

SIMAZINE ADDENDUM

Final Report

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

Contract No. 68-01-6679

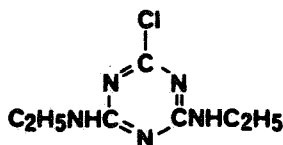
MARCH 13, 1985

Submitted to:
Environmental Protection Agency
Arlington, VA 22202

Submitted by:
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SIMAZINE

SIMAZINE, AQUAZINE, CEKUSAN, FARMCO SIMAZINE, FRAMED, GESATOP, PRINCIP, PRIMATOL S, SIMADEx, SIMANEX, SIM-TROL.



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

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- 3 Warren, J. 1984a. Determination of adsorption/desorption constants of ^{14}C simazine. (No MRID).
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- 6 Warren J. 1984c. Leaching characteristics of aged simazine; Final report #31831. (No MRID)
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- 8 Roux Associates, Inc. 1984a. Sensitivity analysis of areas where simazine has been reported in ground water. (No MRID)
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CASE GS0070 SIMAZINE STUDY 1 PM 04/07/82

CHEM 080807 Simazine

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Bowman, B.R. 1984. Determination of the photolysis rate constants and degradation products of simazine. Unpublished study received Oct. 17, 1984 under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255085.

SUBST. CLASS =

DIRECT RVW TIME = 5 1/2 (MH) START-DATE END DATE

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
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CONCLUSIONS:Degradation - Photodegradation in Water

1. This study is scientifically valid.
2. [^{14}C]Simazine, at 1.12 ppm, was relatively stable to photolysis in unbuffered deionized water (initial pH unspecified), with ~88% of the applied radioactivity remaining as parent after 30 days of irradiation under a mercury-vapor lamp. In a 1% acetone solution, [^{14}C]simazine degraded with a half-life of 12-24 hours. 2-Chloro-4-ethylamino-6-amino-1,3,5-triazine was the major degradate formed, accounting for ~80% of the applied radioactivity after 30 days of irradiation. 
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the temperature was unspecified, the purity of the test substance was not reported, the experiment was not conducted in buffered solutions, and the artificial light source was not related to natural sunlight irradiation.

MATERIALS AND METHODS:

Deionized water, containing 0 or 1% acetone, was treated with [^{14}C]simazine (specific activity 32.2 $\mu\text{Ci}/\text{mg}$, purity unspecified, Ciba-Geigy Corporation), at 1.12 ppm, and 9-ml aliquots were irradiated using a 450-W Ace-Hanovia mercury-vapor lamp (Table 1). Wavelengths $<340\text{ nm}$ were filtered out, and the temperature did not exceed 35 C. Additional samples, with and without acetone, were maintained in darkness. Samples were taken immediately after treatment, and at intervals up to 30 days after treatment.

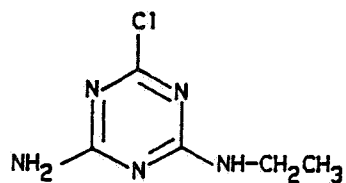
Samples were extracted three times with methylene chloride, and the extracts were combined and concentrated. Aliquots of the concentrated extract and aqueous phase were quantified using LSC. Additional aliquots of the organic phase were spotted onto silica gel TLC plates along with known standards. TLC plates were developed using toluene:acetic acid:ethanol: H_2O (100:100:30:10) and autoradiographed. Radioactive areas were scraped from the plates, and quantified using LSC. Recovery values and detection limits were not reported.

REPORTED RESULTS:

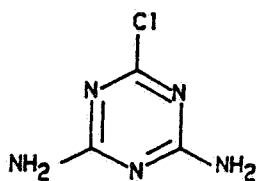
[^{14}C]Simazine degraded with a half-life of 12-24 hours in the sensitized, irradiated solution, >21 days in the sensitized dark control, and >30 days in nonsensitized solutions (Table 2). Half-lives calculated using first-order kinetics were 16 hours and 1323 days for the sensitized and nonsensitized irradiated solutions, respectively. G 28279 (structure shown in Figure 1) was the only degradate found at $>0.1\%$ of the applied radioactivity in the nonsensitized solutions and in the sensitized dark control (maximum of 11% of the applied radioactivity). This was the major degradate formed in the sensitized irradiated solution, accounting for $\sim 80\%$ of the applied radioactivity after 98 hours of irradiation. Three other degradates were identified in this solution, each comprising $\leq 5.6\%$ of the applied radioactivity. Total radioactivity in sensitized and nonsensitized water samples is shown in Table 3.

DISCUSSIONS:

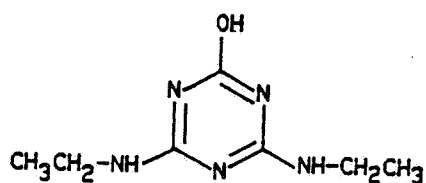
1. The incubation temperature was reported not to have exceeded 35 C, but was not specified.
2. The deionized water used was not buffered, and the initial pH was not reported.
3. Recovery values and detection limits were not provided.
4. The purity of the test substance was not reported.

G-28279

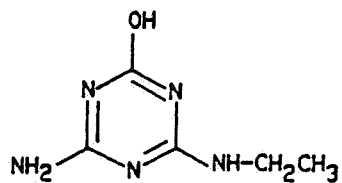
2-chloro-4-ethylamino-6-amino-1,3,5-triazine

G-28273

2-chloro-4,6-bis(amino)-1,3,5-triazine

G-30414

2-hydroxy-4,6-bis(ethylamino)-1,3,5-triazine

GS-17792

2-hydroxy-4-ethylamino-6-amino-1,3,5-triazine

Figure 1. Structures of simazine degradates.

Table 1. Spectral energy of the light source.

λ	Radiated energy of lamp (W)	Intensity ($\mu\text{W}/\text{cm}^2$)		
		50 cm	100 cm	9.2 cm
5780	20.0	768	217	1468
5461	24.5	941	266	1802
4358	20.2	776	220	1489
4045	11.0	422	120	798

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Table 2. Distribution of radioactivity (% of applied) in duplicate samples of sensitized and nonsensitized deionized water treated with [^{14}C]simazine, at 1.12 ppm, and irradiated or maintained in darkness for up to 30 days.

