Shaughnessy No. 080803

Date Out of EAB: 1/29/88

FROM: Patrick W. Holden, Team Leader
Ground Water Team
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

TO: Robert J. Taylor, PM 25
Fungicide-Herbicide Branch
Registration Division (TS-767C)

THRU: Paul F. Schuda, Chief
Exposure Assessment Branch
Hazard Evaluation Division (TS-769C)

Attached, please find the Exposure Assessment Branch review of:

EPA Reg./File #: 100529

Chemical Name: Atrazine

Type Product: Herbicide

Company Name: Ciba-Geigy Corporation

Purpose: Environmental Fate and Leaching Assessment of Atrazine for Consideration for Special Review.

Date Received: 10/25/88 Action Code: _____

Date Completed: 1/29/88 EAB#(s): 80076

Monitoring study requested: yes Total Reviewing Time: 100h

Monitoring study voluntarily: __

Deferrals to: N/A _____ Ecological Effects Branch

_____ Residue Chemistry Branch

_____ Toxicology Branch

REGISTRATION DIVISION DATA REVIEW RECORD

Confidential Business Information — Does Not Contain National Security Information (E.O. 12065)

4/7/5 Hed

1. CHEMICAL NAME: Atrazine

10-27-87

2. IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER
95	350	

TO BE COMPLETED BY PM

5. RECORD NUMBER: 206 274
6. REFERENCE NUMBER: 1
7. DATE RECEIVED (EPA): 10-22-87
8. STATUTORY DUE DATE:
9. PRODUCT MANAGER (PM): Taylor / Arnold
10. PM TEAM NUMBER: 25

TO BE COMPLETED BY PCB

11. DATE SENT TO HED/TSS: 10-24-87
12. PRIORITY NUMBER: 50
13. PROJECTED RETURN DATE: 1-13-88

14. CHECK IF APPLICABLE

- ☐ Public Health/Quarantine
- ☐ Minor Use
- ☐ Substitute Chemical
- ☐ Part of IPM
- ☐ Seasonal Concern
- ☐ Review Requires Less Than 4 Hours

At

15. INSTRUCTIONS TO REVIEWER

A. HED
- ☐ Total Assessment - 3(c)(5)
- ☐ Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977.

B. SPRD (Send Copy of Form to SPRD PM)
- ☐ Chemical Undergoing Active RPAR Review
- ☐ Chemical Undergoing Active Registration Standards Review

C. ☐ BFSD
D. ☐ TSS/RD
E. ☐ Other

F. INSTRUCTIONS

Request for groundwater paper and other necessary work for Atrazine per meeting on 10/20/87. Previous beansheet sent ID # 93 Recd # 206191. See copy attached

16. RELATED ACTIONS — This beansheet is being sent under separate name per request of EAB, for their records

Attention: Al. Lorber

17. 3(c)(1)(D)
- ☐ Use Any or All Available Information
- ☐ Use Only Attached Data
- ☐ Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical.

18. REVIEWS SENT TO
- ☐ TB
- ☐ EEE
- ☐ EF
- ☐ PL
- ☐ RCB
- ☒ EFE
- ☐ CH
- ☐ BFSD

19.	To	TYPE OF REVIEW	NUMBER OF ACTIONS: Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
HED		TOXICOLOGY								
HED		ECOLOGICAL EFFECTS								
HED		RESIDUE CHEMISTRY								
HED	X	ENVIRONMENTAL DATE	1							
RD/TSS		CHEMISTRY								
RD/TSS		EFFICACY								
RD/TSS		PRECAUTIONARY LABELING								
BFSD		ECONOMIC ANALYSIS								

20. ☐ Label Submitted with Application Attached
21. ☐ Confidential Statement of Formula
22. ☐ Representative Labels Showing Accepted Uses Attached
23. Date Returned to RD (to be completed by HED)
24. Include an Original and 4 (four Copies of This Completed Form for Each Branch Checked for Review.

EPA Form 8570-13 (Rev. 11-81) PREVIOUS EDITIONS ARE OBSOLETE.

