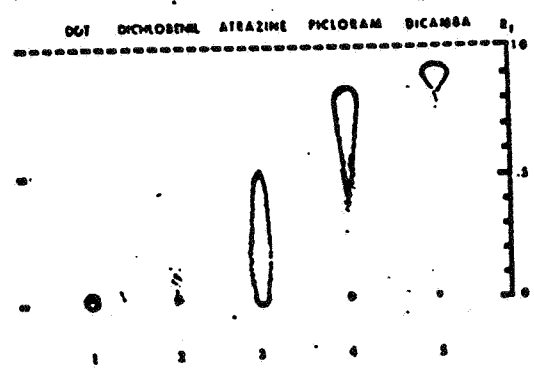


Fig. 1—Movement of five pesticides in Hagerstown silt soil TLC plates, 500 μ by 10 cm. Number below each pesticide refers to the mobility class (22; see also Table 1).

because results from many samples are quickly and reproducibly attainable, and partly because of certain unique properties. For example, 18 soil columns would be required to repeat the soil plate depicted in Fig. 3. Many applications of soil TLC seem feasible, and an introduction to some of these follows.

MATERIALS AND METHODS

Properties of most soils used are given elsewhere (21). Hagerstown silt, the most frequently used soil, was also described earlier (20). Celeryville loam, an Ohio soil, contains 90.4% organic matter, has a pH of 5.0, and has a field moisture capacity of 113%.

The technique of soil thin-layer chromatography has been described in detail (20). Elaboration on special methods or modifications occurs in the Results and Discussion section.

RESULTS AND DISCUSSION

Pesticide Mobility

The most important application of the soil TLC method is for evaluation of pesticide mobility *per se*. In the original publication Helling and Turner (22) tabulated R_f values of 16 herbicides on three soils. They also devised a general classification scheme of five categories based on relative movement on Hagerstown silt plates. Figure 1 is a representative soil TLC plate showing pesticides in each of the five categories. Each is distinctly different in

movement on the plate, and a consensus of mobility literature suggests that the distinctions are indeed valid. Iobenzil is faint because of diffusion and volatility.

The mobilities, as R_f values, of 40 pesticides on Hagerstown silt soil TLC plates are listed in Table 1; previously published data (22) are included for comparison. The group represents 34 herbicides, 4 insecticides, 1 insecticide/acaricide, and 1 fungicide/acaricide. With exceptions (amitrole, bromacil, and Nortron), all 4 and 5 pesticides are organic acids, and only one (4, 5-T) falls below these mobility categories. Theazines, phenylureas, and some miscellaneous compounds generally of intermediate (Class 3) to low (Class 2) mobility. Immobile (Class 1) pesticides include urea cations (diquat, paraquat), chlorinated hydrocarbon pesticides, etc. Dieldrin is ranked above other $R_f = 0$ compounds, since it appeared to diffuse very slightly. Trends indicated here by soil TLC are consistent with published observations of field and laboratory studies. Prior mobility information was found for the following compounds: trietazine, propanil, chlorphenamide, and Morestan.

Soil TLC should be applicable to screening of potential pesticides for their mobility characteristics. Chemicals found to leach readily, for example, might be excluded from further trials if bioactivity is required at the soil surface. For comparison with data from other soils and laboratories, inclusion of a commonly used pesticide as an internal standard is advisable. Monuron has been used in Beltsville, in part because it has intermediate mobility. Presumably in such a screening program, a range of mobilities would be included. Chemicals undergoing preliminary screening are not radioisotopically labeled. Fortunately, bioassays using algae and fungi can now be used for many unlabeled herbicides or fungicides. Recently, Chaman, Gabbott, and Osgerby (10) utilized soil TLC for routine screening of herbicides. They used browntop grass (*Agrostis tenuis*) as their bioassay.

Pesticide Combinations

Increased use of pesticide combinations warrants study of the soil behavior of the components when actually applied together. Persistence, and therefore effectiveness of one component may be altered; e.g., addition of the phytotoxic carbamate PPG-124 to applications of ch

Table 1—Pesticide mobility on Hagerstown silt soil TLC plates

Class 5		Class 4		Class 3		Class 2		Class 1	
TCA	(R. 90)	Picloram	(R. 81)	Propanil	(R. 63)	Siburon	(R. 51)	Chlorobutol	
Dicamba	(R. 88)	Trifluralin	(R. 80)	Propanil	(R. 60)	Propanil	(R. 50)	Diquat	
Dicamba	(R. 86)	MCPA	(R. 78)	4, 5-T	(R. 57)	Propanil	(R. 49)	Chlorophenamide	
Ambroz	(R. 91)	Amitrole	(R. 77)	Propanil	(R. 53)	Propanil	(R. 48)	C-450	
		1, 4-D	(R. 69)	Flumetsuron	(R. 50)	Dichlorobenzil	(R. 47)	Monuron	
		Bromacil	(R. 68)	Dichlorobenzil	(R. 46)	Chlorobutol	(R. 45)	Paraquat	
		Nortron	(R. 65)	Monuron	(R. 44)	Chlorobutol	(R. 44)	Trifluralin	
				Amitrole	(R. 43)	Azoxystrobin	(R. 43)	Isofenphos	
				Propanil	(R. 41)			DGT	
				Trifluralin	(R. 38)				

Average of 3-5 replications.
 Mobility is classified by the system of Helling and Turner (22), based on the following R_f ranges from Hagerstown soil: class 1, 0-0.09; class 2, 0.10-0.34; class 3, 0.35-0.59; class 4, 0.60-0.84; and class 5, 0.85-1.00.

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Table 2—Mobility of herbicides applied in combination, on soil TLC plates

Herbicide	R _F			
	Chlorpropham +PPG-124		Propachlor +PPG-124	
Free acid	0.43	0.41	0.71	0.70
Methyl ester	0.12	0.12	0.42	0.42
Free acid	0.22	0.22	0.32	0.32
Methyl ester	0.12	0.12	0.26	0.27
Free acid	0.05	0.05	0.19	0.20

Herbicide	Atrazine		Propachlor	
	+Prop (1:1)	+Prop (1:2)	+Atra (1:1)	+Atra (1:2)
Free acid	0.48	0.51	0.64	0.64

* Application for all compounds was 0.02 μmol, i.e., 1:1 molar ratio.
 † Propachlor also had 1:2 ratio.

Propachlor prolongs the latter's herbicidal activity (13). Combinations may also be used to control a wider range of target organisms. Table 2 summarizes several experiments with promising herbicidal combinations. For six soils encompassing a wide range in texture and organic-matter content, PPG-124 had no effect on movement of chlorpropham. In additional experiments using Hagerstown soil, neither compound affected the movement of the other when applied at 1:1 or 1:2 molar ratios. Propachlor movement also seems unaffected by combinations with PPG-124. The mobilities of chlorpropham and PPG-124 are similar for many soils; when applied in combination they would thus be expected to remain together in the soil. PPG-124 should be highly effective in prolonging the persistence of chlorpropham. Chlorpropham is less mobile, however, and eventual separation from PPG-124 may occur in the soil profile. Combinations of atrazine and propachlor (Table 2) were also tested. Again, the R_F values of each component are mutually independent. When pesticides are applied at relatively normal rates, this observation may be generally characteristic of combinations. These data represent inherent effects on mobility; biological interactions (which may alter movement patterns in the field) are not reflected.

Formulation

Pesticides are often applied in chemically modified form with other ingredients, usually to facilitate handling and transport into the target organisms. Literature on the influence of formulation on pesticide mobility in soils has recently been summarized (19). Esterification of organic acids generally reduces vertical leaching, although loss by surface runoff and/or volatilization may be amplified. Methyl esters of various ¹⁴C-labeled acids were synthesized using diazomethane in diethyl ether. Movement of a derivative (Fig. 2) relative to the free acid was significantly retarded and was often accompanied by a marked increase in diffusion as with dicamba and fenac. A trace unreacted amiben may have been present as the mobile impurity in the methyl amiben chromatogram. Movement of amiben and its methyl ester was essentially identical to profiles reported by Talbert, Kunyan, and Baker (35) for leaching in slotted soil columns, and to observations by Inceci, Burnside, and Lavy (25). The esters are rapidly hydrolyzed to free acids in moist soil (12, 30, 35), and movement patterns in the field will reflect this conver-

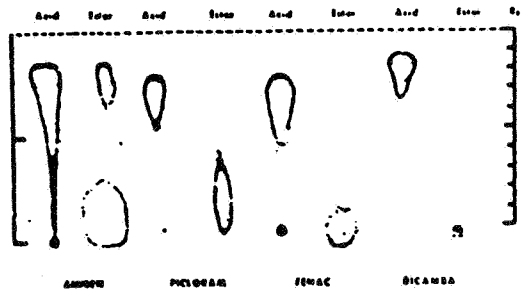


Fig. 2—Movement of acidic herbicides and their methyl esters in a Hagerstown soil plate.

sion. The more common "low volatile" or long-chain ester derivatives would probably exhibit even less solution and vapor phase movement than the esters in Fig. 2.

Adjuvants may, at least temporarily, influence the movement of pesticides into the soil. For example, mobilities of NPA (14, 34) and EPTC (26) were retarded by a variety of carriers. Mobility of diuron could be increased by formulation with 1% solutions of 23 surfactants (6). Several fungicides were mobilized by 1 or 10% Tween 60 solutions, according to soil TLC results.⁷

A brief survey was made of the effect of various surfactants on movement of four herbicides (Table 3). 2,4-D mobility may be enhanced by leaching with 1% Tween 20 and perhaps with the silicones XF-1-1005 and XF-1-3655. The silicones also appeared most effective in mobilizing atrazine, diuron, and diquat. Tween 20 and PM 4579 caused nearly complete loss of the origin spot of diuron, suggesting that these surfactants are effective solubilizers. Diquat transferred was always slight, relative to that remaining immobile. Higher concentrations of each surfactant may have produced a more obvious effect on R_F values (cf. 0.5 and 1% Tween 20), but rainfall would soon dilute the solutions to ≤ 0.5% in the field. Water penetrability, k_w, was slightly reduced by soil- or solvent-incorporated surfactants other than XF-1-1005 and XF-1-3655.

Metabolites

Investigations of the behavior of pesticide metabolites or impurities in soils are relatively uncommon. The unraveling of biochemical pathways leading to breakdown of the pesticide molecule has often been accomplished; but the significance and fate (in soil systems) of products in this sequence is generally less well known.

Several metabolites were compared with their parent herbicide using Hagerstown soil plates. Soil microorganisms can degrade propanil to 3,4-dichloroaniline (DCA). DCA can further condense in soils to 3,3',4,4'-tetrachloroazobenzene (TCAB) and other products, accumulating in increasing proportion to the rate of propanil applied (5, 11, 24; Kaufman, D. D., and D. E. Miller, 1969. Microbial degradation of several aniline based herbicides. Weed Sci.

⁷ Stipes, R. J., and D. R. Oderwald. 1970. *Op. cit.*

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Table 3—Influence of five surfactants on the mobility of 2,4-D, atrazine, diuron, and diquat on Norfolk soil TLC plate.

Name	Class	Description	Conc. % (w/v)	Applied to	R _F *			
					2,4-D	Atrazine	Diuron	Diquat
---	---	---	---	---	0.79	0.69	0.60	0.04
Tween 20	Nonionic	Polyoxyethylene sorbitan monooleate	0.5	Solvent	0.85	0.44	0.56	0.07
Tween 20	Nonionic	Polyoxyethylene sorbitan monooleate	1.0	Solvent	0.96	0.71	0.62	0.09
Tween 20	Nonionic	Polyoxyethylene sorbitan monooleate	0.01	Soil	0.88	0.67	0.58	0.08
Tween 20	Nonionic	Polyoxyethylene sorbitan monooleate	0.5	Soil	0.83	0.66	0.52	0.09
Tween 20	Nonionic	Polyoxyethylene sorbitan monooleate	0.01	Soil	0.85	0.79	0.50	0.07
FD 1879	Nonionic	Alkyl polyoxyethylene ether	0.5	Soil	0.85	0.71	0.59	0.08
XF-1-3655	Nonionic	Silicone	0.5	Solvent	0.84	0.78	0.75	0.13
XF-1-1005	Cationic	Amino dimethylsilane	0.5	Solvent	0.90	0.78	0.75	0.12

* Average of 4 replications (diuron and 1; Tween 20, 2 replications).

Soc. Amer. Abstr., #235.). Average R_F values for propanil (Table 1), DCA, and TCAB (Table 4) indicate that DCA will exhibit only limited movement while TCAB will be immobile. Any TCAB found below the depth of incorporation would have formed *in situ*.

Hydroxyatrazine is formed by hydrolysis of atrazine, ametryne, or atratone in soil. Structurally similar hydroxypropazine and its analogs showed the following decreasing order of adsorption to montmorillonite: -SCH₃ > -OCH₃ > -OH > -Cl (37). By analogy, hydroxyatrazine may be more strongly retained by soils than atrazine (3, 17) and therefore, also be less mobile. Results (Tables 1 and 4) confirm this hypothesis for atrazine (-Cl), but ametryne (-SCH₃) and atratone (-OCH₃) are more, not less, mobile than hydroxyatrazine. Atratone mobility (R_F ≈ .55) was evaluated by an algae bioassay technique.⁸ These mobility data seem reasonable if one assumes adsorption to be, in part, a function of basicity; Weber (38) found the order to be -OH > -OCH₃ > -SCH₃ > -Cl. It is clear, however, that hydroxyatrazine will leach less than its potential precursors.