Sampling interval	Simazine	G 28279 ^a	G 28273	Unknown	G 30414	GS 17792
<u>Sensitized - Dark Control</u>						
0 days	110.2	1.7	--	--	--	0.1
	131.9	1.8	--	--	--	0.1
1 day	117.5	1.6	--	--	--	--
	113.0	1.6	--	--	--	--
3 days	106.4	1.5	--	--	--	--
	100.9	1.2	--	--	--	--
7 days	102.3	1.7	--	--	--	--
	108.9	1.5	--	--	--	--
14 days	95.5	1.3	--	--	--	--
	93.9	1.4	--	--	--	--
21 days	95.8	1.3	--	--	--	--
	95.5	1.0	--	--	--	--
<u>Sensitized - Irradiated</u>						
0 hours	112.4	3.3	0.2	0.2	0.1	0.1
	108.2	2.8	0.2	0.2	0.1	0.1
4 hours	86.8	13.2	--	--	0.1	--
	92.9	12.4	--	--	0.1	--
12 hours	68.9	37.4	0.6	0.4	0.2	--
	67.7	35.8	0.6	0.5	0.3	--
24 hours	49.1	48.0	1.3	1.1	2.3	--
	46.8	44.9	1.2	1.0	2.2	--
48 hours	35.0	63.6	2.6	2.0	2.7	0.5
	36.8	65.2	2.3	1.5	3.2	0.7
98 hours	24.8	82.1	5.6	3.0	4.1	0.9
	26.4	77.8	4.8	2.4	3.3	0.7

Table continued on Page 6.

Table 2 Continued.

Sampling interval	Simazine	G 28279 ^a	G 28273	Unknown	G 30414	GS 17792
<u>Nonsensitized - Dark Control</u>						
0 days	99.2	1.5	--	--	--	--
	96.7	1.5	--	--	--	--
1 day	120.5	2.2	--	--	--	--
	106.6	2.0	--	--	--	--
3 days	111.8	2.0	--	--	--	--
	119.9	2.1	--	--	--	--
7 days	100.4	1.6	--	--	--	--
	116.4	2.0	--	--	--	--
14 days	105.6	1.6	--	--	--	--
	97.1	1.5	--	--	--	--
30 days	96.5	1.6	--	--	--	--
	98.1	1.6	--	--	--	--
<u>Nonsensitized - Irradiated</u>						
0 days	99.1	1.4	--	--	--	--
	101.9	1.5	--	--	--	--
1 day	94.9	2.6	--	--	--	--
	99.8	2.7	--	--	--	--
3 days	106.1	4.2	--	--	--	--
	113.4	4.9	--	--	--	--
7 days	117.9	8.0	--	--	--	--
	104.1	5.9	--	--	--	--
14 days	107.4	10.8	--	--	--	--
	91.3	9.3	--	--	--	--
30 days	88.5	11.0	--	--	--	--
	86.8	10.6	--	--	--	--

^a Structures of degradates shown in Figure 1.

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Table 3. Total radioactivity (ppm) in sensitized and nonsensitized deionized water treated with [^{14}C]simazine, at 1.12 ppm, and irradiated or maintained in darkness for up to 30 days.^a

Sampling interval	Irradiated				Dark Control			
	Sensitized ^b		Nonsensitized		Sensitized ^b		Nonsensitized	
	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase	Organic phase	Aqueous phase
0 hours	0.99	0.001	0.95	0.02	0.92	0.001	0.92	0.002
4 hours	0.93	0.013	-- ^c	--	--	--	--	--
12 hours	0.86	0.070	--	--	--	--	--	--
24 hours	0.72	0.15	0.87	0.010	0.85	0.005	0.89	0.006
48 hours	0.78	0.21	--	--	--	--	--	--
72 hours	--	--	0.88	0.014	0.95	0.007	0.93	0.007
98 hours	0.61	0.31	--	--	--	--	--	--
7 days	--	--	0.79	0.021	1.02	0.008	0.85	0.007
14 days	--	--	0.96	0.031	1.02	0.008	0.94	0.008
21 days	--	--	0.96	0.043	1.04	0.009	--	--
30 days	--	--	--	--	--	--	0.94	0.007

^a Values are averages of duplicate samples.

^b 1% Acetone.

^c Not sampled.

CASE GS0070

SIMAZINE

STUDY 2

PM 04/07/82

CHEM 080807

Simazine

BRANCH EFB

DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID

CONTENT CAT 01

Burkhard, N. 1978. Photolysis of simazine (Gesatop) on soil surfaces under artificial sunlight conditions; Project report 54/78. Unpublished study received Oct. 17, 1984 under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255085.

SUBST. CLASS = S.

DIRECT RVW TIME = 7

(MH) START-DATE

END DATE

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CONCLUSION:Degradation - Photodegradation on Soil

This study is scientifically invalid because the sampling protocol was inadequate (one sampling interval) to accurately establish the pattern of decline of simazine and patterns of formation and decline of degradates on irradiated soil. In addition, this study would not meet EPA Data Requirements for Registering Pesticides (1983) because the test substance was not completely characterized, and the test soil was not demonstrated to be representative of soils in the United States.

MATERIALS AND METHODS:

Les Evouettes loam soil (38.4% sand, 49.4% silt, 12.2% clay, 3.6% organic matter, pH 6.1) was treated with ring-labeled [^{14}C]simazine (Gesatop, specific activity 15.05 uCi/mg, purity and source unspecified) at 10 ppm. Samples were mixed, or adjusted to 12% moisture and mixed, then placed in metal boxes (0.6- to 0.7-cm depth). The samples were maintained at $45 \pm 5^\circ\text{C}$ at a distance ~ 23 cm below the light source (xenon lamp, 940 ± 50 J/m 2 /s) for 24 hours (one hour of exposure to this light source was determined, by measurement, to be equivalent to ~ 2 hours of natural sunlight). Wavelengths < 290 nm were filtered out. Additional treated samples were maintained in darkness as controls.

Samples taken at 0 and 24 hours were extracted with acetone and methanol in a Soxhlet apparatus. The acetone extracts were analyzed by GC. Methanol extracts were spotted onto silica gel TLC plates which were developed two-dimensionally, using ethyl acetate for the first development, and toluene:acetic acid:ethanol:water (50:50:15:5) for the second development. Radioactive areas were quantified using LSC.

REPORTED RESULTS:

For irradiated and nonirradiated samples of moist and dry soil, recoveries ranged from 100.5 to 102.1% of the applied radioactivity (Table 1). The recovery of parent compound and one degradate after irradiation for 24 hours is shown in Table 2.