2

REGISTRATION DIVISION DATA REVIEW RECORD

Confidential Business Information — Does Not Contain National Security Information (E.O. 12065)

MICAL NAME: Atrazine

IDENTIFYING NUMBER	3. ACTION CODE	4. ACCESSION NUMBER
93	350	

TO BE COMPLETED BY PM

5. RECORD NUMBER: 206,191
6. REFERENCE NUMBER:
7. DATE RECEIVED (EPA): 10-22-87
8. STATUTORY DUE DATE:
9. PRODUCT MANAGER (PM): Taylor Grubbs
10. PM TEAM NUMBER: 25

TO BE COMPLETED BY PCB

11. DATE SENT TO HED/TSS:
12. PRIORITY NUMBER:
13. PROJECTED RETURN DATE:

ECK IF APPLICABLE

- Public Health/Quarantine
- Substitute Chemical
- Seasonal Concern
- ☐ Minor Use
- ☐ Part of IPM
- ☐ Review Requires Less Than 4 Hours

STRUCTIONS TO REVIEWER

HED
- ☐ Total Assessment - 3(c)(5)
- ☐ Incremental Risk Assessment - 3(c)(7) and/or E.L. Johnson memo of May 12, 1977.

SPRD (Send Copy of Form to SPRD PM)
- ☐ Chemical Undergoing Active RPAR Review
- ☐ Chemical Undergoing Active Registration Standards Review

C. ☐ BFSD
D. ☐ TSS/RD
E. ☐ Other

F. INSTRUCTIONS

Do risk assessment and groundwater paper on Atrazine as discussed in meeting on 10-20-87. Preparation for policy group. Attention: M. Firestone, M. Farber

ELATED ACTIONS

c)(1)(D)
- Use Any or All Available Information
- ☐ Use Only Attached Data
- Use Only the Attached Data for Formulation and Any or All Available Information on the Technical or Manufacturing Chemical.

18. REVIEWS SENT TO
- ☐ TB
- ☐ EEB
- ☐ EF
- ☐ PL
- ☐ RCB
- ☒ EFB
- ☐ CH
- ☐ BFSD

NUMBER OF ACTIONS

TYPE OF REVIEW	Registration	Petition	EUP	SLN	Sec. 18	Inert	MNR. USE	Other
TOXICOLOGY								
ECOLOGICAL EFFECTS								
RESIDUE CHEMISTRY								
ENVIRONMENTAL DATE	1							
CHEMISTRY								
EFFICACY								
PRECAUTIONARY LABELING								
ECONOMIC ANALYSIS								

☐ Label Submitted with Application Attached

21. ☐ Confidential Statement of Formula

22. ☐ Representative Labels Showing Accepted Uses Attached

23. Date Returned to RD (to be completed by HED)

24. Include an Original and 4 (four) Copies of This Completed Form for Each Branch Checked for Review.

Form 8570-13 (Rev. 11-81) PREVIOUS EDITIONS ARE OBSOLETE.

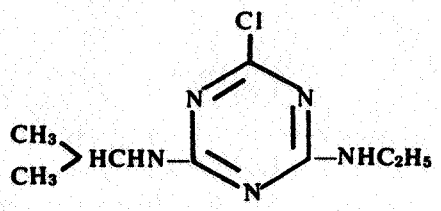
An Assessment of the Potential of Atrazine
to Contaminate Ground Water Based Upon Available
Environmental Fate and Ground Water Monitoring Data

1. Chemical:

Chemical name: 2-chloro-4-ethylamino-6-isopropyl-amino-1,3,5-triazine

Common name: atrazine

Structure:



2. Test Material: N/A

3. Study/Action Type:

Evaluation of atrazine environmental fate and ground water monitoring data with reference to potential for contamination of ground water from agricultural use of atrazine. The purpose of this evaluation is to facilitate a decision on whether atrazine should undergo Special Review.

4. Study ID:

Please see the attached review for identification of all studies which were cited.

5. Reviewed By:

Michael R. Barrett, Chemist
Ground Water Team
EAB/HED

Signature: _____

Date: _____

6. Approved By:

Patrick Holden, Team Leader
Ground Water Team
EAB/HED

Signature: C. Eidanfer

Date: 1/29/88

7. Conclusions:

Refer to the attached review.