An early intermediate in the metabolism of 2,4-D by many microorganisms is 2,4-dichlorophenol (27). Fortunately, there is no present evidence of its accumulation in soils. When added to soil or soil isolates, the dichlorophenol was quickly degraded (1, 7, 8, 28); 2,4,5-trichlorophenol, a potential metabolite of 2,4,5-T, was not so readily degraded. From the mobility data in Table 4, any free 2,4-dichlorophenol should show intermediate mobility, increasing as soil organic matter decreased. Its high volatility as well as the diffuse soil TLC patterns suggest that vapor phase movement may be substantial. 2,4,5-T is consistently less mobile than 2,4-D (21) and perhaps the trichlorophenol would also be less mobile than the dichlorophenol.

The chlorinated dioxins are highly toxic chemicals asso-

⁸ Helling, C. S., et al. 1971. *Op. cit.*

Table 4—Mobility of herbicide metabolites and impurities on soil TLC plates

Soil	R _F of						
	BCA	TCAB	Hydroxyatrazine	2,4,5-T	2,4-dichlorophenol	2,7-Diuron	2,3,7,8-Dioxin
Norfolk soil	0.57	0.00	0.14	0.73	0.66	0.00	0.00
Lakeland soil	0.22	0.00	0.28	0.49	0.30	0.00	0.00
Hagerstown soil	0.22	0.00	0.28	0.34	0.20	0.00	0.00
Barrow soil	0.22	0.00	0.28	0.40	0.17	0.00	0.00
Colebrookville sand	0.22	0.00	0.28	0.17	0.00	0.00	0.00

* Average of 2-2 replications (diuron, 2-4 replications).

ciated with the hydropericardium factor or chick ed. factor (23). They are sometimes found as impurities commercially processed fats and fatty acids, and have been detected in minute quantities in formulated 2,4,5-T samples. Study of the mobility of two important dioxins, 2,3,7,8-dichlorodibenzo-p-dioxin and 2,3,7,8-tetrachlorodibenzo-p-dioxin, was included in a broader USDA program describing their fate in the soil environment. Both dioxins properly described, on the basis of results from a wide range of soils (Table 4), as being immobile. Gas chromatographic analysis of segments from Norfolk and Hagerstown soil TLC plates further confirmed the absence of movement. Their very low water solubility (0.2 ppb for the 2,3,7,8-dioxin) undoubtedly contributes to this. If applied indirectly to soils, they would not move farther in the soil profile, but as with other immobile pesticides could be subject to runoff or wind erosion transport.

Soil pH

Solution or soil pH is known to affect adsorption of many pesticides (4, 29, 39). The dissociation constant, pK_a, of individual compounds appears to be the key to their behavior. For example, the organic acids 2,4-D and 2,4,5-T exhibited negative adsorption when they existed primarily as anions (pH > pK_a) in a clay suspension (16). In general, adsorption is stronger at low than at high pH values. Weber (39) delineated this more precisely for s-triazines on montmorillonite: maximum adsorption occurred at or near the pK_a, with adsorption declining very acid as well as basic suspensions.

Helling (19) summarized the case for adsorption of an important—perhaps dominant—factor influencing pesticide movement. Thus, pH should influence mobility at certain acidity levels, and some studies with simazine and dicamba (2) concur, the latter being readily leached in soils except at pH < 4.2. Movement of 2,4-D was less in H-saturated Berino sandy loam than in Ca or Na saturated soil, using soil TLC plates (15). This relationship measured differences in adsorption and, presumably, mobility.

Soil pH was modified by addition of CaCO₃ (13 mg soil) or 0.01N H₂SO₄ in increments. Soil plates that represented an *in situ* pH gradient were then prepared. In five combinations of two soils (or other adsorbents) were achieved, varying across the plate width, by placing a micro combined glass/calomel electrode. Figure 3 shows the gradation of Hagerstown silt from pH 5.00 to 6.50.

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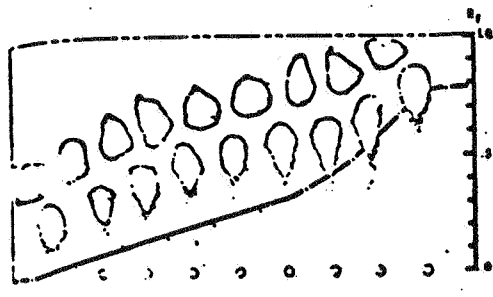


Fig. 3—Effect of soil pH (line) on the mobility of dicamba (upper spots) and fenac (lower spots) in a modified Hagerstown silt plate.

Effect of pH on dicamba and fenac mobility. In this region the effect is clear and direct; from pH 7 to 8, however, movement is unchanged. Gradients of Sterling (pH 6.32 to 7.76) produced increasing movement of dicamba and fenac to ca. pH 6.7. Combination of other similar soils, Dundee sil (pH 5.83) and Sterling sil (pH 7.72), produced results in accordance with the previous observations. Increasing movement of both herbicides in Chillum sil occurred from pH 5.05 to ca. 6.5, with no other change to pH 7.20.

Soil Modifications

Isolation of the properties that influence pesticide movement would greatly assist prediction of pesticide behavior in soils. A logical approach is through the use of modified soils and other model systems, as in the preceding study on soil pH.

ORGANIC MATTER REMOVAL

Organic matter was totally removed (analysis by Walkley-Black method) from Hagerstown silt by ignition at relatively low temperature. Normal soil TLC plates, 500 x 20 x 20 cm, were gradually heated to 400C during 24-hour period. The soil changed in color from light tan to reddish-brown but appeared to retain its structural integrity. Water penetrability was higher than in unmodified plates. Movement of eight herbicides on an oxidized Hagerstown plate is depicted in Fig. 4, and should be compared with R_f values in Table 1. A striking increase in the mobility of chloropropham (CIPC), to R_f 0.74, suggests that soil organic matter is quite significant in preventing leaching of this compound. Lateral movement, presumably diffusion, is noteworthy especially concerning the short (61 min) development time. Movement of the related herbicide propham (IPC) is also increased, to R_f 0.74, again accompanied by marked diffusion. Picloram (0.55), monuron (0.55), and diuron (0.33) were also highly mobile in oxidized soil. Atrazine was unaffected, and fenac and diphenamid movement was retarded by the treatment. Retardation in mobility, though surprising, may reflect preferential adsorption to active clay sites made available by destruction of associated soil organic matter.

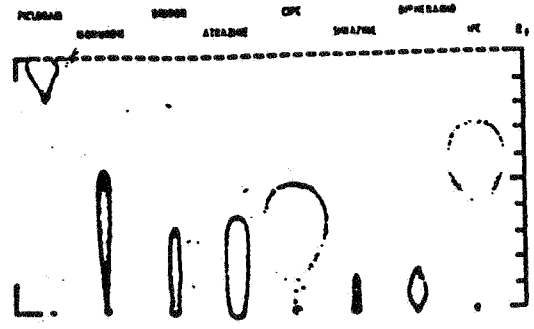


Fig. 4—Effect of organic matter oxidation on mobilities of eight herbicides in a Hagerstown silt plate.

Hagerstown silt was also modified by treatment with acidified 30% H₂O₂, with 85% loss of soil organic matter. Plates produced from this soil readily slaked in water, and water penetration was very slow because the soil was highly dispersed. Most compounds diffused extensively during the ca. 24-hour development. Simazine and diphenamid mobilities were slightly reduced; mobilities of other compounds were relatively unchanged. Soil plates were also sprayed directly with H₂O₂, but this produced an uneven surface. Pesticide movement on sprayed plates was somewhat greater than on untreated plates. By comparison, the dry-ignition method for removing soil organic matter was much simpler and presumably better than the H₂O₂ method. No known method for organic-matter removal can be guaranteed not to affect the inherent mineralogical properties, however.

MODEL CLAYS

Two common soil clays, montmorillonite and kaolinite, were also used as adsorbent phases in TLC studies. Both were of commercial origin: natural calcium montmorillonite was Panther Creek (Aberdeen, Miss.), the kaolinite was Hydrite RS. The acids dicamba, MCPA, and 2,4-D are highly mobile (Fig. 5), while fenac is somewhat less

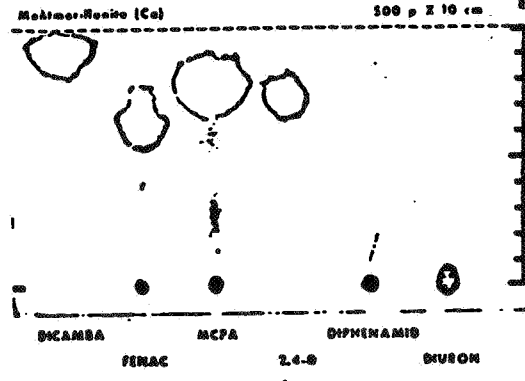


Fig. 5—Movement of herbicides in a calcium montmorillonite TLC plate.

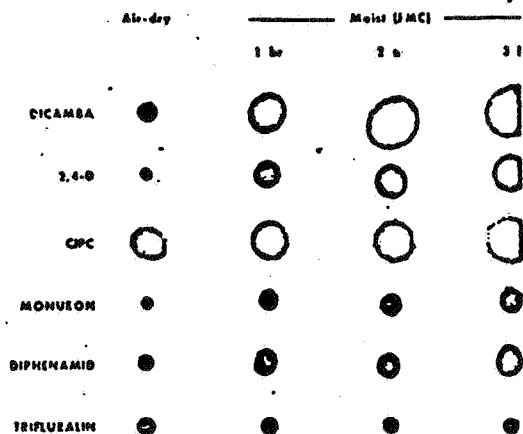


Fig. 7.—Diffusion of herbicides in moist and dry Hagerstown silt plates, 500 μ.

mobile on montmorillonite. Since the clay is slightly alkaline and possesses a high cation-exchange capacity, it is not unexpected that the dissociated acids leach readily (16). Fenac is less acidic than the others (32, 36), which may account in part for their differential movement. Mobility of monuron (not shown) and diuron is reduced relative to Hagerstown silt plates, while diphenamid is rendered completely immobile. The latter is especially difficult to explain, since there was no apparent correlation between clay content and diphenamid R_f on five montmorillonitic soils (21). Diphenamid differs from other compounds in Fig. 5 in that it has two aromatic rings; this may increase molecular size sufficiently to increase Van der Waals forces and to produce a positive entropy effect, both of which favor adsorption (18). Chlorpropham was somewhat mobile ($R_f = .40$).

In contrast to its behavior on montmorillonite, diphenamid is fairly mobile (average $R_f = 0.54$ for two plates) in kaolinite (Fig. 6). There is a tendency for most compounds shown to move readily as chromatographic spots in contrast to the streaking pattern often occurring in soils. Acidic compounds (including the weakly acidic Monuron) continue to be most mobile in both soil and clay TLC systems. Chlorpropham on another kaolinite plate was immobile to mass transfer movement but exhibited limited diffusion. Movement of this compound was negatively correlated with clay content in nine kaolinitic soils, but not with clay in a group of montmorillonitic soils (21). Diquat was immobile ($R_f = 0.01$) on kaolinite, as expected from adsorption data (9). The separation of several impurities of 2,4-D suggests that kaolin eluted with water may be a useful system for conventional TLC.

Diffusion

From earlier research with soil TLC (22), it was clear that pesticide movement occurred by two processes, mass transfer and diffusion. R_f values of relatively nonvolatile compounds tend to represent the former process. Diffusion

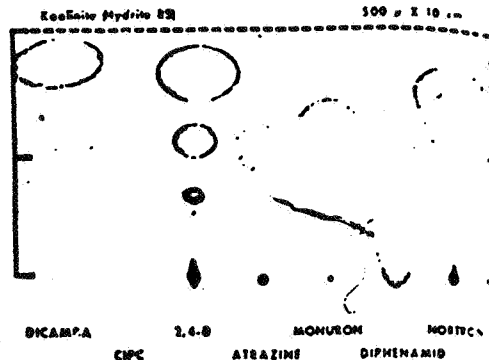


Fig. 6.—Movement of herbicides in a kaolinite TLC plate.

was examined by applying six herbicides to 500 μ x 10-cm Hagerstown silt plates. Before autoradiography, plates were maintained air-dry or at field moisture capacity for 1, 2, or 3 hours (Fig. 7). Only chlorpropham diffused in dry soil and this movement increased in the presence of water. Diffusion of all compounds was, as expected, a function of time. Trifluralin was immobile. Other compounds that diffuse extensively in Hagerstown silt include diuron, benil (Fig. 1), various methyl esters (Fig. 2), Nemag, EPTC, and propham. Soil TLC may prove a useful technique for determining diffusion coefficients of pesticides in soils.

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Pesticide Mobility in Soils III. Influence of Soil Properties¹

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ABSTRACT

Soil parameters influencing pesticide movement were tested using simple correlation and multiple linear regression analyses. Mobilities of 12 pesticides on 14 soils were first characterized by soil thin-layer chromatography. Mobility of ionic compounds was inversely related to adsorption of ionic compounds, field moisture capacity, organic matter and cation contents, and cation-exchange capacity. Mobility of acidic compounds (dicamba, picloram, fenac, and 2,4-D) was directly related with soil pH and inversely with picloram adsorption. Pesticide mobility tended to be directly related to increased water flux.