DISCUSSION:

1. The duration of the study was not sufficient to establish the half-life of simazine. In addition, there was only one sampling interval (24 hours).
2. The CEC of the test soil was not reported.
3. The purity of the test substance was not specified.
4. The test soil, reported to be a silty loam, is a loam according to the USDA soil textural classification system. In addition, the source of the test soil was Switzerland, and it was not demonstrated to be representative of soils in the United States.
5. The soil samples exposed to light were maintained at $45 \pm 5^\circ\text{C}$, which is outside the range of most environmental conditions. The temperature at which the dark controls were maintained was not specified.

Table 1. Total radioactivity (% of applied) in irradiated and dark control soil samples.

Sample	Sampling interval (hours)	<u>Extractable</u>		Unextractable	Total
		Acetone	Methanol		
<u>Dry soil</u>					
Irradiated	0	93.1	4.6	4.3	102.0
	24	76.7	12.0	11.8	100.50
Nonirradiated	24	84.6	8.0	8.5	101.10
<u>Moist soil^a</u>					
Irradiated	0	93.1	4.6	4.4	102.1
	24	61.5	17.1	22.2	100.8
Nonirradiated	24	69.1	15.0	17.4	101.50

^a The soil moisture was adjusted to 12%.

Table 2. Recovery of simazine and G-30414^a (% of applied) from soil treated at 10 ppm and irradiated or maintained in the dark for 24 hours.

Sample	Sampling interval (hours)	Simazine	G-30414
<u>Dry soil</u>			
Irradiated	0	93.1	ND ^b
	24	90.9	3.1
Nonirradiated	24	81.7	5.7
<u>Moist soil^c</u>			
Irradiated	0	93.1	ND
	24	71.9	3.5
Nonirradiated	24	62.0	4.7

^a 2-Hydroxy-4,6-bis(ethylamino)-1,3,5-triazine (structure shown in Study 1).

^b Not detected; detection limit is 1.0% of the applied radioactivity.

^c The soil moisture was adjusted to 12%

CASE GS0070 SIMAZINE STUDY 3 PM 04/07/82

CHEM 080807 Simazine

BRANCH EFB DISC

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01
Warren, J. 1984a. Determination of adsorption/desorption constants of ¹⁴C simazine.
Unpublished study received Oct. 17, 1984, under 100-541; submitted by Ciba-Geigy
Corporation, Greensboro, NC. Accession No. 255085.

SUBST. CLASS = S.

DIRECT RVW TIME = 6 1/2 (MH) START-DATE END DATE

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CONCLUSIONS:

Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Simazine adsorption increased directly with soil organic matter content and CEC. Freundlich K values ranged from 4.66 for loam (2.9% organic matter, CEC 20.6 meq/100 g) to 0.36 for the loamy sand (0.3% organic matter CEC 5.9 meq/100 g). Desorption K values were consistently higher than those for adsorption indicating that the adsorption process was not completely reversible. As the soil organic matter and CEC values decreased, the adsorption decreased and desorption increased.
3. This study partially fulfills EPA Data Requirements for Registering Pesticides (1983) by providing information on the mobility of simazine (unaged) in two loam and two loamy sand soils.

MATERIALS AND METHODS:

One gram samples (sieved to <1 mm) of four sterilized soils (Table 1) were added to aqueous solutions of ring-labeled [^{14}C]simazine (specific activity 32.2 $\mu\text{Ci}/\text{mg}$, purity unspecified, source unspecified) at 0.074, 0.37, 0.74, and 1.24 ppm. The resulting suspensions were shaken in darkness for 48 hours, centrifuged, filtered, and analyzed by LSC. A volume of distilled water equal to the volume of filtrate collected, was added to each sample, after which they were shaken, in darkness, for 72 hours. The samples were centrifuged, filtered, and aliquots of the filtrate were analyzed by LSC.

REPORTED RESULTS:

Freundlich K values ranged from 4.66 for the Iowa-3 loam (2.9% organic matter, CEC 20.6 meq/100 g) to 0.366 for the Missouri loamy sand (0.3% organic matter, CEC 59 meq/100 g) indicating a significant correlation between organic matter content and CEC and adsorption of simazine by soils (Table 2). Desorption K values were consistently higher (from 17.1 for the Iowa-3 loam to 1.12 for the Missouri loamy soil) than those for adsorption indicating that the adsorption process was increasingly irreversible as the CEC and organic matter content increased.

DISCUSSION:

The purity of the test substance was not reported.

Table 1. Soil characteristics.

Soil type	pH	Organic matter	Sand	Silt	Clay	CEC (meq/100 g)
		<u> </u>	<u>%</u>	<u> </u>	<u> </u>	
Iowa-3 loam	6.1	2.9	49.6	33.2	17.2	20.6
New York loam	5.4	1.9	50.8	36.0	13.2	11.2
Iowa-1 loamy sand	6.6	1.6	83.6	9.2	7.2	7.6
Missouri loamy sand	7.8	0.3	83.6	9.2	7.2	5.9

Table 2. Freundlich K and 1/n values for the adsorption and desorption of simazine on four soils.

Soil	K _d	1/n
<u>Adsorption</u>		
Iowa-3 loam	4.66	0.75
New York loam	1.42	0.88
Iowa-1 loamy sand	1.13	0.787
Missouri loamy sand	0.366	0.78
<u>Desorption</u>		
Iowa-3 loam	17.1	0.88
New York loam	6.17	0.95
Iowa-1 loamy sand	5.12	0.90
Missouri loamy sand	1.12	0.81

CASE GS0070 SIMAZINE STUDY 4 PM 04/07/82

CHEM 080807 Simazine

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Warren, J. 1984b. Leaching characteristics of parent simazine. Unpublished study received Oct. 17, 1984, under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255085.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 (MH) START-DATE END DATE

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CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. [¹⁴C]Simazine was moderately to very mobile in four soils; after leaching 12-inch soil columns with 20 inches of water, 57.5, 12.8, 10.6, and 3.5% of the applied radioactivity remained in the top 2 cm of Iowa-3 loam, New York loam, Iowa-1 loam, and Missouri loamy sand soil columns, respectively. Recovery of radioactivity in the leachate ranged from <0.01% of the applied (Iowa-3 loam) to 85.2% (Missouri loamy sand).
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the test substance was not completely characterized, and K_d values were not reported.

MATERIALS AND METHODS:

Four test soils (Table 1) were air dried and sieved through a 20 mesh screen. Subsamples of each soil were treated with [^{14}C]simazine (label position(s) not specified, specific activity 32.2 $\mu\text{Ci}/\text{mg}$, purity unspecified, Ciba-Geigy Corp.) at 10 ppm. Soil columns (3-inch inside diameter, 24-inch length) were filled with test soil to 12 inches and the soil moisture adjusted to field capacity. A uniform layer of [^{14}C]simazine treated soil (~10.0 g) was placed in the columns and covered with a 10 g layer of untreated soil. Each column was leached with 20 inches (~50 cm) of deionized water at 1.0-inch (2.5 cm)/hour.