8. Recommendations: N/A

9. Background: N/A

10. Discussion: N/A

11. Completion of One-Liner: N/A

12. CBI Appendix: N/A

An Assessment of the Potential of Atrazine to Contaminate Ground Water Based Upon Available Environmental Fate and Ground Water Monitoring Data

EXECUTIVE SUMMARY

Atrazine is a persistent, soil-applied herbicide which has been used extensively in the United States since the 1950s. There is an extensive data base on the behavior of atrazine in soil and water. This data base indicates that atrazine has a high potential to leach to ground water.

Atrazine has a sufficiently low vapor pressure, sufficiently high water solubility, etc., such that its leaching potential should be considered. Soil adsorption of atrazine is moderate; some atrazine in soil would be expected to partition into the soil water and be available for leaching. Available data indicate that atrazine is moderately to highly persistent (half-lives of several weeks to months) in nearly all mineral soils. Available hydrolysis data imply that atrazine could be still more persistent in ground water. Currently, atrazine has been detected in ground water in 18 states. Concentrations in ground water derived from point sources frequently exceed 20 ug/L (ppb). Levels of atrazine in ground water from 14 of 18 of the states for which monitoring data are available have been found to exceed the proposed lifetime health advisory (3 ug/L) in one or more samples. Many of these findings of atrazine in ground water are believed to be associated with normal agricultural use and subsequent leaching to ground water (nonpoint source). The available data are insufficient to determine whether, in general, atrazine residues in ground water will continue to increase with current agricultural practices; however, this possibility needs to be considered. The data indicate widespread contamination of ground water with atrazine and imply that a substantial number of people might be exposed to levels exceeding the proposed lifetime health advisory of 3 ppb. It is recommended that the registrant conduct a large-scale retrospective ground-water monitoring study to assess the true extent of contamination by atrazine nationwide.

INTRODUCTION

Atrazine is a member of a large chemical family of pesticides, the triazine herbicides, which have maintained a prominent position in the U.S. herbicide market since the 1950s. In general, the triazine herbicides have characteristics such as high persistence in soils, slow hydrolysis, low vapor pressure, moderate solubility in water, and moderate adsorption to soil organic matter and clay. These properties make triazine herbicides candidates for consideration as potential contaminants of ground water. Atrazine, in particular, has been found to enter ground water in a number of locations throughout the United States from point or nonpoint sources.

CHEMICAL AND PHYSICAL PROPERTIES INFLUENCING THE LEACHING POTENTIAL OF ATRAZINE

Atrazine has a solubility of 33 ppm in water at 27 C. It is highly soluble in many organic solvents (Ciba-Geigy Corporation, 1971). The octanol-water partition coefficient of atrazine is 476 (Kenaga and Goring, 1980). At field application rates, the potential concentration of atrazine in soil water and ground water is very low relative to its solubility in water; therefore, water solubility does not limit the leaching of atrazine through the soil profile and subsurface strata into ground water. Water solubility of the primary degradates of atrazine in soil [deethylated atrazine, deisopropylated atrazine, and 2-hydroxyatrazine (Khan et al., 1981; Khan and Saidak, 1981)]; should be greater than for the parent; therefore, presumably the movement of these degradates through soil and subsurface strata are also not limited by their water solubilities. Atrazine solubility in water is high relative to the the proposed lifetime health advisory for atrazine in drinking water which is 3 ug/L (0.003 ppm) (U.S. Environmental Protection Agency, ODW, 1987) or only one-ten-thousandth of the solubility limit of atrazine in water.

The hydrolysis rate of atrazine in natural waters is highly variable but it could take years to degrade in ground water (Table 1). Evidence for nonbiological hydrolysis of atrazine in soils is the finding of Skipper et al. (1967) that there was no difference in the degradation rate of atrazine to hydroxyatrazine between nonsterile and sterilized (autoclaved for 12 h at 121 C) soils (including a sandy loam with 2.7% organic matter, 18.7 me/100 g CEC and pH 6.1 and a silty clay loam with 8.0% organic matter, 35.8 me/100 g CEC, and pH 6.3) maintained at 30 C (apparently) with the water content at 100 percent "field capacity" for each soil. The presence of adsorbents in soil appears to catalyze atrazine hydrolysis resulting in a much higher reaction rate than in water alone (Hance, 1967; Armstrong et al., 1967; Armstrong and Chesters, 1968). Therefore, with the paucity of adsorbents in ground water matrices (and presumably les microbial degradation) it is likely that atrazine is generally more persistent in ground water than in most soils under typical environmental conditions.