When soils were grouped according to their clay mineralogy, there was a tendency for movement of acidic pesticides to be directly related to non-montmorillonitic clay content and inversely related to non-montmorillonitic clay content.

Regression equations usually contained field moisture capacity, water flux, and often simazine or chlorpropham adsorption for predicting movement. These parameters are highly related with soil organic-matter content, which does not appear in the regression equations. The average deviation

of predicted from observed mobility, across all soils and pesticides, was 0.04 R_p units.

Additional Key Words for Indexing: herbicide, insecticide, leaching, movement of pesticides, clays, organic matter, field moisture capacity.

THE observation that pesticides applied to coarse-textured, sandy soils are subject to greater leaching than those found in soils of higher clay and organic content is now virtually a truism. Numerous references supporting this are found in two recent reviews (1, 8). Adsorption of pesticides to various soils usually follows the inverse generalization, supporting the contention that adsorption governs

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Table 1—Soil properties

Soil Name	Soil Number	Origin (State)	Micros in					pH	CEC	Water Run-off on soil TLC*	Adsorption			
			Organic matter	Clay	Field capacity	Av. dry	mg/100 g				Picloram	Simazine	Diuron	Chlor-propham
Marble of Lakeland of Christian I	36	Maryland	0.11	11.3	4.5	0.17	5.1	0.2	11.8	6	5	3	10	
Ascalon soil	11	Colorado	1.44	26.4	14.0	1.30	7.3	12.7	6	13	10	36		
Sawling of Dundee soil	4	Mississippi	1.47	29.0	24.3	2.03	5.0	14.1	7.5	6	30	17	31	
Whedden soil	27	Maryland	1.05	25.2	22.7	0.61	5.6	10.3	5.3	13	25	16	42	
Duffield soil	42	Maryland	1.20	22.7	21.5	1.30	5.3	10.9	5.1	6	22	16	31	
Belleville soil	7	Maryland	2.42	22.0	22.5	0.50	5.3	4.7	4.5	11	30	15	40	
Hagerstown soil	41	Maryland	2.30	20.5	20.0	0.07	6.0	10.7	4.6	3	20	25	56	
Chilham soil	27	Maryland	1.00	22.1	24.5	0.05	6.0	7.0	5.2	9	25	20	40	
Irwell soil	29	?	1.27	22.2	21.2	1.04	5.4	17.0	0.9	12	35	47	75	
Barnes of Parkley soil	33	West Virginia	0.82	20.5	20.0	1.72	7.1	22.7	5.2	7	35	46	70	

* Distribution is measured in the test. † Abbreviations: lat = lateratified, Va = Virginia, Mo = Missouri, Ga = Georgia, Nc = North Carolina.

movement. Thus, those soil factors influencing pesticide adsorption—especially soil organic matter, clay, and (sometimes) soil pH—have often been related to movement. Movement of organophosphorus insecticides (15) and s-triazine herbicides (5) was inversely related to their adsorption to four soils.

Statistical analyses are sometimes used to confirm and measure the significance of soil parameters on properties such as pesticide adsorption (14) and bioactivity (12). Atrazine retention against leaching in a miscible displacement experiment was highly correlated with organic matter content, surface area, and cation exchange capacity (CEC), according to Snelling, Hobbs, and Powers (16). Adsorption itself was negatively correlated with movement of 29 nonionic herbicides, although leaching was performed with ethanol/water in a partition thin-layer chromatographic (TLC) system (5).

The objective of the present study was to examine soil from the standpoint of parameters influencing pesticide mobility. The use of soil TLC (9, 10) permitted examination of pesticide movement in many soils, facilitating the subsequent correlation and regression analyses.

MATERIALS AND METHODS

Soils—The properties of soils used in this and other (9, 10, 11) studies are indicated in Table 1. Characteristics and the

† Pesticide chemicals mentioned in this text are given in Table 1 of a preceding publication (9).

methods used to determine them include: organic matter the Walkley-Black procedure (13); clay content, by the drometer method; cation-exchange capacity (CEC), by Ca saturation and titration method (13); field moisture capacity (FMC), after drainage of excess water in soil columns; pH, electrometrically in a 1:1 soil/water paste. Mineralogy the clay fraction was determined using X-ray diffraction standard preparatory procedures. All soils used, except H. town, Lakeland, and Duffield, were previously characterized by Harris and Sheets (7).

Adsorption Experiments—The procedure of Harris and Sheets (7) was used. Duplicate 1-g (oven-dry basis) samples of soil (sieved at 250 or 500 μ) were shaken 2 hours with 1 ml herbicide solution in 13 by 100 mm test tubes having lined screw caps. The herbicides and their concentrations (ppm) were: picloram (400), diuron (25), chlorpropham (80), and simazine (4), all in 0.01M CaCl₂. Suspensions were centrifuged 30 min at 3,300 × g and the decantates were for 20 min at 9,000 × g. The ¹⁴C-simazine decantate was analyzed by liquid scintillation counting. The others, non-radioactive, were analyzed using ultraviolet spectroscopy with λ_{max} of each: picloram (222 mμ), diuron (252 mμ), chlorpropham (238 mμ). Before analysis they were diluted 66 ×, 4 ×, or 6 ×, respectively. Adsorption is therefore presented (Table 4) as the percentage of herbicide removed to the near-saturated solutions. Length of shaking, from 15 to 2 hours, did not affect picloram adsorption onto Hagerstown soil.

Soil Thin-layer Chromatography—The technique has been described in detail (9, 11). For these experiments 13 different radioactive pesticides were applied in a statistically random order across two 20 by 20-cm soil plates. Monuron (an internal standard) occurred once on each plate. Four such replicates were made per soil. The development time was recorded on each plate; water flux data (Table 1) is based directly on time, an average from eight plates.

Table 2—Mobility of 13 pesticides on 14 soils, using soil thin-layer chromatography

Soil Name	Soil Number	R _f of												
		Diuron	Picloram	Paraquat	2,4-D	Monuron	Atrazine	Dibromochloroacetic acid	Simazine	Diuron	Chlor-propham	Atrazine	Diuron	
Marble of Lakeland of Christian I	36	1.00	0.90	0.84	0.80	0.80	0.74	0.60	0.60	0.51	0.37	0.20	0.04	
Ascalon soil	11	1.00	0.95	1.00	1.00	0.97	0.90	0.90	0.80	0.59	0.20	0.10	0.00	
Sawling of Dundee soil	4	0.99	0.97	0.90	0.87	0.87	0.80	0.60	0.55	0.35	0.20	0.10	0.00	
Whedden soil	27	0.95	0.95	0.72	0.67	0.67	0.50	0.50	0.50	0.35	0.20	0.10	0.00	
Duffield soil	42	0.90	1.00	0.74	0.60	0.60	0.65	0.65	0.65	0.35	0.15	0.10	0.00	
Belleville soil	7	0.90	0.70	0.50	0.41	0.30	0.34	0.30	0.30	0.22	0.10	0.10	0.00	
Hagerstown soil	41	0.95	0.95	0.84	0.60	0.60	1.00	0.90	0.65	0.30	0.10	0.10	0.00	
Chilham soil	27	0.90	0.90	0.62	0.30	0.30	0.30	0.30	0.31	0.22	0.10	0.10	0.00	
Irwell soil	29	0.97	0.9	0.60	0.64	0.57	0.36	0.34	0.30	0.10	0.11	0.00	0.00	
Barnes of Parkley soil	33	1.00	0.81	0.67	0.71	0.54	0.50	0.50	0.32	0.15	0.10	0.00	0.00	
Average By		0.95	0.85	0.75	0.72	0.56	0.5	0.44	0.40	0.21	0.23	0.17	0.01	

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Table 3—Simple correlation coefficients (r) among pesticide R_F values and soil properties, for 14 soils

Pesticide	Organic matter	Clay	Moisture at		pH	CEC	Water flux on soil TLC	Adsorption			
			Field capacity	Air-dry				Picloram	Simazine	Chlorpropham	
1	.151	-.015	-.192	.328	.416*	.794	-.304	-.207	-.174	.275	-.078
2	-.231	-.227	-.007	.047	-.484	-.015	-.645*	-.413	-.382	-.189	-.412
3	-.077	-.003	-.252	.263	.761**	-.308	-.395*	-.337*	-.379	-.069	-.298
4	-.262	-.109	-.435	.130	-.618*	-.144	-.643**	-.641	-.471	-.131	-.504
5	-.726**	-.708**	-.926**	-.595*	-.115	-.704**	-.673**	-.235	-.856**	-.729**	-.801**
6	-.636*	-.489*	-.874**	-.647	-.112	-.357*	-.749**	-.216	-.870**	-.616*	-.846**
7	-.444	-.369*	-.766**	-.549*	-.886	-.844*	-.717**	-.207	-.764**	-.302	-.646*
8	-.337*	-.353*	-.838**	-.399	-.150	-.531	-.733**	-.324	-.625**	-.303	-.793**
9	-.718**	-.712**	-.928**	-.563*	-.169	-.688**	-.644*	-.308	-.837**	-.716**	-.911**
10	-.608*	-.649*	-.898**	-.498	-.087	-.330	-.792**	-.340	-.723**	-.370*	-.651**
11	-.261*	-.617*	-.831**	-.518	-.120	-.618*	-.458	-.107	-.747**	-.365*	-.766**
12	-.174	-.344	-.513	-.348	-.118	-.341	-.809**	-.677	-.608	-.155	-.379

* Significant at 5% level. ** Significant at 1% level.

RESULTS AND DISCUSSION

The 14 surface soils used in this study of mobility versus soil properties were selected to include a broad range in clay (11 to 51%) and organic matter (0.1 to 8.0%) contents, and in pH (4.3 to 7.7). Other properties in Table 2 such as moisture capacity, CEC, and adsorption of various pesticides, are usually correlated with clay and/or organic matter. As expected, they also vary widely in magnitude.

The soils can be grouped broadly into five montmorillonitic soils (numbers 4, 11, 13, 16, 29) and nine non-montmorillonitic soils. The latter characteristically contain kaolinite and vermiculite and are from the eastern USA.

A summary of pesticide mobility appears in Table 2. The soils are ranked according to increasing organic-matter content. For pesticides from 2,4-D to azinphosmethyl there is a general trend toward reduced mobility with increased organic matter. Relative order of pesticide mobility is usually the same among soils. The pesticides, which are ranked (with the exception of diphenamid) by decreasing mobility on Hagerstown, have average R_F values for the 14 soils that correspond to the order of Table 2, except that diphenamid (0.44) is slightly less mobile than simazine (.46). Thus, both the "relative mobility classification" concept (1), and the use of Hagerstown soil to define this classification, appear justified.

Simple Correlation

Correlation coefficients of pesticide mobility and soil properties are presented in Table 3. Trifluralin is omitted; it was immobile in all soils. Fine clay content was also omitted because correlations were nonsignificant.

Mobilities of 10 of the 12 pesticides were directly correlated with water flux. Flux was negatively correlated (-.577*) with field capacity but was not as closely related to other soil parameters. Field capacity itself was highly positively correlated with movement of nonionic pesticides. As expected, field capacity was also highly correlated with more fundamental parameters—organic matter, clay, CEC. These parameters were generally negatively correlated with movement of nonionic pesticides.

Soil pH was important only for movement of the acidic compounds, though picloram was significantly correlated at the 10% level. That is, the higher the pH, the slower the movement of these compounds. This corroborates

data obtained for dicamba and fenac by direct modification of soil pH (10).

Pesticide movement is often thought to be governed largely by its adsorption to soil. Adsorption (Table 3) was an accurate single-factor predictor of the movement of most nonionic compounds. Prediction of movement was often best for chemically similar pesticides, e.g., simazine (-.885**) or atrazine (-.870**) mobility with simazine adsorption. Chlorpropham's adsorption was less well correlated with its own mobility than with the mobility of three other herbicides. Perhaps this reflects the extensive diffusion chlorpropham undergoes, a process more likely subject to variability in soil TLC than the mass transfer movement that characterizes other compounds. Picloram adsorption is significantly related only to fenac mobility, although movement of 2,4-D and picloram tend also to be inversely related. Picloram adsorption data (Table 1) seemed erratic, perhaps because it was always rather low. It is clear from correlations of movement with adsorption and other soil parameters that acidic pesticides behave in a strikingly different manner than do nonionic compounds.

Adsorption itself was highly correlated with soil organic-matter content: simazine (.671**), diuron (.961**), chlorpropham (.884**), Picloram adsorption was nonsignificantly correlated, however. Adsorption of diuron (.695**) and chlorpropham (.650*) was related to total clay content; simazine was less closely related (.534). All three compounds were correlated with CEC. These trends substantially agree with Harris and Sheets (7), who correlated adsorption and phytotoxicity with properties of 32 soils, many identical to those used in this study.

To summarize the simple correlation results of Table 3 for 14 soils, mobility of nonionic compounds was directly related to water flux and inversely related to adsorption of similar compounds, field moisture capacity, organic-matter and clay contents, and CEC. Mobility was generally not related to adsorption of a dissimilar compound (picloram), fine clay content, pH, and moisture content of air-dry soil. Mobility of acidic compounds was directly related to water flux and pH, and inversely related to picloram adsorption.

The relationship of mobility and water flux was unexpected and therefore prompted the direct experimentation reported earlier (9). It was concluded from the latter that there may be some direct relationship between mobility and flux, or penetrability. Because of continued uncer-

Table 4—Simple correlation coefficients (r) among pesticide R_f values and soil properties, for soils grouped by clay mineral.