The leachate from each column was collected and analyzed by LSC. The soil columns were divided into 12 segments, with each segment being analyzed for radioactivity by combustion and radioanalysis.

REPORTED RESULTS:

[^{14}C]Simazine was very mobile in the Missouri loamy sand, and moderately mobile in the Iowa-1 loamy sand and New York loam, and Iowa-3 loam soil. Recovery in the leachate of radioactivity applied to the columns ranged from >85% for the Missouri loamy sand to <0.01% for the Iowa loam (Table 2).

Mobility and distribution of the [^{14}C]simazine residues in the soil columns correlated with the organic matter content of the soils. In the Iowa-3 soil (2.9% organic matter) >42% of the applied radioactivity was recovered in the top 1-inch segment while in the New York, Iowa-1, and Missouri soils the radioactivity was distributed throughout the column (Table 3).

DISCUSSION:

1. The test substance was not completely characterized.
2. Values of soil/water relationships (K_d) were not reported.

Table 1. Soil characteristics.

Soil type	pH	Organic matter	Sand	Silt	Clay	CEC (meq/100 g)
		<hr/>	% <hr/>			
Iowa-3 loam	6.1	2.9	49.6	33.2	17.2	20.6
New York loam	5.4	1.9	50.8	36.0	13.2	11.2
Iowa-1 loamy sand	6.6	1.6	83.6	9.2	7.2	7.6
Missouri loamy sand	7.8	0.3	83.6	9.2	7.2	5.9

Table 2. Radioactivity (% of applied) recovered in the leachate from soil columns treated with [^{14}C]simazine at 10 ppm.

Soil	Radioactivity
Iowa-3 loam	<0.01
New York loam	20.1
Iowa-1 loamy sand	16.8
Missouri loamy sand	85.2

Table 3. Distribution of radioactivity (% of applied) in soil column segments after treatment at 10 ppm and leaching with 20 inches of water.

Soil segment (inches)	Iowa-3 loam	New York loam	Iowa-1 loamy sand	Missouri loamy sand
0-1	38.6	7.0	8.2	2.4
1-2	18.9	5.8	2.4	1.1
2-3	12.3	4.8	2.2	1.5
3-4	5.5	5.7	2.7	1.8
4-5	4.2	6.3	5.7	1.5
5-6	3.7	7.5	6.0	1.3
6-7	2.8	6.0	6.4	1.3
7-8	2.0	7.0	7.1	1.4
8-9	1.2	6.4	9.3	1.6
9-10	1.2	7.1	7.9	1.9
10-11	0.2	6.2	7.2	2.5
11-12	0.04	5.4	6.9	3.6

CASE GS0070

SIMAZINE

STUDY 5

PM 04/07/82

CHEM 080807

Simazine

BRANCH EFB

DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID

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SUBST. CLASS = S.

DIRECT RVW TIME = 5 1/2 (MH) START-DATE

END DATE

REVIEWED BY: G. Moore

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CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Aged (30 days) residues of simazine were mobile in sand leached with 0.5 inches of water for 45 days. In the leachate, ~42% of the applied radioactivity was recovered, with ~28% being parent compound and 3.7% being 2-chloro-4-ethyl-amino-6-amino-1,3,5-triazine. In silt loam soil leached similarly, 8.7% of the applied radioactivity was recovered in the leachate, of which 6.6% was parent simazine and 0.8% was 2-chloro-4-ethylamino-6-amino-1,3,5-triazine.
3. This study would not fulfill EPA Data Requirements for Registering Pesticides (1983) because K_d values were not reported, radioactive residues in the soil columns were not characterized, and the test soils were not demonstrated to be representative of those in the United States.

MATERIALS AND METHODS:

Two test soils (Table 1) were treated with ring-labeled [^{14}C]simazine (Gesatop, >99% pure, specific activity 2.44 $\mu\text{Ci}/\text{mg}$, Ciba-Geigy Corp.) at 10 kg ai/ha. After adjusting the soil moisture to 50% of 0.33 bar with distilled water, the soils were aged in darkness for 30 days at $25 \pm 1^\circ\text{C}$. Volatiles were trapped during the aging period in gas adsorption bottles filled with ethylene glycol, 0.1 N sulfuric acid, and 2 N sodium hydroxide. Soil columns (40-cm length, 4-cm inside diameter) were filled to 28 cm with untreated soil. A 2-cm layer of treated, aged soil covered with a filter paper disc was placed on top of the column after which it was leached with 22.5 inches of water over 45 days.

Samples of the treated, aged soil were extracted with methanol:water (8:2). The soil column segments were extracted similarly, then additionally extracted with methanol in a Soxhlet apparatus for 4 hours. Aliquots of the extracts were quantified by LSC. In addition, the extracted soil samples were combusted to determine nonextractable radioactivity. Leachate samples were extracted with methylene chloride followed by ethyl acetate. The extracts were developed on silica gel TLC plates with ethyl acetate and chloroform:methanol:formic acid:water (80:15:4:2). The detection limit was 0.1% of the applied radioactivity.

REPORTED RESULTS:

From the Collombey sand and the Les Evouettes silt loam soil, 99.7 and 102% of the applied radioactivity was recovered by combustion of unleached, treated, aged samples (Table 2). Of the radioactivity recovered ~87% was methanol extractable with ~10% being non-extractable.

After leaching the Collombey sand and Les Evouettes silt loam soil columns, 61.1 and 91.3% of the applied radioactivity, respectively was recovered in the soil (Table 3).

The extractable radioactivity in the Collombey sand leachate was identified by TLC as 28.5% of the applied (parent compound), 3.7% 2-chloro-4-ethylamino-6-amino-1,3,5-triazine (structure given in Study 1) and 1.22 unidentified compounds. The silt loam leachate had 6.6% parent simazine, 0.8% 2-chloro-4-ethylamino-6-amino-1,3,5-triazine, and 0.1% unidentified compounds. The distribution of the radioactivity in the various leachate samples collected is shown in Table 4.

DISCUSSION:

1. Values of soil/water relationships (K_d) were not presented.
2. The source of the test soils was Switzerland, and they were not demonstrated to be representative of soils in the United States.
3. Radioactive residues in the soil column were not characterized.

Table 1. Soil characteristics.