Table 1. Hydrolysis Rates of Atrazine in Aqueous Media

Hydrolysis Half-Life, Days	pH	Temp, °C	Conditions	Medium	Reference
0.10	7	25	--	"Natural Water"	Mabey & Mill (1978)
2.5%/3 Mo.[a]	--	12	Nonsterile[b]	Simulated aquifer	Wehtje et al. (1981)
7.5	--	107	--	Bentonite clay suspension	Hance (1967)
4.2×10^4		20	--	Bentonite clay suspension	Hance (1967)
"very long"	6	--	--	Buffer solution	Hance (1967)
"very long"	--	--	Nonsterile	Distilled water	Hance (1967)
20	2 or 12	25	Nonsterile	Buffer solution	Armstrong et al. (1967)
200	4 or 11	25	Nonsterile	Buffer solution	Armstrong et al. (1967)
> 1000	6 or 10	25	Nonsterile	Buffer solution	Armstrong et al. (1967)
209	3.9	25	Nonsterile	Buffer solution	Armstrong et al. (1967)
22	3.9	25	Sterilized[c]	Soil + water	Armstrong et al. (1967)
84	5	20	Nonsterile	Buffer solution	Burkhard & Guth (1981)
42	5	30	Nonsterile	Buffer solution	Burkhard & Guth (1981)
> 200	7	20 or 30	Nonsterile	Buffer solution	Burkhard & Guth (1981)
35	2.9	25	Nonsterile	Buffer solution with 500 ppm fulvic acid	Khan (1978)
742	7.0	25	Nonsterile	Buffer solution with 500 ppm fulvic acid	Khan (1978)
525	--	12	In situ	Confined aquifer; atraz. loss presumed to be hydr.	Perry & Eiden(1987)[d]

[a]The amount degraded after 3 months.
[b]Cultures of aquifer microbes were added.
[c]Soil (silt loam, 13% organic matter) was boiled for 15 minutes and presumably was not completely sterilized.
[d]Charles Perry, U.S. Geological Survey, Lawrence, KS; and Catherine Eiden, EAB, OPP, Environmental protection Agency; personal communication.

Adsorption of pesticides to soil is generally inversely proportional to pesticide mobility in the soil profile. Soil adsorption also influences pesticide persistence. Adsorption of atrazine is a significant dissipation process. Adsorption partition coefficients or K_d values (coefficient of proportion of solution concentration to concentration adsorbed at the soil-water interface at equilibrium) range from 0.40 to 91.8 and are < 10 for most soils except peat soils (Table 2). The K_{oc} (the K_d divided by the proportion of organic matter relative to the total mineral content of the soil) varies from 5.3 to 300 (excluding an extremely low organic matter sand with K_{oc} variably measured as 0 to 2571) with most values in the 15 to 200 range. These values are indicative of a moderate propensity for adsorption of atrazine by soil colloids and are sufficiently low so that it is expected that some leaching of atrazine might be possible if it is sufficiently persistent in soil.

The vapor pressure of atrazine has been reported to be 3.6×10^{-9} atmos at 20 °C (Grayson and Fosbraey 1982), and 7.5×10^{-9} (10 °C), 3.9×10^{-9} (20 °C), 1.8×10^{-9} (30 °C), and 0.30×10^{-9} (50 °C) atmos (Jordan et al., 1970). Cohen et al. (1984) calculated the Henry's Law constant as the vapor pressure of the pesticide divided by its water solubility at the same temperature. Using the above values from the literature for the vapor pressure of atrazine at 20 °C, and the water solubility of atrazine at 27 °C (presumably not substantially different from the water solubility at 20 °C) Henry's Law constant is calculated to be 2.3×10^{-5} to 2.6×10^{-5} atmos-L/mol.