Pesticide	Moisture at				pH	CEC	Water flux on soil TLC	Adsorption		
	Organic matter	Clay	Field capacity	1/2-1/4 dry				Picloram	Simazine	Diuron
	1 Montmorillonitic Soils									
Dicamba	-.674	.721	-.631	.716	-.931*	-.157	.373	-.398	-.504	-.006
Picloram	-.737	-.396	-.629	-.172	-.565	-.161	-.475	-.017*	-.467	-.719
Fenac	-.613	-.316	-.711	-.230	-.716	-.037	-.474	-.878	-.566	-.565
2,4-D	-.543	-.349	-.612	-.666	-.477	-.343	-.666	-.938*	-.603	-.612
Monuron	-.683	-.009	-.707	-.656	-.523	-.699	-.377	-.737	-.613*	-.765
Atrazine	-.479	-.060	-.764	-.773	-.737	-.304	-.340	-.655	-.922*	-.375
Diphosamid	-.526	-.318	-.146	-.373	-.517	-.778	-.427	-.051	-.611*	-.211
Simazine	-.386	-.018	-.534	-.663	-.635	-.141	-.366	-.314	-.965**	-.319
Diuron	-.666	-.172	-.763	-.676	-.479	-.515	-.420	-.796	-.624	-.637
Chlorpropham	-.631*	-.111	-.876	-.161	-.366	-.190	-.535	-.061**	-.519	-.627*
Asiaphos methyl	-.523	-.631	-.531	-.390	-.695	-.327	-.532	-.476	-.619*	-.681
Diquat	-.363	-.669	-.423	-.211	-.616	-.065	-.357	-.650	-.679	-.737
	9 Non-montmorillonitic Soils									
Dicamba	-.195	-.118	-.366	-.667	-.633	-.126	-.373	-.395	-.175	-.214
Picloram	-.117	-.336	-.565	-.146	-.369	-.137	-.719*	-.287	-.474	-.069
Fenac	-.687	-.018	-.539	-.063	-.773*	-.176	-.666*	-.615	-.607	-.136
2,4-D	-.163	-.197	-.375	-.667	-.628	-.019	-.773*	-.457	-.634	-.054
Monuron	-.736*	-.625**	-.941**	-.698*	-.139	-.664*	-.743*	-.672	-.913**	-.700*
Atrazine	-.664	-.716*	-.661**	-.663	-.615	-.163	-.661**	-.103	-.694**	-.509
Diphosamid	-.596	-.661*	-.661**	-.540	-.110	-.504	-.636**	-.334	-.829**	-.27
Simazine	-.613	-.647	-.699**	-.535	-.173	-.462	-.666**	-.399	-.912**	-.26
Diuron	-.669*	-.615**	-.960**	-.626	-.166	-.694	-.743*	-.697	-.923**	-.667*
Chlorpropham	-.579	-.696*	-.973**	-.534	-.063	-.389	-.636**	-.272	-.625**	-.316
Asiaphos methyl	-.618	-.644*	-.664**	-.541	-.169	-.563	-.598	-.610	-.666**	-.374
Diquat	-.192	-.316	-.536	-.263	-.633	-.176	-.926**	-.617	-.187	-.107

* Significant at 5% level. ** Significant at 1% level.

tainty, two soils giving extreme values of flux, Christiansa 1 and Lakeland sl, were consecutively omitted, and correlations were rerun on the 13 and 12 remaining soils. Omission of the loam had little effect, but when Lakeland was also removed, water flux was then significantly related (5% level) only to picloram, 2,4-D and chlorpropham movement. Flux was correlated (inversely) with a single soil parameter, field moisture capacity.

The principal changes noted in eliminating Christiansa 1 were nearly always increased correlation of picloram mobility with factors such as organic matter, field capacity, and adsorption of pesticides. This acidic (pH 4.4) soil caused unusual retardation of picloram movement, probably depressing the 14-soil correlation coefficients. Christiansa soil appeared to contain a relatively high iron content. Hydrated iron oxides and low pH were both shown to enhance picloram adsorption (4).

The original 14 soils were subdivided, as previously described, into montmorillonitic and nonmontmorillonitic soils. The rationale behind these distinctions is that montmorillonite is an expandible layer silicate clay with high cation-exchange capacity, conditions favorable for positive adsorption of neutral or cationic pesticides and for negative adsorption of anionic species. The nonmontmorillonitic soils contain kaolinite and/or vermiculite clays that generally adsorb nonionic pesticides less, but anionic species more than montmorillonite. Simple correlation coefficients for each group appear in Table 4.

The number of significant correlations in the montmorillonite group is small, probably because the degrees of freedom have been greatly reduced.⁴ Soil organic matter is negatively correlated with chlorpropham R_f and is likely important in movement of diuron, 2,4-D, monuron, and perhaps picloram and atrazine. Montmorillonitic clay was

nearly correlated (5% level) with retardation of diuron movement, in contrast to the effect of nonmontmorillonite clays. This trend is expected, since diquat is more strongly adsorbed to montmorillonite than to kaolinite or vermiculite (3, 17). Clay content had the opposite effect on K_d values for acids, especially dicamba: movement tended to be directly related to montmorillonitic clay, suggesting probable negative adsorption. Dicamba was not adsorbed by montmorillonite, vermiculite, and several soils, but was adsorbed by kaolinite in one study (2). Soil pH was correlated (.951*) only with dicamba movement. Adsorption of picloram, simazine, and chlorpropham was negatively correlated with their observed mobilities and those of related compounds. The relationship between picloram adsorption and chlorpropham movement, and vice versa is not understood.

Soil organic matter, in a group of nine nonmontmorillonitic soils, was significantly correlated with reduction of monuron and diuron movement. Atrazine was just below significance (-.664 vs. the required .666*). The remaining nonionic pesticides had r values much higher than that of ionic compounds. Clay was highly negatively correlated with monuron and diuron movement, and less well with movement of other nonionic compounds. Although picloram is not significantly correlated with clay, the r (-.356) is opposite that in the previous soil group (.394) suggesting that the kaolinite/vermiculite group is less negatively charged, as expected.

Soil pH was correlated with fenac R_f and nearly correlated (5% level) with 2,4-D R_f. This continues the general observation that pH is primarily related to movement of acidic compounds.

In contrast to montmorillonitic soils, water flux was correlated with movement of nearly all pesticides in the second soil group. From the previous discussion, this reflects artificially strong influence of soils 10 and 11, especially as they are now in a group of 9 rather than 14.

⁴ For significance at the 10% level, r ≥ 0.805 and 0.582 for the groups of five and nine soils, respectively.

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3- Multiple regression data relating pesticide mobility (Y) with soil parameters (X), for 14 soils

Regression equation	R ²
$\hat{Y} = 0.80 + 0.0251X_{pH} + 0.0011X_{clay}$	0.528
$\hat{Y} = 0.80 + 0.0072X_{FMC}$	0.606
$\hat{Y} = 0.0 + 0.1884X_{pH} + 0.0130X_{clay}$	0.700
$\hat{Y} = 0.21 + 0.0007X_{pH} + 0.0000X_{clay}$	0.880
$\hat{Y} = 0.00 + 0.0473X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.72 + 0.0004X_{pH} + 0.0004X_{clay}$	0.905
$\hat{Y} = 0.10 + 0.0042X_{pH} + 0.0011X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
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$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
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$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900
$\hat{Y} = 0.00 + 0.0000X_{pH} + 0.0000X_{clay}$	0.900

at 5% level. **Significant at 1% level. ***Significant at 0.1% level. Independent variables are significant at 10% level.

Absorption of simazine, diuron, and chlorpropham was correlated with reduced movement of chemically similar compounds. Picloram adsorption was related only to mobility (10% level) in this soil group.

Multiple Linear Regression

Multiple linear regression equations were also developed (Table 5) for prediction of mobility and to determine the relative importance of the soil parameters, when considered together. Independent variables were added only so long as significance at the 10% level or better was indicated by the calculated F. The first parameter added is always giving the largest r value.

It is significant to note that soil pH appears only among organic acids as an important parameter affecting pesticide mobility. Although pH is absent from picloram's equation in Table 5, the next variable added to the regression equation would have been pH. This, however, is strongly evidenced by Christiana loam. By omitting this soil the same regression equation was obtained for picloram

$$Y = 0.99 - 0.0034X_{CIPC} + 0.0035X_{CEC} \quad (R^2 = 0.828)$$

The multiple coefficient of determination, R², indicates 82.8% of the variation in picloram mobility can be predicted from data on chlorpropham (CIPC) adsorption and CEC. The improvement is marked over the use of water flux (R² = 0.416) for 14 soils. Omission of Christiana loam had much less effect on regression equations for other compounds. Water flux remained a significant term in all equations.

Independent variables that appear in Table 5 are always derived parameters; i.e., they are correlated with the fundamental soil components, clay and organic

matter, and/or with soil pH. Since measurements of chlorpropham or simazine adsorption reflect interaction with several soil parameters, and since adsorption appears to be a key factor affecting pesticide movement, it is not surprising that these data are useful predictors of mobility. Of the more common measurements of soil properties, field moisture capacity (FMC) is perhaps the most useful predictor of mobility.

When the regression equations of Table 5 are actually used to predict pesticide R_p, the average absolute deviation from the observed mobility was only 0.04. For all pesticides except fenac (deviation was 0.07), estimated R_p deviated from 0.02-0.05, averaged across 14 soils. If every independent variable in Table 3 is included, the average deviation is 0.02, indicating the improved accuracy of this prediction.

The average relative contribution of each variable to the R_p of a pesticide is expressed by comparing their standardized partial regression coefficients, b'. For dicamba movement in 14 soils, b' is 0.85 and -0.45 for pH and clay, respectively; pH is thus ca. twice as important as clay content. With 2,4-D, the order is chlorpropham adsorption > pH > simazine adsorption > water flux. These first three terms account for ca. 75% of soil-to-soil variability in 2,4-D mobility. For monuron and atrazine, the relative contributions were FMC > simazine adsorption > water flux. With simazine movement, b' values were -0.69 (simazine adsorption) and 0.42 (water flux).

ACKNOWLEDGEMENT

I thank E. J. Koch, Biometrical Services, ARS, USDA, Beltsville, Md. for his assistance with experimental design and statistical analysis.

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9. Helling, C. S. 1971. Pesticide mobility. I. Parameters of soil thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35:732-737 (this issue).
10. Helling, C. S. 1971. Pesticide mobility in soils II. Applications of soil thin-layer chromatography. Soil Sci. Soc. Amer. Proc. 35:737-743 (this issue).
11. Helling, C. S., and B. C. Turner. 1968. Pesticide mobility. Determination by soil thin-layer chromatography. Science 162:562-563.

249

DATA EVALUATION RECORD

STUDY 17

CHEM 080803

Atrazine

\$163-1

FORMULATION—90—FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00098254

Hardies, D.E. and D.Y. Studer. 1982. Soil thin-layer chromatography of PPG-1292: BRC 22593. Unpublished study received April 5, 1982 under 2F2666; submitted by PPG Industries, Inc., Barberton, OH; CDL:070755-J.

DIRECT REVIEW TIME = 10

REVIEWED BY: W. Hurtt

TITLE: Staff Scientist

EDITED BY: K. Patten

TITLE: Task Leader

APPROVED BY: W. Spangler

TITLE: Project Manager

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TEL: 468-2500

APPROVED BY: S. Termes

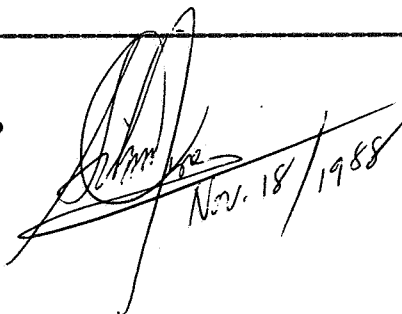
TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 557-2243

SIGNATURE:

CONCLUSIONS:



Nov. 18/1988

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because the soils were sieved through a 0.3-mm sieve, which may have removed a significant portion of the sand fraction and reduced the apparent mobility of atrazine. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the test substance was not completely characterized and the temperature at which the soil TLC plates were developed was not reported.

SUMMARY OF DATA BY REVIEWER:

Using soil TLC techniques and Helling's mobility classification system, unaged [¹⁴C]atrazine (radiochemical purity not specified, specific activity 8.31 mCi/mole) was determined to be of low mobility in silt loam (R_f 0.31) and silty clay loam (R_f 0.29) soils, intermediately mobile in sandy loam soil (R_f 0.62), and mobile in sandy clay loam soil (R_f 0.77). Mobility was the lowest in silty clay loam soil, which contained

the most organic matter and most clay of the four soils; mobility was greatest in the sandy clay loam and sandy loam soils, which had the least organic matter and most sand of the four soils.

DISCUSSION:

1. The soils were sieved through a 0.3-mm sieve which may have removed a significant portion of the sand, thereby reducing the apparent mobility of atrazine on the soil TLC plates. Since a 2-mm sieve is considered the standard for soil texture analysis and soil TLC studies, the results of the texture analyses and the mobility studies may have been biased towards fine-textured soils and lower mobility of atrazine, respectively.
2. The test substance was not completely characterized. Although information concerning the specific activity of [¹⁴C]atrazine was provided, data concerning radiochemical purity and location of the [¹⁴C]label were not provided.
3. The temperature at which the TLC plates were developed was not specified.
4. The mobility of aged [¹⁴C]atrazine was not addressed.