Soil type	pH	Organic matter	Sand	Silt	Clay	CEC (meq/100 g)
		%				
Collombey sand	7.8	2.2	87.0	10.2	2.8	14.0
Les Evouettes silt loam	6.1	3.6	38.4	49.4	12.2	9.0

Table 2. Radioactivity recovered (% of applied) from [^{14}C]simazine treated, aged soil samples before leaching.

Soil type	Total ^a (by combustion)	Extractable	Nonextractable ^b	Volatiles/ CO_2
Collombey sand	99.7	87.1	9.8	5.2
Les Evouettes silt loam	102.0	88.0	11.1	1.2

^a Total radioactivity determined by combustion of unextracted samples.

^b Radioactivity determined by combustion of the extracted sample.

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Table 3. Distribution of radioactivity (% of applied) in leached soil columns treated with [^{14}C]simazine.

Soil layer (cm)	Collombey sand			Les Evouettes silt loam		
	Extractable	Nonextractable	Total	Extractable	Nonextractable	Total
0-2	2.1	7.9	10.0	1.6	9.8	11.4
2-4	0.8	1.9	2.7	1.1	3.9	5.0
4-6	0.9	1.4	2.9	1.6	4.0	5.6
6-8	1.1	1.4	2.5	1.9	3.6	5.5
8-10	1.2	1.4	2.6	2.2	4.6	6.8
10-12	1.2	1.4	2.6	2.2	3.5	5.7
12-14	1.4	1.3	2.7	2.6	3.8	6.4
14-16	1.7	1.3	3.0	3.0	3.8	6.8
16-18	2.1	1.5	3.6	3.1	3.3	6.4
18-20	2.5	2.2	4.7	3.5	2.5	6.0
20-22	2.7	2.0	4.7	3.2	1.8	5.0
22-24	2.8	2.2	5.0	4.1	1.7	5.8
24-26	2.9	2.0	4.9	3.6	1.3	4.9
26-28	2.9	1.8	4.7	4.1	1.4	5.5
28-30	3.8	1.3	5.1	3.6	0.9	4.5
Total	30.1	31.0	61.1	41.4	49.9	91.3

Table 4. Distribution of radioactivity (% of applied)^a in leachate from soil columns treated with [¹⁴C]simazine.

Water applied (inches)	Collombey sand	Les Evouettes silt loam
0-5.0	ND ^b	ND
5.0-10.0	0.14	ND
10.0-15.0	1.29	ND
15.0-20.0	2.08	0.33
20.0-22.5	1.53	1.03
Total	5.04	1.36

^a Values represent the average recovery from 10 samples taken in 0.5-inch increments.

^b Not detected; detection limit is 0.1% of the applied radioactivity.

CASE GS0070 SIMAZINE STUDY 6 PM 04/07/82

CHEM 080807 Simazine

BRANCH EFB DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID CONTENT CAT 01

Warren J. 1984c. Leaching characteristics of aged simazine; Final report #31831. Unpublished study received Oct. 17, 1984, under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255085.

FICHE/MASTER ID No MRID CONTENT CAT 01

Warren J. 1985. Leaching characteristics of aged simazine (supplementary investigation for ABC Project No. 31831); Final report #32483. Unpublished study received Jan. 23, 1985 under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 256317.

SUBST. CLASS = S.

DIRECT RVW TIME = 10 (MH) START-DATE END DATE

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Two hardcopies were combined for this review because one (Report #32483) contains two additional replicates of the experiment performed in the other (Report #31831).

CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. The portion of the study pertaining to soil columns A, B, and C is scientifically invalid because the recovery of [^{14}C]simazine was too low (67, 67 and 57% for columns A, B, and C, respectively). The portion of the study pertaining to soil columns D and E is scientifically valid.
2. Aged (30-day) residues of [^{14}C]simazine were relatively mobile in loamy sand soil columns (12-inches high) leached with 20 inches of water over a 29 day period. Soil in the columns retained 43.9 to 47.4% of the applied radioactivity while ~52% was recovered in the leachate.

-2-

3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because simazine degradates in the soil column after leaching were not identified, K_d values were not reported, and the soil aging conditions were not reported.

MATERIALS AND METHODS:

Missouri loamy sand soil (83.6% sand, 9.2% silt, 7.2% clay, 0.3% organic matter, pH 7.8, CEC 5.9 meq/100 g) was treated with ring-labeled [^{14}C]simazine (specific activity 32.2 uCi/mg, purity unspecified, Ciba-Geigy Corp.) in acetone at 8.2 ppm, and aged for 30 days (incubation conditions such as light, temperature, soil moisture were not reported). Soil columns (24-inch length, 3-inch diameter) were filled to 12 inches with untreated soil and the soil moisture was adjusted to ~0.33 bar. A uniform (8 to 11-g) layer of aged treated soil was placed in each column and covered with a 10-g layer of untreated soil. The columns were leached with 20 inches of water over 29 days.

Aged and unaged, treated soil samples (unleached) were extracted three times with methanol:water (8:2), the supernatant was filtered, and aliquots were analyzed for radioactivity by LSC. The extract was concentrated and brought back to volume with water, after which the aqueous phase was extracted three times with methylene chloride. Aliquots of the organic and aqueous phase were analyzed by LSC. Additional aliquots were concentrated, developed on silica gel TLC plates with toluene:acetic acid:ethanol:water (10:10:3:1) and compared with known standards.

After leaching, the columns were segmented, and each segment was analyzed for total radioactivity by combustion and radioassay. Aliquots of the leachate samples were analyzed by LSC. The leachates were combined and extracted three times with methylene chloride and the organic and aqueous phases were analyzed by radioassay and TLC as previously described.

REPORTED RESULTS:

In treated soil samples, 104% (8.5 ppm) of the applied [^{14}C]simazine was recovered after aging for 30 days. Of the radioactivity detected, 87.1% was identified as parent simazine and 10.9% as the simazine degradate 2-chloro-4-ethylamino-6-amino-1,3,5-triazine (G-28279, structure shown in Study 1).

Recovery of radioactivity from columns A, B, and C was 67, 67 and 57% of applied, respectively (Table 1). The recovery of applied radioactivity from columns D and E was 95.9 and 98.9%, respectively. The leachate from both columns contained ~52% of the applied radioactivity of which 41.7% (column D) and 43.4% (column E) was identified as parent simazine. In column D, 6.1% of the applied radioactivity was identified as G-28279, while 5.6% was identified as this degradate in column E. The distributions of radioactivity detected in the soil column leachate is shown in Table 2.