ATRAZINE PERSISTENCE IN SOIL

Numerous studies have examined the persistence of atrazine in natural soils at controlled moisture and temperature levels in the range of conditions found in the natural environment (Table 3). First order half-lives or times required for 50 percent disappearance listed in Table 3 range from 20 to 1800 days in soils of a wide variety of textural classifications containing from 0.55 to 13 percent organic matter. Differences in the dissipation rate of atrazine occurred as the temperature and soil water content varied; Nicholls et al. (1982), Walker (1978), and Walker and Zimdahl (1981) have quantified this effect in particular soils in simulation models. The available data in the literature also show marked differences in atrazine dissipation rates in different soils kept under the same temperature and moisture regimes and when the same soil is altered in pH or adsorption properties by the addition of appropriate materials. Allen and Walker (1987) have demonstrated that the rates of degradation of metribuzin, a triazine herbicide, in 12 mineral soils are correlated with soil texture and the Freundlich adsorption constant for metribuzin and were able to describe most of the variation in first order rate constants by multiple regression analysis. The available data indicate that similar relationships of atrazine persistence to the physical and chemical characteristics of soils are likely to

Table 2. Soil Adsorption Coefficients for Atrazine on a Total Soil (K_d) and Soil Organic Matter (K_{oc}) Basis[a]

K_d	K_{oc}	Texture	Organic Matter, %	CEC, Meq/100 g	Reference
0.70	5.3	Silt loam	13	--	Armstrong et al. (1967)
0.40	40	Loamy sand	4	--	Armstrong et al. (1967)
0.17	8.5	Clay	2	--	Armstrong et al. (1967)
1.3	52	Sandy loam	2.5	--	Moyer et al. (1972)
6.03	155.8	Silty clay loam	3.9	--	Davidson et al. (1980)
0.89	98.9	Sandy clay loam	0.90	--	Davidson et al. (1980)
0.62	124.0	Sandy loam?	0.50	--	Davidson et al. (1980)
0.62	110.7	Sand	0.56	--	Davidson et al. (1980)
1.0	--	Clay	--	42	Talbert & Fletchall (1965)
21.5	--	Peat	--	118	Talbert & Fletchall (1965)
91.8	--	Peat moss	--	106	Talbert & Fletchall (1965)
4.32	--	Silty clay loam	4.2	21	Talbert & Fletchall (1965)
6.03	156	Silty clay loam	3.9	55	Rao & Davidson (1979)
0.89	98.9	Sandy loam	0.90	6.8	Rao & Davidson (1979)
0.62	111	Fine sand	0.56	5.2	Rao & Davidson (1979)
1.00	23	Silty clay loam	4.4	--	Lavy (1968)
0.47	16	Sandy loam	2.9	--	Lavy (1968)
0.26	15	Sandy loam	1.7	--	Lavy (1968)
2-11.6	43-252	Silty clay loam	4.6	--	Weidner (1974)
1.4-8.7	48-300	Sandy loam	2.9	--	Weidner (1974)
0-1.8	0-2571	Gravelly sand	0.07	--	Weidner (1974)
2.88	51.4	Silt loam	5.6	--	Wagenet et al. (1987)
1.98	55.0	Silt loam	3.6	--	Wagenet et al. (1987)
0.86	39.1	?	2.2	--	Wagenet et al. (1987)
3.2±2.9	163 ± 80	56 different soils (average)[b]	--	--	Rao & Davidson (1980)

[a]Coefficients are calculated from the Freundlich equation, S = KCN where K and N are constants and S = ug/atrazine per g of soil (K_d) or per g of soil organic matter (K_{oc}) adsorbed and C is the ug atrazine per g of equilibrium solution (usually at a concentration of 1 ppm, a concentration likely to occur in soil solution after agricultural applications).
[b]This average includes some of the previously listed soils.