MATERIALS AND METHODS

MATERIALS AND METHODS:

In a soil TLC study, four unaged soils (a sandy loam, a sandy clay loam, a silty loam, and a silty clay loam; described in Tables I-IV) were air-dried and sieved through a 0.3-mm sieve. TLC plates were prepared from each soil by making a slurry of ≈ 10 g of soil and ≈ 5 g of water which was layered on glass plates (0.5-mm thick) and allowed to dry. The plates were spotted with ≈ 0.05 μCi ring-labeled [^{14}C]atrazine (radiochemical purity not specified, specific activity 8.31 mCi/mole; Pathfinder Laboratories) and ≈ 0.05 μCi PPG-1292 (dichloroacetyl-1,2- ^{14}C), a reference pesticide (radiochemical purity not specified, specific activity 4.2 mCi/mole; California Bionuclear). The soil plates were developed over a 15-cm ascending path in distilled water at an unspecified temperature, and the radioactive areas were visualized in a spark chamber. The leading edges of the radioactive areas were used for R_f value calculations.

Atrazine

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Pages 254 through 262 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.
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DATA EVALUATION RECORD

STUDY 18

CHEM 080803

Atrazine

\$163-1

FORMULATION—00—ACTIVE INGREDIENT

FICHE/MASTER ID 00105942

Leake, C., D. Lines, and K. Tiffen. 1981. The leaching of NC 21314 in four soil types using soil TLC. METAB/81/40. Unpublished study prepared and submitted by FBC Chemicals, Inc., Wilmington, DE.

FICHE/MASTER ID 00114299

Leake, C., L. Sommerville, D. Lines, et al. 1982. The leaching of Amitraz in four soil types using soil TLC. METAB/82/16. Unpublished study prepared by FBC Chemicals, Ltd., England, and submitted by FBC Chemicals, Inc., Wilmington, DE.

DIRECT REVIEW TIME = 10

REVIEWED BY: W. Hurtt

TITLE: Staff Scientist

EDITED BY: K. Patten

TITLE: Task Leader

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation
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TEL: 468-2500

APPROVED BY: S. Termes

TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 557-2243

SIGNATURE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because the soils were sieved through 0.25- or 0.5-mm sieves, which may have removed a significant portion of the sand fraction and reduced the apparent mobility of atrazine. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the soils were not completely characterized and the temperature at which the soil TLC plates were developed was not reported.

SUMMARY OF DATA BY REVIEWER:

Ring-labeled unaged [¹⁴C]atrazine (purity 86%, specific activity 19.1 μCi/mg) was found to be intermediate in mobility (R_f 0.54-0.56) by Helling's classification system when averaged over four sieved soils (a sand, a sandy loam, a silt loam, and a clay) in two studies employing soil TLC analysis. The soils in both studies were sieved through a 0.25- or a 0.5-mm sieve. The mobility of atrazine was the highest in the sand and lowest in the clay soils that had the lowest and highest, respectively, clay and organic matter content. For the individual soils, the mobility classifications of atrazine were: sand, mobile to very mobile (R_f 0.91 and 0.95); sandy loam, intermediate (R_f 0.42 and 0.43); silt loam, intermediate (R_f 0.49 and 0.50); and clay, intermediate (R_f 0.36 and 0.38).

DISCUSSION:

1. The soils were improperly sieved; the sandy loam and sand were sieved through a 0.5-mm sieve, and the clay and silt loam soils were sieved through a 0.25-mm sieve. Since a 2-mm sieve is considered the standard for soil texture analysis and soil TLC studies, the results of the texture analyses and the mobility studies may have been biased towards fine-textured soils and lower mobility of atrazine, respectively.
2. The soils were not completely characterized. The CEC values were not determined, and the sum of sand, silt, and clay did not add up to 100% for any of the four soils. Thus, it is not possible to assess the accuracy of the textural classifications.
3. The temperature at which the TLC plates were developed was not specified.
4. The mobility of aged [¹⁴C]atrazine was not addressed.

MATERIALS AND METHODS

MATERIALS AND METHODS:

In a soil TLC study, four unaged soils (a sand, a sandy loam, and silt loam, and a clay; described in Appendix I) were air-dried and sieved through one of two sieves. The clay and silt loam soils were sieved through a 0.25-mm sieve, and the sandy loam and sand were sieved through a 0.5-mm sieve. The soil was mixed with water to form a paste and layered on glass TLC plates at 0.5-mm thickness for the clay and silt loam soils and at 1-mm thickness for the sand and sandy loam soils. Ring-labeled [¹⁴C]atrazine (purity 86%, specific activity 19.1 μCi/mg; Petrochemicals Division, Cleveland, UK) was spotted on the plates along with the following ¹⁴C-labeled reference compounds: paraquat (purity 95%, specific activity 167 μCi/mg or 242 μCi/mg), NC 21314 (purity 95%, specific activity 86.4 μCi/mg), 2,4-D (purity 98%, 242 μCi/mg), and amitraz [1,5-di-(2,4-dimethylphenyl)-3-methyl-1,3,5-triazapenta-1,4-diene; purity 97%, specific activity 9.0 μCi/mg]. The plates were developed in 0.01 M CaCl₂ at an unspecified temperature, dried, and exposed to x-ray film to locate the labeled pesticides.

Atrazine

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- Identity of product inert ingredients.
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- Description of the product manufacturing process.
- Description of quality control procedures.
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- The product confidential statement of formula.
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DATA EVALUATION RECORD

STUDY 19

CHEM 080803

ATRAZINE

§163-1

FORMULATION—RADIOLABELED ACTIVE INGREDIENT

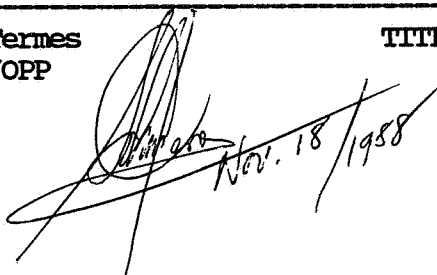
FICHE/MASTER ID 40431329

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. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided. If the requested data is acceptable, this study can be considered to fulfill data requirements for the mobility of atrazine in soils (163-1).

Reported Results

Sorption coefficients (K) were calculated from frontal R_f values for ^{14}C -labeled atrazine ran against ^{14}C -labelled reference standards of Amiben, Prometon, 2,4-D, and Ethion. The calculated K values were used to classify the mobility of atrazine in the four different soils studied:

Plainfield sand highly mobile
Mississippi silt loam mobile
California sandy loam intermediate mobility
Hagerstown silty clay loam . intermediate mobility

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MATERIALS AND METHODS

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

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

Experimental procedure: 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

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

R_f = relative migration of the compound compared 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 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.

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PERTINENT DATA TABLES AND FIGURES

Atrazine

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DATA EVALUATION RECORD

STUDY 20

CHEM 080803

ATRAZINE

§163-1

FORMULATION—RADIOLABELED ACTIVE INGREDIENT

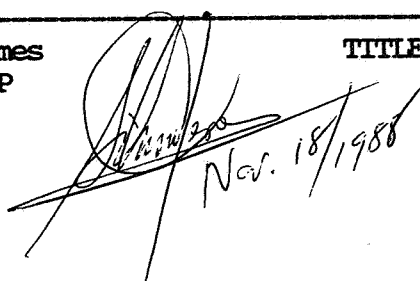
FICHE/MASTER ID 40431330

Saxena, A.M. 1987. Determination of the mobility of soil-aged ^{14}C -atrazine residues by soil thin-layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. HLA 6015-186. Completed October 15, 1987. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

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

If the requested information is acceptable, this study may fulfill data requirements for the mobility of atrazine in soils (163-1).

The reported data indicate that the most mobile component of soil-aged atrazine was the unchanged (parent) atrazine.

MATERIALS AND METHODS

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

Soil: California loam soil

<u>Physical Characteristics</u>	<u>Value</u>
Sand.....	51%
Silt.....	37%
Clay.....	12%
Organic matter.....	1.4%
pH.....	7.6
Cation exchange capacity.....	7
FMC 0.33 bar.....	12%

<u>Microbial characteristics</u>	<u>Value</u>
Aerobic plate.....	12,000,000 count/g
Anaerobic plate.....	460,000 "
Aerobic spore.....	8,800 "
Anaerobic spore.....	170 "
Yeast.....	200 "
Mold.....	29,000 "

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

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

Experimental procedures

- a) Soil fortification: Approximately 21.7 g of sieved soil (20.0 g on a dry basis) were placed in a biometer flask. Then, 200 mL of the ¹⁴C-atrazine fortification solution (11.0×10^6 dpm = 225 ug; theoretical concentration of 11.3 ppm of ¹⁴C-atrazine in dry soil). After the methanol evaporated, the soil was hand-tumbled to homogenize the soil. Water was added to bring the moisture content to 75% of the FMC at 0.33 bar.
- b) Aerobic incubation: A 10% NaOH solution (10 mL) were added to the side arm of the biometer flask. Both the flask and the side arm were sealed (rubber stoppers) and incubated in the darkness at 25 ± 1 deg. C for 32 days. The NaOH solution was removed (and replaced with fresh solution) after 1, 7, 14, 21, 28, and 32 days. Radioactivity in duplicate aliquots was determined by LSC; the measured radioactivity in the NaOH trap was indicative of the amount of CO₂ or volatile products (or both) that

formed. After 32 days, the aged soil was removed from the biometer flask and ground and homogenized with a mortar and pestle. Five aliquots of the aged soil (about 0.15 g each) were oxidized to determine the amount of ^{14}C -activity remaining in the soil.

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

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

- c) Aged-soil TLC: The soil was sieved (1.18 mesh screen). A strip of tape was placed approximately 17.5 cm from one edge of a plate (20 x 20-cm). A slurry of soil and water was applied to a thickness of approximately 1.0 mm and allowed to dry. The plate was separated into seven channels (by cutting grooves), each approximately 2.5 cm wide.

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

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

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

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

Where, K = sorption coefficient
R_f = Relative mobility of the compound compared to water
φ = Pore fraction of the soil (assumed to be 0.5)
D = Specific gravity of the solids in soil (2.5)

REPORTED RESULTS AND DISCUSSION

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

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

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

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

Atrazine

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Pages _____ through _____ are not included.

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 - 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.
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MATERIALS AND METHODS

Test material: ^{14}C -G-28273, specific activity 14.1 uCi/mg, radio-purity 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).

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

Experimental procedure: 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 frontal R_f value, a mobility class was assigned. A sorption coefficient (K) was determined by

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

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-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.

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 293 through 295 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.
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 - A draft product label.
 - The product confidential statement of formula.
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DATA EVALUATION RECORD

STUDY 22

CHEM 080803

G-28279 (degradate of ATRAZINE)
2-amino-4-chloro-6-ethylamino-s-triazine

§163-1

FORMULATION—RADIOLABELED MATERIAL

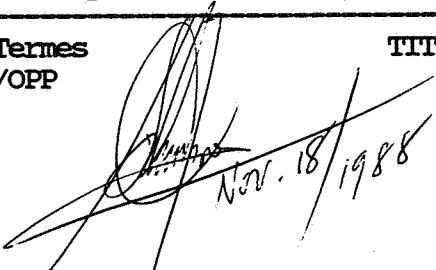
FICHE/MASTER ID 40431331

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. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes
ORG: EFGWB/EFED/OPP
TEL: 557-2243

TITLE: Chemist

SIGNATURE:



CONCLUSIONS:

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided. If the requested data is acceptable, this study can be considered to fulfill data requirements for the mobility of atrazine degradates in soils (163-1).

Sorption coefficients (K) were calculated from R_f values for ¹⁴C-labeled G-28279 ran against ¹⁴C-labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion. The calculated K values were used to classify the mobility of G-28279 in the four different soils studied:

Plainfield sand highly mobile
Mississippi silt loam low mobility
California sandy loam low mobility
Hagerstown silty clay loam . intermediate mobility

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).

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

Experimental procedure: 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 value, 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 of 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.

PERTINENT DATA TABLES AND FIGURES

Atrazine

Page _____ is not included in this copy.

Pages 300 through 302 are not included.

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DATA EVALUATION RECORD

STUDY 23

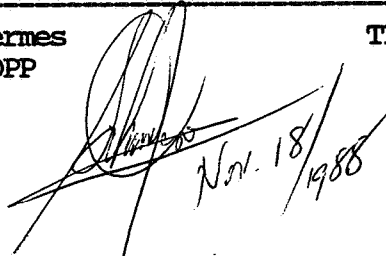
CHEM 080803 G-30033 (degradate of ATRAZINE) §163-1
2-amino-4-chloro-6-isopropylamino-s-triazine

FORMULATION—RADIOLABELED MATERIAL

FICHE/MASTER ID 40431334
Blair, J.E. 1986. Determination of the mobility of G-30033 in selected soils by soil thin-layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-306. Completed February 27, 1986. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes TITLE: Chemist
 ORG: EFGWB/EFED/OPP
 TEL: 557-2243

SIGNATURE:



CONCLUSIONS:

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided. If the requested data is acceptable, this study can be considered to fulfill data requirements for the mobility of atrazine degradates in soils (163-1).

Sorption coefficients (K) were calculated from R_f values for ¹⁴C-labeled G-30033 ran against ¹⁴C-labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion. The calculated K were used to classify the mobility of G-30033 in the four different soils studied:

Plainfield sand highly mobile
Mississippi silt loam mobile
California sandy loam mobile
Hagerstown silty clay loam . intermediate mobility

MATERIALS AND METHODS

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

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

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

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

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

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

Atrazine

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Pages 306 through 308 are not included.