DISCUSSION:

1. The test substance was not completely characterized (purity).
2. Values of soil/water relationships (K_d) were not reported.
3. No explanation was provided to account for the difference in recovery of applied radioactivity from columns A, B, and C (average of ~65%) and from columns D and E (average of ~98%).
4. Conditions under which the treated soil samples were aged (light, temperature, soil moisture, were not reported.
5. Simazine degradates remaining in the soil column were not identified after leaching.

-4-

Table 1. Radioactivity (% of applied) in leachate and soil from soil columns treated with [^{14}C]simazine.

Soil depth (inches)	Soil Column				
	A	B	C	D	E
0-1	1.6	1.5	12	7.2	4.9
1-2	17.0	0.99	1.1	1.4	1.9
2-3	0.76	0.73	0.79	1.8	2.4
3-4	1.2	1.0	0.87	2.5	2.9
4-5	1.0	2.0	0.90	3.6	3.3
5-6	0.80	1.8	1.1	3.6	3.6
6-7	0.98	6.0	1.5	3.5	3.8
7-8	1.5	2.8	1.7	3.4	4.0
8-9	2.2	2.6	2.4	4.4	5.3
9-10	3.6	3.4	2.1	3.9	5.4
10-11	2.6	3.7	2.9	3.4	4.4
11-12	3.2	3.9	5.7	5.2	5.5
Leachate	31.0	37.0	24.0	52.03	51.54
Total	67.44	67.42	52.06	95.93	98.94

-5-

Table 2. Radioactivity (% of applied) in leachate of [^{14}C]simazine treated soil columns.

Leachate (inches)	Soil Column	
	D	E
0-0.5	<0.01	<0.01
0.5-1.0	<0.01	<0.01
1.0-1.5	<0.01	<0.01
2.5-3.5	<0.01	<0.01
3.5-4.0	<0.01	0.03
4.0-4.5	0.04	0.09
4.5-5.0	0.09	0.14
5.0-6.0	0.14	0.16
6.0-7.0	0.36	0.30
7.0-7.5	0.32	0.20
7.5-8.0	0.19	0.12
8.0-8.5	0.25	0.18
8.5-9.5	0.34	0.22
9.5-10.5	1.6	1.3
10.5-11.0	2.6	2.3
11.0-11.5	1.7	1.6
11.5-12.0	1.9	1.8
12.0-13.0	2.2	2.0
13.0-14.0	5.4	5.4
14.0-14.5	5.6	5.6
14.5-15.0	2.8	3.0
15.0-15.5	2.8	2.8
15.5-16.5	2.7	2.8
16.5-17.5	5.5	5.6
17.5-18.0	4.8	4.9
18.0-18.5	2.3	2.3
18.5-19.0	2.2	2.3
19.0-20.0	2.0	2.0
	4.2	4.4
Total	52.03	51.54

CASE GS0070

SIMAZINE

STUDY 7

PM 04/07/82

CHEM 080807

Simazine

BRANCH EFB

DISC --

FORMULATION 00 - ACTIVE INGREDIENT

FICHE/MASTER ID No MRID

CONTENT CAT 01

Guth, J. A. 1983. Leaching characteristics of aged residues of ^{14}C -simazine (G-27692, Primatol) in two soils. Unpublished study received Oct. 17, 1984, under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255085.

SUBST. CLASS = S.

DIRECT RVW TIME = 7

(MH) START-DATE

END DATE

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CONCLUSIONS:Mobility - Leaching and Adsorption/Desorption

1. This study is scientifically valid.
2. Aged (294 days) residues of [^{14}C]simazine were slightly mobile in loamy sand and silt loam soils. Soil columns (11.8-inch height) leached with ~8 inches of water retained 67.2 and 65.7% of the applied radioactivity in the upper 4 inches (10 cm) of the loamy sand and silt loam soil, respectively.
3. This study does not fulfill EPA Data Requirements for Registering Pesticides (1983) because the soil columns were not eluted with a sufficient amount of water to fully assess simazine mobility in soil, K_d values were not presented, the test soils were not demonstrated to be representative of those in the United States, and the aging period for the treated soil samples was too long.

MATERIALS AND METHODS:

Two test soils (Table 1) were treated with ring-labeled [^{14}C]simazine (Primatol, >99% pure, specific activity 5.54 mCi/g, Ciba-Geigy Corp.) at 10.0 Kg ai/ha. Soil moisture was adjusted to 70% of 0.33 bar and the samples were incubated in darkness at 25 C for 294 days. Volatiles were trapped during the aging period in two gas washing bottles containing 2 N NaOH. Soil columns (40-cm length, 4-cm inside diameter) were filled to 28 cm with untreated soil. A 2-cm layer of treated, aged soil, covered with a filter paper disc, was placed on top of the column, after which it was leached with ~8 inches of water over 16 days.

Samples of the unleached, treated aged soil were extracted five times with methylene chloride, four times with methanol:water (8:2, v:v), and with methanol in a Soxhlet apparatus for 16 hours. Radioactivity in the extracts was quantified by LSC and characterized by TLC [developed on silica gel plates with ethyl acetate, toluene:acetone (85:15), and chloroform:methanol:formic acid:water (80:15:4:2)]. Unextractable radioactivity in the samples was determined by combustion. After segmenting the leached columns (2-cm segments) the soil samples were analyzed for extractable and unextractable radioactivity as previously described. Total radioactivity in the leachate from the columns was quantified by LSC, but degradates were not identified or quantified because of the low specific radioactivity of the samples.

REPORTED RESULTS:

After aging for 294 days, 97.5% (72.0% extractable, 20.3% nonextractable, 5.2% volatiles) of the applied radioactivity was recovered from the Collombey loamy sand. In the Les Evouettes silt loam, 97.4% (73.3% extractable, 23.4% nonextractable, 0.7% volatiles) of the applied radioactivity was recovered. In the Collombey loamy sand, 63.4% of the applied radioactivity was identified as parent compound, while in the Les Evouettes silt loam, 55.2% was parent simazine. Other degradates identified in the soils are shown in Table 2.

After leaching the soil columns, 92.0 and 94.0% of the applied radioactivity was recovered from the Collombey loamy sand and the Les Evouette silt loam, respectively. In the loamy sand, 67.2% of the applied was detected in the upper 10 cm of the column, while 65.7% was found in the silt loam soil (Table 3). Of the radioactivity recovered in the columns 48.9% was extractable, and 43.1% nonextractable in the loamy sand, and 39.6% extractable, and 54.4% nonextractable in the silt loam soil. Other degradates identified in the leached soil samples are shown in Table 4. Total radioactivity detected in the column leachate was 0.948 and 0.352% of the applied for the Collombey loamy sand and the Les Evouettes silt loam soils, respectively.