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DATA EVALUATION RECORD

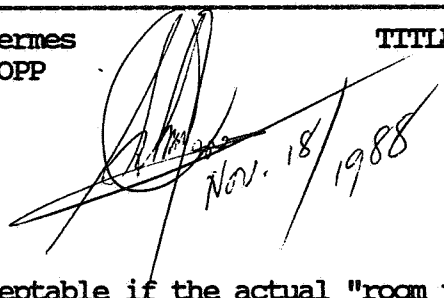
STUDY 24

CHEM 080803 G-34048 (degradate of ATRAZINE) §163-1
2-ethylamino-4-hydroxy-6-isopropylamino-s-triazine

FORMULATION—RADIOLABELED MATERIAL

FICHE/MASTER ID 40431332
Blair, J.E. 1986. Determination of the mobility of G-34048 in selected soils by soil thin-layer chromatography. Conducted by Hazleton Laboratories America, Inc., Madison, WI. Laboratory Study No. 6015-302. Completed March 7, 1986. Submitted by Ciba-Geigy Corporation, Greensboro, NC.

REVIEWED BY: Silvia C. Termes TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-2243



SIGNATURE:

CONCLUSIONS:

This study may be acceptable if the actual "room temperature" at which the plates were developed can be provided. If the requested data is acceptable, this study can be considered to fulfill data requirements for the mobility of atrazine degradates in soils (163-1).

Sorption coefficients (K) were calculated from R_f values for ^{14}C -labeled G-34048 ran against ^{14}C -labeled reference standards of Amiben, Prometon, 2,4-D, and Ethion. The calculated K were used to classify the mobility of G-34048 in the four different soils studied:

- Plainfield sand low mobility
- Mississippi silt loam immobile
- California sandy loam immobile
- Hagerstown silty clay loam . low mobility

MATERIALS AND METHODS

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

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

Experimental procedure: 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-34048, 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 by autoradiography. The frontal R_f values were calculated from each autoradiography by measuring the distance from the origin to the leading edge of the radioactivity and dividing by the distance from the origin to the solvent front. For each soil, G-34048 was determined in triplicate and each standard once. Based on frontal R_f value, a mobility class was assigned. A sorption coefficient (K) was calculated from the relative mobility by

$$K = \frac{1/R_f - 0.2/3}{D (1 - 0.2/3)}$$

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

REVIEWER'S COMMENTS

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

PERTINENT DATA TABLES AND FIGURES

Atrazine

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DATA EVALUATION RECORD

STUDY 25

CHEM 080803

Atrazine

\$163-1

FORMULATION—00—ACTIVE INGREDIENT

FICHE/MASTER ID 00116619

Kinne, L., J. Reynolds, L. Froelich, et al. 1982. Soil mobility of FMC 57020. M-4862. Unpublished study prepared and submitted by FMC Company, Philadelphia, PA.

DIRECT REVIEW TIME = 10

REVIEWED BY: W. Hurtt

TITLE: Staff Scientist

EDITED BY: K. Patten

TITLE: Task Leader

APPROVED BY: W. Spangler

TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD

TEL: 468-2500

APPROVED BY: S. Termes

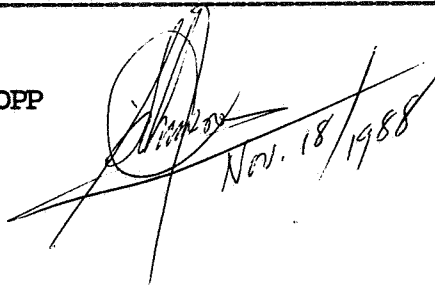
TITLE: Chemist

ORG: EFGWB/EFED/OPP

TEL: 557-2243

SIGNATURE:

CONCLUSIONS:



Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because the soils were sieved through a 0.25- or 0.5-mm sieve which may have removed a significant portion of the sand fraction and reduced the apparent mobility of atrazine. In addition, this study would not fulfill EPA Data Requirements for Registering Pesticides because the temperature information was not provided for the column leaching or soil TLC studies.

SUMMARY OF DATA BY REVIEWER:

Based on soil TLC experiments, ring-labeled unaged [¹⁴C]atrazine (radiochemical purity 94.7%) was found to be intermediate in mobility in sandy, silt, and clay loam soils (R_f 0.35-0.47) and mobile in a "fine" sand soil (R_f 0.73) by Helling's classification system. All soils were sieved through a 0.25- or 0.5-mm sieve prior to TLC analyses. The mobility of atrazine was the highest in the "fine" sand which had the lowest organic

matter content (1.3%) and clay content (3.6%), and mobility was lowest in the sandy loam (R_f 0.35) which had the highest organic matter content (3.2%) but only a moderate level of clay (10.8%).

Based on column leaching experiments, ring-labeled unaged [^{14}C]atrazine (radiochemical purity 94.7%) was found to be very mobile in soil columns of "fine" sand. Approximately 65% of the recovered radioactivity was found in the leachate and $\approx 35\%$ was found to be relatively uniformly distributed throughout the 30-cm column length.

DISCUSSION:

General

1. The soils were not sieved with the standard 2-mm sieve. The "fine" sand and sandy loam soils were sieved through a 0.5-mm sieve and the silt and clay loam soils were sieved through a 0.25-mm sieve such that a significant portion of the sand fraction (0.05-2.00 mm) may have been removed with a resulting possible decrease in apparent mobility of atrazine.
2. None of the four soils had an organic matter content $\leq 1\%$. Since the "fine" sand and sandy loam soils were marginally high to high in organic matter content for coarse textured soils (1.3 and 3.2%, respectively), the apparent mobility of atrazine may have been represented as too low.
3. The temperature at which the TLC and column leaching studies were conducted was not reported.
4. One of the four soils was designated as a "fine" sand which is not a recognized soil classification name on the USDA textural classification triangle.
5. The mobility of aged [^{14}C]atrazine was not addressed.

Column Leaching

1. It could not be determined whether the material balance was complete because it was not stated whether recovered radioactivity was percent of that applied or percent of that recovered.
2. Column leaching studies were only conducted with the "fine" sand soil.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Soil TLC

In a soil TLC study, four unaged soils were air-dried for 24 hours and sieved. The "fine" sand and sandy loam soils were sieved through a 0.5-mm sieve, and the silt and clay loam soils were sieved through a 0.25-mm sieve. The soils were mixed with water to form a slurry and layered on glass TLC plates at a thickness of 2 mm for the sand and sandy loam soils and 0.25 mm for the silt and clay loam soils. Following air-drying overnight, the plates were spotted with ring-labeled [¹⁴C]atrazine (radiochemical purity 94.7%, specific activity 8.31 mCi/mmol; Pathfinder Labs) and three ¹⁴C-labeled reference pesticides (FMC-57020, paraquat, and 2,4-D) and developed at an unspecified temperature to a distance of 10 cm in distilled water. The plates were dried and exposed to X-ray film for 3-7 days to locate the labeled pesticides.

Column Leaching

In a column leaching study, unaged "fine" sand (prepared for experimental use as described for soil TLC) was packed to depth of 30 cm in 25-mm glass columns which were then saturated with water. A glass wool plug was placed on top of the soil, and ≈6 g of soil treated with 10 μCi of ring-labeled [¹⁴C]atrazine or one of the three reference pesticides (properties as previously described for soil TLC) was added to each column. The columns were eluted with 250 mL of water (equivalent to 50.8 cm times area) and the eluate was collected in 5-mL fractions. After elution, the columns were cut into 6-cm segments and air-dried. Portions of each soil segment were combusted for total radioactivity and those segments having radioactivity ≥10% of that applied to the column were solvent-extracted, concentrated, and subjected to HPLC analysis with ISC. Radioactivity in the eluate fractions was determined by ISC.

Atrazine

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Pages 319 through 322 are not included.

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DATA EVALUATION RECORD

STUDY 26

CHEM 080803

Atrazine

§163-1

FORMULATION—00—ACTIVE INGREDIENT

FICHE/MASTER ID 00160292

Davidson, J., P. Rao, L. Ou, et al. 1980. Adsorption, movement, and biological degradation of large concentrations of selected pesticides in soils. EPA-600/2-80-124. Prepared by Soils Science Dept., Univ. of FL in conjunction with the Municipal Environmental Research Lab., U.S. Environmental Protection Agency, Cincinnati, OH.

DIRECT REVIEW TIME = 8

REVIEWED BY: W. Hurtt TITLE: Staff Scientist

EDITED BY: K. Patten TITLE: Task Leader

APPROVED BY: W. Spangler TITLE: Project Manager

ORG: Dynamac Corporation
Rockville, MD

TEL: 468-2500

APPROVED BY: S. Terres
TITLE: Chemist
ORG: EFGWB/EFED/OPP
TEL: 557-2243

SIGNATURE:

CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

This study is unacceptable because insufficient experimental details were provided to assess the adequacy of the results in fulfilling EPA Data Requirements for Registering Pesticides based upon mobility (batch equilibrium). It is primarily a summary of a large number of experiments concerned with the behavior of high concentrations of pesticides in soil and, as such, does not provide specific details relevant to the batch equilibrium experiments. Although methodology for a column leaching study was included, identifiable results of the experiments were not provided.

SUMMARY OF DATA BY REVIEWER:

Based on batch equilibrium experiments, ring-labeled [¹⁴C]atrazine was mobile to very mobile in silty clay loam, sandy loam, sandy clay loam, and "fine" sand soils when equilibrated for 48 hours at 23°C at five concentrations between 10 and 1000 μM. The equilibrations were conducted in soil:solution ratios of 5 or 10 g soil:10 mL solution. Freundlich K_{ads} values were 9.12 (mobile) for the silty clay loam and were 0.69-0.85 (very mobile) for the remaining three coarser textured soils. K_{oc} values ranged from 99 (sandy loam) to 156 (silty clay loam). Adsorption values (K_{ads} and K_{oc}) were the highest for the silty clay loam soil having the highest clay and organic carbon content.

DISCUSSION:

1. The original document was concerned primarily with the behavior of high concentrations of five pesticides in soil as affected by a number of variables; therefore, insufficient specific details concerning the batch equilibrium experiment were provided to assess the applicability of the study for fulfilling data requirements based upon soil mobility (batch equilibrium).
2. The mobility of aged [¹⁴C]atrazine was not addressed.
3. Desorption of atrazine was not determined for any of the soils.
4. The test substance was not characterized.
5. The sum of sand, silt, and clay for the "sandy clay loam" was only 90%; therefore, the textural classification could not be confirmed. Also, one of the four soils was designated as a "fine" sand which is not a recognized soil classification name in the USDA Soil Textural Classification System.
6. The studies were not conducted in a 0.01 N calcium ion solution.
7. The soil was not combusted at the end of the experiment to confirm that the material lost from solution was adsorbed to the soil and to provide a complete material balance.
8. The pH of the test solution was not reported.
9. Methodology was provided for column leaching studies in the original document, but identifiable results of the experiments were not provided.

MATERIALS AND METHODS

MATERIALS AND METHODS:

In a batch equilibrium study, four soils (a "fine" sand, a sandy loam, a sandy clay loam, and a silty clay loam) were air-dried and sieved through a 2-mm screen. Duplicate soil samples were shaken with ring-labeled [¹⁴C]atrazine (test substance not further characterized) for 48 hours at 23 ± 1°C. The soil:solution ratio was 5 or 10 g soil:10 mL solution. Five unspecified concentrations of atrazine between 10 and 1000 μM were used in these experiments. After centrifuging at 800x g for 10 minutes, the [¹⁴C]-activity in the supernatant was determined by LSC.

SECTION 4

MATERIALS AND METHODS

SOILS

Soils used in this study were selected on the basis of their geographic and taxonomic representation of major soil orders in the United States. State Conservationists for the Soil Conservation Service in selected regions were asked to identify the major soil series in their area for a selected soil order and to ship 735 kg (air-dry) of the Ap horizon of that soil. A soil profile description, sample site location, previous crop and management history, and climatic conditions at the site were provided with each soil series selected and studied. Soils selected were: Webster silty clay loam (Typic Haplaquolls) from Iowa, Cecil sandy loam (Typic Hapludults) from Georgia, Glendale sandy clay loam (Typic Torrifuvents) from New Mexico, Eustis fine sand (Typic Quartzipsaments), and Terra Ceia muck (Typic Mediasaprists) from Florida.

The soils were air-dried and sieved to pass a 2-mm screen prior to being stored. Selected physical and chemical properties of the mineral soils are given in Table 1. Terra Ceia muck is characterized by 81% organic matter, 19% total mineral content, CEC of 350 meq/100g and pH of 6.4.

PESTICIDES

The pesticides used in this study were selected based upon their present and anticipated usage as well as their different chemical properties. The production and use of herbicides has increased significantly in the past few years and at the present time herbicides represent the largest group of pesticides on the market. Because of this market shift in pesticide production, the herbicides were identified as a group of chemicals requiring major attention. The following description of each pesticide used in the study illustrates the diversity in chemical properties and toxicity of the selected compounds. It was believed that this range in chemical properties (Table 2) provided the necessary information needed to evaluate the problems associated with introducing large pesticide concentrations into the soil environment.

- 1) Atrazine (Herbicide): (2-chloro-4-ethylamino-6-isopropylamino-s-triazine). Low solubility in water (Table 2), but highly soluble in chloroform, methanol, and ether. Losses due to chemical and microbial degradation are significant. Leaching from soils may be limited due to adsorption on certain soil constituents. Acute oral LD₅₀ to rats 3080 mg/kg.

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TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF THE MINERAL SOILS USED IN THIS STUDY

SOIL	PARTICLE SIZE FRACTION (%)		PI (1:1 paste) Water IN KCl	CIC (meq/100g)	Organic C (%)	Base Saturation (%)	Extractable Acidity (meq/100g)		
	Sand	Silt	Clay						
Webster	18.4	45.3	38.3	7.3	6.5	54.7	3.87	91	5.15
Cecil	65.8	19.5	14.7	5.6	4.8	6.8	0.90	31	4.68
Glendale	50.7	16.4	22.9	7.4	6.5	35.8	0.50	90	3.74
Eustis	93.8	3.0	3.2	5.6	4.1	5.2	0.56	10	4.68

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- 2) Methyl Parathion (Insecticide): (0-0-dimethyl-0-p-nitrophenyl phosphorothioate). Technical grade is a liquid. Low solubility in water (Table 2), but soluble in most organic solvents. Highly toxic and degrades readily in a soil environment producing some metabolites that are equally toxic. Acute oral LD₅₀ to rats is 9-25 mg/kg.
- 3) Terbacil (Herbicide): (3-tert-butyl-5-chloro-6-methyl uracil). Soluble in water (Table 2) and soluble in most organic solvents. Mobile in soils due to relatively low adsorption. Acute oral LD₅₀ for rats between 5,000-7,000 mg/kg.
- 4) Trifluralin (Herbicide): (α,α,α-trifluoro-2,6-dinitro-N, N-dipropyl-p-toluidine). Almost insoluble in water (Table 2) but very soluble in most organic solvents. Volatile unless incorporated into the soil immediately following application. Microbial and photo-degradation play a significant role in dissipation from soil. Adsorption on organic matter and clay colloids retards leaching from soils. Acute oral LD₅₀ for rats greater than 10,000 mg/kg.
- 5) 2,4-D (Herbicide): (2,4-dichlorophenoxyacetic acid). Somewhat soluble in water (Table 2), and very soluble (30-60%) in acetone and alcohols. Undergoes microbial degradation in soils, but losses due to photodecomposition are minimal. Because of low adsorption in soils, it is readily leached. Acute oral LD₅₀ for formulations are in the range of 300-1000 mg/kg rats, guinea pigs, and rabbits.

Formulated and technical grade materials fortified with ¹⁴C materials were used to study mobility, adsorption-desorption, microbial degradation and accumulation of metabolites in soils at various pesticide concentrations. Stock solutions of each pesticide were prepared in 0.01N CaCl₂ using the commercial stock solution made up to the aqueous solubility limit of the pesticide. Solutions of lower concentrations were prepared by successive dilutions of the original stock solution. A mixture of antibiotics consisting of Penicillin G at 1 μg/ml and Polymixin B sulfate at 5 μg/ml (Sigma Chemical Co., St. Louis, MO) was added to all pesticide solutions to prevent microbial degradation during storage and use.

The commercial formulation of 2,4-D was Ded-Weed 40 (Thomson-Hayward Chemical Co., Kansas City, MO), a dimethylamine salt of 2,4-D (41% acid equivalent). The stock solution of commercially formulated atrazine was prepared using AATREX 80W (80% wettable powder; Ciba-Geigy Corp., Greensboro, NC). A concentrated xylene solution of methyl parathion (80% solution; Monsanto Co., Agricultural Division, St. Louis, MO) was diluted in 0.01N CaCl₂ to give the desired stock concentration. The commercial form of trifluralin was Treflan (Elanco Products Co., a division of Eli Lilly and Co., Indianapolis, IN; 44.5% trifluralin and 55.4% inert ingredients). The technical grade form of each pesticide was at least 97% pure. All pesticide solutions were spiked with the appropriate uniformly ring-labeled ¹⁴C compound (except for trifluralin) to give specific activities in the range of 2-5 nCi/ml. Trifluralin was ¹⁴C-labeled at the -CF₃ position.

ADSORPTION ISOTHERMS

Equilibrium adsorption isotherms for all soil-pesticide combinations were measured using the batch procedure. Equilibrium was achieved by

shaking duplicate samples of 5 or 10 g of soil with 10 ml of pesticide solution in Pyrex screw-cap glass test tubes for 48 hrs. Preliminary experiments had indicated that there was no measurable increase in pesticide adsorption beyond this time. Following equilibration, the test tubes were centrifuged at 800 g for 10 minutes and the ^{14}C -activity in 1-ml aliquots of the clear supernatant solution was assayed by liquid scintillation counting. Decreases in pesticide solution concentration were attributed to adsorption by the soil. All adsorption experiments were performed at a constant temperature ($23 \pm 1^\circ \text{C}$).

PESTICIDE DISPLACEMENT THROUGH SOILS

Pesticide movement through water-saturated columns of Webster, Cecil, and Eustis soils was studied using the miscible displacement technique described by Davidson et al. (1968). Air-dry soil was packed in small increments into glass cylinders (15 cm long; 45 cm² cross-sectional area). Medium porosity fritted glass plates served to retain the soil in the column. The soil was initially saturated with 0.01 N CaCl_2 solution. A known volume of pesticide solution at a desired concentration was introduced into the soil at a constant flux using a constant-volume peristaltic pump. After a specific volume of pesticide solution had been applied, the pesticide solution was subsequently displaced through the soil column with 0.01 N CaCl_2 at the same flux. Effluent solutions were collected in 5 or 10 ml aliquots using an automatic fraction collector. A pulse of $^3\text{H}_2\text{O}$ (specific activity = 5 nCi/ml) was also displaced through each soil column to characterize the transport of non-adsorbed solutes. The activity of ^{14}C and ^3H in effluent fractions was assayed by liquid scintillation. The counting efficiencies exceeded 90% for ^{14}C and 50% for ^3H in all cases.

The column experiments consisted of displacing 2,4-D amine solutions at two concentrations (50 and 5,000 $\mu\text{g/ml}$) through columns of Cecil, Eustis and Webster soils, and 5 and 50 $\mu\text{g/ml}$ solutions of atrazine through a Eustis soil. All displacements were performed at a Darcy flux of approximately 0.22 cm/hr to ensure near-equilibrium conditions for pesticide adsorption during flow. The total volume of water held in the soil column was gravimetrically determined at the end of each displacement by extruding the soil from the glass cylinders and oven-drying. The number of pore volumes (V/V_0) of solution displaced through the column was calculated by dividing the cumulative outflow volume (V) by total water volume (V_0) in the soil column. Effluent pesticide concentrations are expressed as relative concentrations (C/C_0), where C and C_0 are, respectively, effluent and input concentrations. Plots of C/C_0 versus V/V_0 are referred to as breakthrough curves (or BTC).

Air-dry soil was packed into 3.2-cm diameter lucite cylinders composed of 1-cm sections supported by a V-shaped container that permitted observation of the wetting front position with time. Technical or analytical grade pesticide was dissolved in benzene and was spiked with ^{14}C -labeled compound. The benzene solution was mixed with air-dry soil (to give 200 or 2,000 μg of pesticide/g of soil and 10 nCi/g soil) and the benzene evaporated. In order to simulate a waste disposal site, the pesticide-spiked soil was packed into the top 1.5 cm of the soil column. Infiltration

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

SECTION 2
CONCLUSIONS

1. Equilibrium adsorption isotherms for pesticides and soils considered in this study were nonlinear. The Freundlich equation described the full range of pesticide solution concentrations (zero to aqueous solubility limit) studied. The adsorption "sites" for the pesticide were apparently never saturated in any soil-pesticide system investigated.

2. Pesticide mobility was inversely related to the pesticide concentration in the soil solution phase when the adsorption isotherm was nonlinear ($N < 1.0$). 2,4-D at 5,000 µg/ml was nearly as mobile as the chloride ion. The dependence of the mobility on pesticide solution concentration could be predicted and described by the equilibrium adsorption isotherm.

3. $^{14}\text{CO}_2$ evolution rate from a ^{14}C -ring labeled pesticide was a good indicator of pesticide degradation rate in soils containing large pesticide concentrations. Total CO_2 evolution, however, did not always represent the actual degradation of a pesticide. For this reason, the biological activity of soils containing low pesticide concentrations may, in many cases, be unrelated to the behavior and degradation of pesticides at large concentrations in the soil.

4. Moderately persistent pesticides such as atrazine and trifluralin, degrade slowly forming a number of metabolites when present in soils at high and low concentrations. These pesticides and metabolite products have the potential to become "bound" to the soil matrix. Bound residue was defined in this study to be the ^{14}C -labeled material remaining in the soil after recommended extraction procedures had been employed.

5. The less persistent pesticides such as 2,4-D and methyl parathion may or may not degrade when applied to a soil at high concentrations. Factors that determine the degradation rate were pesticide concentration, chemical formulation, nutrients in the soil, soil type, soil pH, temperature, soil-water content, soil organic matter content, texture, and the presence of a microbial population capable of degrading the pesticide. If the pesticide was degraded, the time required for degradation to begin was longer for large concentrations (>50 ppm) than for low concentrations. The lag period was directly related to pesticide concentration.

6. Pesticide mobility and degradation were described using adsorption and biological degradation parameters measured during this study. Conceptual or process based mathematical models were used to describe pesticide

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mobility. The models were well suited for estimating the concentration distribution and mobility of pesticides associated with waste disposal sites.

7. Bound residues were formed at all concentrations studied (10 to 20,000 ppm). The percent of binding was higher for low concentrations; however, the amount bound (atrazine or trifluralin) increased as the pesticide concentration increased. The toxicity and chemical nature of the "bound residues" were not studied in detail.

8. At low pesticide concentrations (<50 ppm), microbial activity (indicated by total CO₂ evolution, and bacterial, fungal and actinomycete population) was generally not affected. Microbial activity may be enhanced or inhibited when a large amount of pesticide is applied to a soil. When degradation occurred at large concentrations, microbial activity was enhanced. Moreover, formulation chemicals may stimulate microbial activity by serving as energy or nutrient sources. If pesticide degradation does not occur, microbial activity may be either enhanced or inhibited.

9. Based on the results of this study, groundwater contamination may be a significant problem when highly soluble pesticides are placed in waste disposal sites subject to considerable leaching. The potential for groundwater contamination, on the other hand, is not as great for pesticides with low solubilities.

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PERTINENT DATA TABLES AND FIGURES

TABLE 5. FREUNDLICH CONSTANTS CALCULATED FROM EQUILIBRIUM ADSORPTION ISOTHERMS FOR VARIOUS SOIL-PESTICIDE COMBINATIONS

PESTICIDE	SOIL	K_M^{\dagger}	K_G^{\ddagger}	N	$K_{OC}^{\ddagger\ddagger}$
Atrazine	Webster	9.12	6.03	0.73	155.8
	Cecil	0.84	0.89	1.04	98.9
	Glendale	0.69	0.62	0.93	124.0
	Eustis	0.85	0.62	0.79	110.7
	Average ± % CV*	2.87 ± 145	2.04 ± 131	0.87 ± 16	122.3 ± 20
Methyl Parathion	Webster	18.67	13.39	0.75	346.0
	Cecil	4.81	3.95	0.85	438.6
	Glendale	6.05	3.57	0.61	714.5
	Eustis	3.30	2.72	0.86	486.4
	Average ± % CV	8.21 ± 86	5.91 ± 85	0.77 ± 15	496.4 ± 32
Terbacil	Webster	2.96	2.46	0.88	63.6
	Cecil	0.39	0.38	0.99	42.2
	Glendale	0.42	0.38	0.93	76.0
	Eustis	0.15	0.12	0.88	21.4
	Average ± % CV	0.98 ± 135	0.83 ± 130	0.92 ± 6	50.8 ± 47
Trifluralin	Webster	2.49	2.93	1.15	75.7
	Cecil	0.43	0.46	1.05	50.7
	Glendale	1.31	1.60	1.18	177.8
	Eustis	0.23	0.24	1.06	43.2
	Average ± % CV	1.11 ± 92	1.31 ± 94	1.11 ± 6	86.8 ± 72
2,4-D Amine	Webster	7.27	4.62	0.70	119.4
	Cecil	0.84	0.65	0.83	72.2
	Glendale	--	--	--	--
	Eustis	1.14	0.76	0.73	135.7
	Average ± % CV	3.08 ± 118	2.01 ± 112	0.75 ± 9	109.1 ± 30

K_M^{\dagger} Freundlich constant when solution and adsorbed phase concentrations are expressed as $\mu\text{M/l}$ and $\mu\text{M/kg}$ of soil.

K_G^{\ddagger} Freundlich constant for solution and adsorbed phase concentrations are as $\mu\text{g/ml}$ and $\mu\text{g/g}$ of soil [$K_G = K_M (\text{MW}/1,000)^{1-N}$], when MW is the pesticide's molecular weight.

$K_{OC}^{\ddagger\ddagger}$ Freundlich constant for solution and adsorbed phase expressed as $\mu\text{g/ml}$ and $\mu\text{g/g}$ of organic carbon.

*CV is the coefficient of variation, % CV = (standard deviation/average x 100).