DISCUSSION:

1. The soil columns were not leached with a sufficient amount of water (~8 inches) to adequately assess simazine mobility in soils.
2. The source of the test soils was Switzerland, and they were not demonstrated to be representative of soils in the United States.
3. Values of soil/water (K_d) relationships were not provided.
4. The treated soil samples were aged for 294 days; samples should be aged for 30 days or one half-life (whichever is shorter).

Table 1. Soil characteristics.

Soil type	pH	Organic matter	Sand	Silt	Clay	CEC (meq/100 g)
		<u> </u>	<u> </u>	<u> </u>	<u> </u>	
		%	%			
Collombey loamy sand	7.1	3.28	79.9	14.9	5.2	12.1
Les Evouettes silt loam	5.6	3.10	10.4	71.6	18.0	11.0

Table 2. Distribution of radioactivity (% of applied) in aged soil samples treated with [^{14}C]simazine at 10 Kg/ha.

Compound	Collombey loamy sand	Les Evouettes silt loam
Simazine	63.4	55.2
G-28279 ^a	3.7	3.9
G-28516 ^b	NDC	ND
G-28273 ^d	1.1	0.7
G-30414 ^e	ND	11.0
GS-17792 ^f	ND	1.7
GS-177919	ND	0.8
Unknown	3.8	--

^a 2-Chloro-4-ethylamino-6-amino-1,3,5-triazine.

^b 2-Chloro-4-ethylamino-6-N-ethanolamine-1,3,5-triazine.

^c Not detected; detection limit is 0.1% of the applied radioactivity.

^d 2-Chloro-4,6-bis(amino)-1,3,5-triazine.

^e 2-Hydroxy-4,6-bis(ethylamino)-1,3,5-triazine.

^f 2-Hydroxy-4-ethylamino-6-amino-1,3,5-triazine.

^g 2-Hydroxy-4,6-diamino-1,3,5-triazine.

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Table 3. Distribution of radioactivity (% of applied) in leached soil columns treated with [^{14}C]simazine at 10 Kg/ha.

Soil layer (cm)	Collombey sand		Les Evouettes silt loam	
	Extractable	Nonextractable	Extractable	Nonextractable
0-2 ^a	17.6	28.1	2.5	26.9
2-4	4.0	3.2	3.1	3.9
4-6	2.6	1.5	3.8	4.5
6-8	3.8	1.8	5.3	4.6
8-10	3.2	1.4	6.1	5.0
10-12	2.8	1.6	5.8	3.2
12-14	2.5	1.0	5.2	2.3
14-16	2.2	0.9	3.9	1.6
16-18	2.1	0.9	2.0	1.1
18-20	2.1	0.7	0.7	0.5
20-22	2.1	0.6	0.4	0.3
22-24	1.4	0.4	0.3	0.2
24-26	1.0	0.3	0.2	0.1
26-28	0.8	0.3	0.2	0.1
28-30	0.7	0.4	0.1	0.1
Total	48.9	43.1	39.6	54.4

^a Treated segment.

Table 4. Distribution of radioactivity (% of applied) in leached soil columns treated with [^{14}C]simazine at 10 Kg/ha.

Compound ^a	Collombey loamy sand	Les Evouettes silt loan
Simazine	42.6	21.7
G-28279	4.1	4.6
G-28516	ND ^b	0.2
G-28273	1.1	1.1
G-30414	1.1	9.3
GS-17792	ND	2.3
Unknown	ND	0.4

^a Degradates identified in Table 2.

^b Not detected; detection limit is 0.1% of the applied radioactivity.

CASE GS0070

SIMAZINE

STUDY 8

PM PM# 04/07/82

CHEM 080807

Simazine

BRANCH EFB

DISC --

FORMULATION 90 - FORMULATION NOT IDENTIFIED

FICHE/MASTER ID No MRID

CONTENT CAT 02

Roux Associates, Inc. 1984a. Sensitivity analysis of areas where simazine has been reported in ground water. Unpublished study received Dec. 5, 1984 under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255834.

FICHE/MASTER ID No MRID

CONTENT CAT 02

Roux Associates, Inc. -1984b. Survey of activities in selected states regarding monitoring for pesticides in ground water. Unpublished study received Dec. 5, 1984 under 100-541; submitted by Ciba-Geigy Corporation, Greensboro, NC. Accession No. 255833.

SUBST. CLASS = S.

DIRECT RVW TIME = 5 1/2 (MH) START-DATE

END DATE

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Two hardcopies were combined for this review because they both pertained to the same pesticide monitoring survey.

CONCLUSION:Exposure - Groundwater

This study cannot be validated because the sampling protocols and analytical methods were not reported.

MATERIALS AND METHODS:

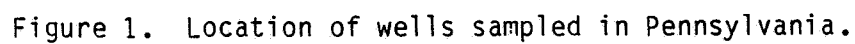
Twenty-one states were surveyed during September, 1984, to determine the nature and extent of groundwater monitoring for pesticides. A summary of the groundwater programs identified is shown in Table 1. Based on the results of the telephone survey, results of analyses for simazine in groundwater samples were provided for California, Maryland, and Pennsylvania. Twenty-eight wells were sampled in Maryland, and 84 were sampled in Pennsylvania; sampling locations for these states are shown in Figures 1 and 2. In California, 217 wells were sampled, of which 166 were located in the San Joaquin Valley (exact sampling locations not provided). The analytical methods were not reported.

REPORTED RESULTS:

Simazine was found at 0.5-3.5 ppb in 5 of 217 wells sampled in California, and at 0.1 ppb in one of 28 wells sampled in Maryland. Simazine concentrations in groundwater samples from Pennsylvania are shown in Table 2.

DISCUSSION:

1. Information on simazine concentrations in California groundwater was reported to have been obtained from a published report issued by the U.S. Office of Pesticide Programs entitled "Potential for Pesticide Contamination of Ground-Water Resulting from Agricultural Uses". Data for simazine in Maryland and Pennsylvania were generated by the U.S. Geological Survey, and were provided in the following reports: "Results of Maryland Ground-Water Pesticide Reconnaissance, Fall 1983", U.S. Geological Survey, Water Resources Division, Towson, Maryland, January, 1984; and "Water Resources Data, Pennsylvania, Water Year 1983, Volume 2. Susquehanna and Potomac River Basins", by J.W. Buchanan, W.C. Loper, W.P. Schaffstall, and R.A. Hainly, U.S. Geological Survey Water-Data Report PA-83-2.
2. The sampling protocols and analytical methods were not reported for any location.
3. Exact sampling locations were not provided for California, and the data were presented only as a range. All of the sampling locations shown in Table 2 (Pennsylvania) were not identified on the site map (Figure 1); this discrepancy was not explained.