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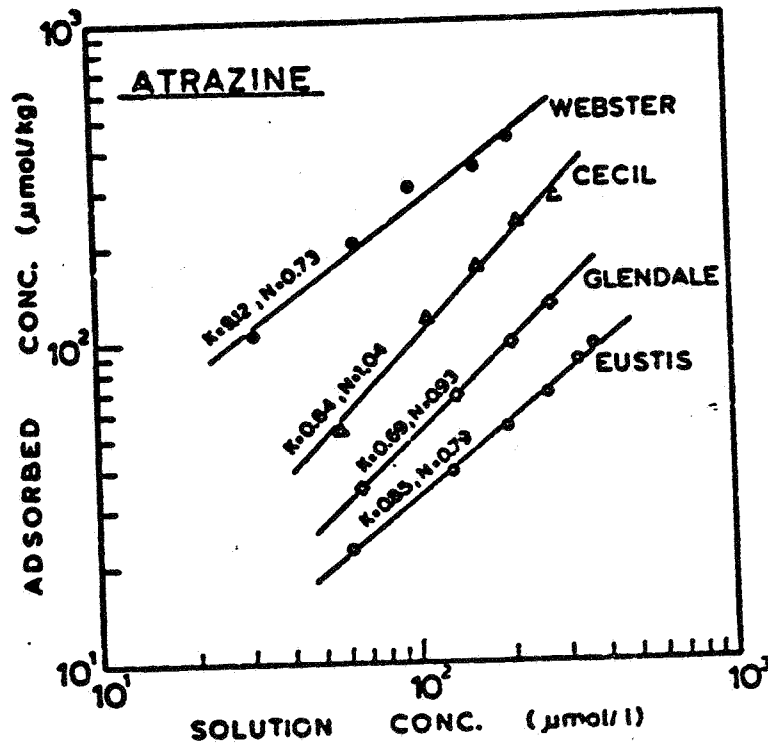


Figure 4. Adsorption isotherms for atrazine and Webster, Cecil, Glendale and Eustis soils. Freundlich constants (K and N) for each isotherm, determined by least-squares fit to the data, are also shown.

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DATA EVALUATION RECORD

STUDY 27

CHEM 080803

Atrazine

\$163-1

FORMULATION--90--FORMULATION NOT IDENTIFIED

FICHE/MASTER ID 00027140

Lavy, T.L. 1974. Mobility and deactivation of herbicides in soil-water systems. Project A-024-NEB. Nebraska Water Resources Research Institute. Available from: National Technical Information Service, Springfield, VA.

FICHE/MASTER ID 00027139

Weidner, C.M. 1974. Degradation in groundwater and mobility of herbicides. Masters thesis: University of Nebraska, Lincoln, NE.

DIRECT REVIEW TIME = 6

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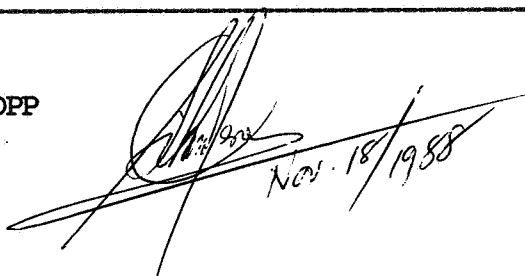
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CONCLUSIONS:



Mobility - Leaching and Adsorption/Desorption

The batch equilibrium portion of this study is unacceptable because it could not be determined if the 14-hour equilibration period was long enough to establish equilibrium between the soil and water phases and the soil:solution slurries were stored in a refrigerator for 24 hours prior to analysis of the supernatant for total radioactivity. The column leaching portion of this study is unacceptable because material balances were not provided. In addition, this study does not fulfill EPA Data Requirements for Registering Pesticides because: Batch equilibrium - distribution coefficients (K_d) were calculated instead of Freundlich K values, the CECs of the soils were not reported, the equilibration temperature was not specified, the test substance was not completely

characterized, the soils were not analyzed after equilibration to confirm adsorption and to provide a material balance, desorption of atrazine was not studied, and the study was not conducted using a 0.01 N calcium ion solution; and Column leaching - the soil columns were only 8 inches in length instead of 12 inches, the soil columns were leached with only 10 inches of water instead of 20 inches, the CECs of the soils were not reported, and the purity and specific activity of the test substance were not specified.

SUMMARY OF DATA BY REVIEWER:

Based on batch equilibrium experiments, [¹⁴C]atrazine (500 dpm/mL, not further characterized), at 1, 2, 5, and 10 ppm, was very mobile in gravelly sand soil (K_d values of 0-1.00) and was mobile to very mobile in sandy loam and silty clay loam soils (K_d values of 1.40-8.70 and 2.00-11.60, respectively).

Based on column leaching experiments, [¹⁴C]atrazine (90,000 dpm, not further characterized) was very mobile in gravelly sand, mobile in sandy loam soil, and slightly mobile in silty clay loam soil columns (8-inches) leached with 10 inches of water; 95.1%, 18.3% and 1.5% of the applied radioactivity, respectively, was present in the leachates.

DISCUSSION:

Batch equilibrium

1. It could not be determined if the 14-hour equilibration period was long enough to establish equilibrium between the soil and water phases.
2. After equilibration and centrifugation, the soil:solution slurries were stored in a refrigerator for 24 hours prior to analysis of the supernatant for total radioactivity. During the storage period, the distribution of atrazine between the soil and solution phases may have changed as a result of exposure to lower temperatures.
3. Distribution coefficients (K_d) were calculated instead of Freundlich K values.
4. The CECs of the soils were not reported.
5. The equilibration temperature was not specified.
6. The test substance was not completely characterized. It was stated that the solution was 500 dpm/mL, indicating that the test substance was radiolabeled; in the general methods section, the study author stated that ring-labeled [¹⁴C]atrazine was used in "many of the studies" in the original report. The purity and specific activity of the test substance were not reported. In addition, it was not reported whether or not nonradiolabeled atrazine was also used.

7. The soils were not analyzed after equilibration to confirm adsorption and to provide a material balance.
8. Desorption of atrazine was not studied.
9. The study was not conducted using a 0.01 N calcium ion solution.

Column leaching

1. Material balances were not provided. Radioactivity in the soil columns was presented only in terms of percent of the recovered from the soil columns.
2. The soil columns were only 8 inches in length instead of 12 inches.
3. The soil columns were leached with only 10 inches of water instead of 20 inches.
4. The CECs of the soils were not reported.
5. The purity and specific activity of the test substance were not specified.

Other

Four experiments in the original documents were not reviewed. One experiment was a study of degradation of atrazine in groundwater samples; this experiment is unacceptable as a hydrolysis study because the solutions were not sterile and it was not stated whether or not the solutions were incubated in the dark. A second experiment was not reviewed because it contains bioassay data only. A third experiment was a study of the movement of atrazine injected below the soil surface of a field plot and is not pertinent to environmental fate data requirements. A fourth experiment was a study of the effectiveness of charcoal and exchange resins in removing herbicide residues from aqueous solutions and is also not pertinent to environmental fate data requirements.

MATERIALS AND METHODS

MATERIALS AND METHODS:

Batch equilibrium

Sieved (2-mm) silty clay loam, sandy loam, and gravelly sand soils (Table 1) were treated with aqueous solutions containing [¹⁴C]atrazine (500 dpm/mL, not further characterized) at 1, 2, 5, and 10 ppm (soil:solution ratio 1:10). The soil:solution slurries were shaken for 14 hours (equilibration temperature not reported). The soil:solution slurries were centrifuged, then refrigerated for 24 hours. The supernatants were analyzed for total radioactivity by LSC.

Column leaching

[¹⁴C]Atrazine (90,000 dpm, not further characterized) was added at 1 ppm to the top half-inch of columns (60-mm diameter, 8-inch length) of silty clay loam, sandy loam, and gravelly sand soils (Table 1). The soil columns were leached with 10 inches of distilled water at a rate of 0.5 cm/hour for a total of 50 hours. The leachate fractions were collected at 90 minute intervals. After leaching, the soil columns were divided into 0.5-inch segments.

The leachate fractions were analyzed for total radioactivity by LSC. The soil segments were analyzed by LSC following combustion.

MATERIALS AND METHODS

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

PERTINENT DATA TABLES AND FIGURES

Table 6. Analysis of soils used to conduct adsorption and leaching studies.

Soil Type	Soil Depth (in.)	pH	CN	PERCENT			Moisture at 1/3 at m
				Sand	Silt	Clay	
Sharpsburg clay loam	0-6	5.2	4.55	10	57	33	28.2
Jones sandy loam	0-6	5.7	2.91	64	25	11	13.3
Jones gravely sand	24-40	6.3	0.07	93	2	5	9.1

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II. Research performed under objective b) measure the mobility of four herbicides (alachlor, atrazine, butylate and picloram) in three Nebraska profiles.

A. Ed Study to Show Relative Adsorption of Atrazine, Alachlor, Butylate and Picloram to Three Soil Types.

Herbicide solutions used for this study were prepared in distilled water at 1, 2, 5, and 10 ppm of atrazine, alachlor, butylate and picloram. Each solution contained approximately 500 dpm/ml initially. The soils used in this study were Sharpsburg silty clay loam, Jansen sandy loam, and Jansen gravelly sand. All soil was passed through a 2 mm sieve before use. For each of three replications, one-half gram soil samples were weighed into screw top vials to which was added 5 ml herbicide solution. The vials were sealed and shaken for 14 hours on a gyrotory shaker before being centrifuged at 1400 rpm for approximately one hour. To facilitate the settling of the soil particles the samples were placed in a refrigerator for 24 hours. Aqueous 1 ml samples were counted using the liquid scintillation counter. Care was taken not to include settled soil particles in the liquid sample. Ed values were then calculated for each treatment using the following equation:

$$E_d = \frac{\text{dpm standard} - \text{dpm equilibrium solution}}{\text{dpm equilibrium solution}} \times \frac{\text{ml solution}}{\text{g. adsorbent}}$$

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Ed values in Table 9 show that atrazine is adsorbed on the Sharpsburg topsoil more readily than any other combination. Greater adsorption occurred when low concentrations of herbicides were present. Alachlor and butylate

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were also adsorbed to a considerable degree. Pinalom showed relatively little adsorption to any of the soils used. Much less adsorption occurred in the Jensen gravelly sand (subsoil) than in the other two soils which were both topsoils. Data in Table 6 reflects large differences in the clay and organic matter between the topsoils and subsoil.

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Table 9. Kd values showing relative adsorption of four herbicides at four different concentrations on three different soil types.

HERBICIDE	SOIL TYPE	CONCENTRATION (PPM)			
		1	2	3	10
Atrazine	Sharpsburg silty clay loam	11.40	2.40	2.40	2.00
	Jackson sandy loam	9.70	2.20	1.90	1.40
	Jackson gravelly sand	1.00	0.00	0.00	0.04
Alachlor	Sharpsburg silty clay loam	4.31	4.07	2.32	2.00
	Jackson sandy loam	3.15	3.20	2.76	2.40
	Jackson gravelly sand	0.74	0.94	0.70	0.78
Dactylate	Sharpsburg silty clay loam	3.13	3.06	4.90	4.83
	Jackson sandy loam	4.26	4.28	4.11	3.84
	Jackson gravelly sand	1.38	1.49	1.31	1.06
Picloram	Sharpsburg silty clay loam	1.15	1.22	1.24	1.07
	Jackson sandy loam	0.74	0.91	0.89	0.83
	Jackson gravelly sand	0.00	0.00	0.16	0.23

$$K_d = \frac{\text{mg adsorbed} - \text{mg available in solution}}{\text{mg available in solution}} = \frac{\text{mg adsorbed}}{\text{mg available in solution}}$$

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8. Leaching Studies with Atrazine, Alachlor, Butylate and Picloram.

Glass leaching columns were used to evaluate the relative mobility of atrazine, alachlor, butylate, and picloram under laboratory conditions. Topsoils of a Sharpsburg silty clay loam and a Jansen sandy loam, and a Jansen gravelly sand subsoil were used in this study. The glass columns (60 mm diameter x 240 mm length) were packed with 20 cm of soil to an average bulk density of 1.15, 1.34, and 1.57 g/cm³ for the Sharpsburg, Jansen sandy loam and Jansen gravelly sand respectively. Soils for the columns were at 2/3 field capacity moisture content before being packed into the columns.

Herbicides containing a ¹⁴C-label were added to soil in the top 1/2 inch of each column. The 1 ppm concentration contained 90,000 dpm.

Distilled water was then leached through the columns (approximately 4-field capacities or 25 cm) at a rate of 0.3 cm/hr. The leachate was collected with a fraction collector at 90 minute intervals and assayed with a liquid scintillation spectrometer. After leaching, the soil in the column was sectioned into 1 cm intervals and assayed for ¹⁴C-material.

Data in Table 18 show that Sharpsburg topsoil retains the majority of atrazine, alachlor and butylate in the upper half of the soil column as the water passes through. The Jansen topsoil was considerably more adsorptive than the deeper gravelly subsoil. Picloram was very mobile in all soils with most of the ¹⁴C appearing in the leachate. All herbicides moved readily through the Jansen gravelly sand.

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A comparison of these Kd and leaching studies is encouraging. The Kd studies indicate that atrazine is adsorbed to a greater extent than the other compounds. Leaching studies show those herbicides which are not readily adsorbed move readily through the soil column. Thus it appears that Kd studies can be used as guides in predicting the mobility of herbicides in the field.

The extreme mobility of picloram under these experimental conditions confirm current recommendations for disallowing its use in cropland areas.

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