-4-

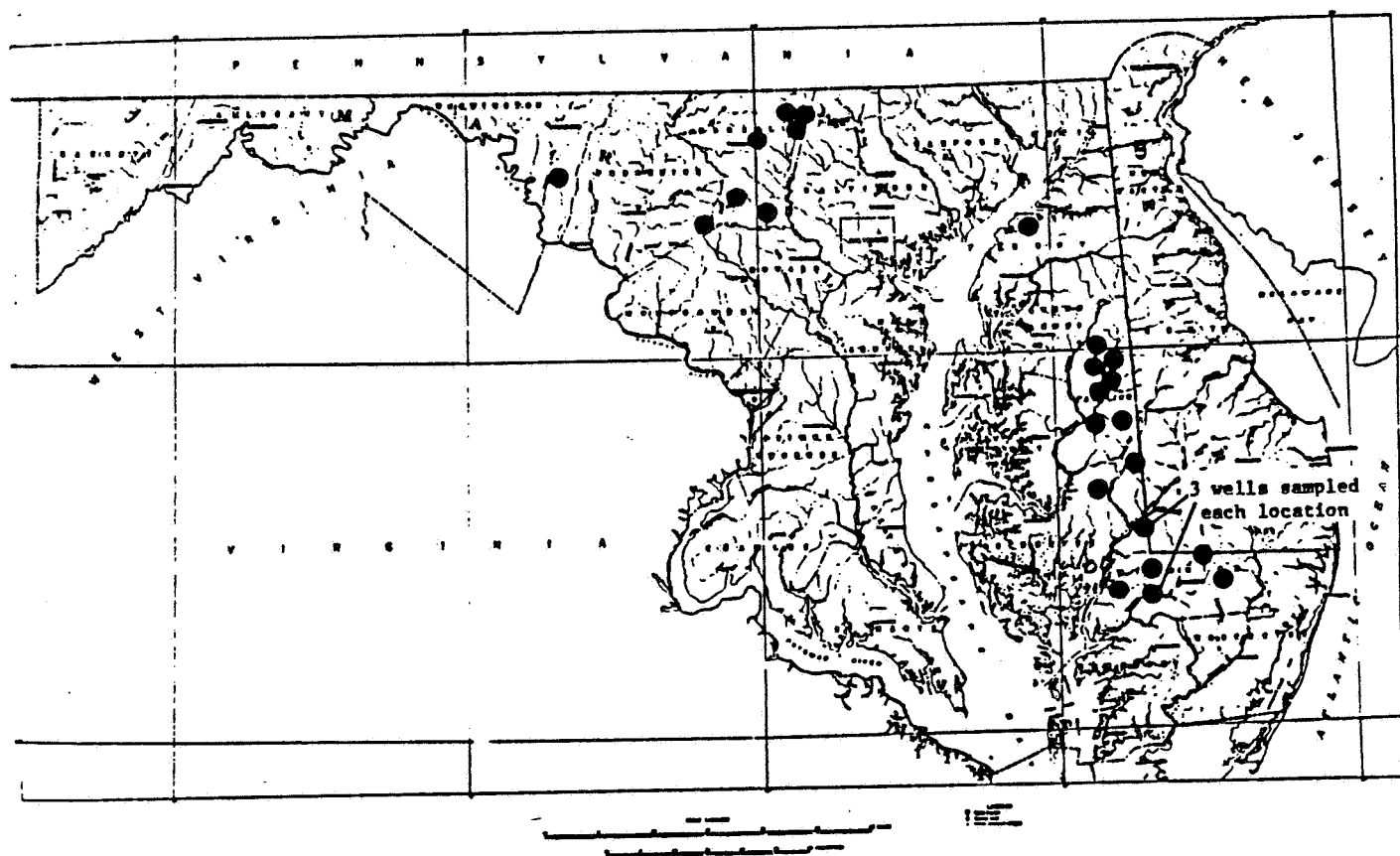


Figure 2. Location of wells sampled in Maryland.

Table 1. State summary of ground water programs.

State	Ground-water monitoring programs	Monitoring programs that include pesticides	Pesticides identified in ground-water	Simazine identified in ground water	Reports or data available
California	X	X	Temik, Telon, Others	X	X
Delaware	X	X	Simazine, Others		-- ^a
Florida	X	X	Temik, Atrazine		X
Idaho	X	-- ^b	Temik, EDB, Others		
			DDT, Lindane, Others		
			Toxaphene		
Illinois	X				
Indiana	-- ^b				
Kentucky					
Maryland	X	X	Simazine, Atrazine, Others	X	
Michigan	X				
New Jersey	X	X	Temik, Others		X
New York	X	X	Temik, Carbofuran		X
			Others		
North Carolina	X				
Ohio	X	-- ^b			
Oregon	-- ^b				
Pennsylvania	X	X	Simazine, Propazine, Others	X	X
			Atrazine		
South Carolina	X	-- ^b	DBCP, EDB		
Texas	X		Cotton defoliant		X
Utah	X				
Virginia	X				
Washington	X	X	Chlordane		
			Picloram, EDB		X
			Tordon		
West Virginia	X	-- ^b	Chlordane		

^a Not available at time of reporting (October, 1984).^b Planned programs.

Table 2. Simazine concentrations (ppb) in groundwater samples from Pennsylvania.

Sampling date	Sampling location	Depth below land surface (feet)	Depth of well (feet)	Simazine
3/2/83	1651	69.79	105	0.30
3/3/83	1643	36.50	100	0.40
7/13/83	1643	37.27	100	0.20
3/1/83	1650	73.68	125	0.20
3/2/83	1646	72.43	125	0.30
4/27/83	1646	69.94	125	0.50
5/24/83	1646	72.02	125	0.20
7/13/83	1646	72.80	125	0.20
3/2/83	1649	36.14	85	0.20
3/3/83	1645	51.73	80	0.50
6/27/83	1550	--	--	0.21
6/27/83	1551	--	--	1.10
3/21/83	1552	--	--	0.20
3/23/83	1562	--	--	1.60
6/29/83	1562	--	--	0.59
3/22/83	1580	--	--	0.20
3/21/83	1640	--	--	0.31
6/29/83	1640	--	--	3.40