Table 3. Persistence of Atrazine in Soil Media Under Controlled Conditions

Half-Life(*) or 50% degrad. time, days	Soil Characteristics: Texture	Organic Matter, %	pH	Soil Water, %	Soil Water Tension	Temp., °C	Comments	Reference
300	sandy loam	2.7	6.1		20-28% FC			Skipper et al. (1967)
300	silty clay loam	8.0	6.3		20-28% FC			Skipper et al. (1967)
115*	loamy sand	4	4.9	saturated		22	High applic. rate	Armstrong et al. (1967)
220*	silt loam	13	6.9	saturated		22	(5-48 ppm)	Armstrong et al. (1967)
1000-1800*	clay	2	7.3	saturated		22		Armstrong et al. (1967)
41*	loam (A)	2.5	8.0	17		25		Walker & Zimdahl (1981)
28*	silt loam (B)	1.1	7.3	17		25		Walker & Zimdahl (1981)
47*	sandy loam (C)	2.6	6.4	17		25		Walker & Zimdahl (1981)
181*	Soil A			17		5	Selected data, experiments	Walker & Zimdahl (1981)
133*	Soil B			17		5	at 5-35 °C and 2.5-17%	Walker & Zimdahl (1981)
179*	Soil C			17		5	soil water were included	Walker & Zimdahl (1981)
103*	Soil A			5.1		5		Walker & Zimdahl (1981)
55*	Soil B			5.1		5		Walker & Zimdahl (1981)
94*	Soil C			5.1		5		Walker & Zimdahl (1981)
> 63	clay loam				100% FC	—		Anderson et al. (1980)
> 365	silt	2.9	5.7		100% FC	14		Bellinck & Mayaudon (1979)
16-20*	loam	0.55	5.4	160	—	12-36	The first 2 "soils" were sediments.	Jones et al. (1982)
13-15*	sandy loam	0.85	4.4	160	—	12-36	Diff. half-lives were calc. depend	Jones et al. (1982)
110-330*	sandy loam	0.91	5.5	17	60% WHC	12-36	on whether unextracted ^{14}C-residue	Jones et al. (1982)
36-385*	silty clay loam	0.91	6.4	50	100% WHC	12-36	was assumed to contain parent.	Jones et al. (1982)
38*	silty clay	3.8	5.2		0.1 bar	30		Dao et al. (1979)
37*	silty clay	2.9	5.8		0.1 bar	30		Dao et al. (1979)
64*	fine silt loam	2.9	6.3		0.1 bar	30		Dao et al. (1979)
21-28							For deethyl & deisopropyl metabolites.	Winkelmann & Klaine (1987)
180							For hydroxyatrazine.	Winkelmann & Klaine (1987)
37*	silt loam	1.6	5.1-5.8	20	pF 2.5	22		Hance (1979)
37*	silt loam	1.6	6.3-7.0	20	pF 2.5	22		Hance (1979)
28*	silt loam	1.6	7.9-7.7	20	pF 2.5	22	Soil pH was adjusted by lime or	Hance (1979)
27*	silt loam	1.6	8.2-7.8	20	pF 2.5	22	sulfuric acid amendments; the pH	Hance (1979)
29*	silt loam	4.0	5.2-4.6	33	pF 2.5	22	values given are for the beginning	Hance (1979)
32*	silt loam	4.0	6.1-5.3	33	pF 2.5	22	and end of the incubation period.	Hance (1979)
36*	silt loam	4.0	7.2-6.3	33	pF 2.5	22		Hance (1979)

Table 3. Persistence of Atrazine in Soil Media Under Controlled Conditions (Cont'd)

Half-Life(*) or 50% degrad. time, days	Soil Characteristics: Texture	Organic Matter %	pH	Soil Water %	Soil Water Tension	Temp. °C	Comments	Reference
40*	silt loam	4.0	8.0-6.8	33	pF 2.5	22		Hance (1979)
71*	sandy loam (A)	2.5	7.3	20	83% FC	20		Moyer et al. (1972)
355*	A + 2.5% charcoal	—	—	20	83% FC	20		Moyer et al. (1972)
98*	A + 10% clay	—	—	20	83% FC	20		Moyer et al. (1972)

be found. Atrazine clearly is sufficiently persistent in most soils for the possibility of leaching to ground water in measurable quantities to be considered. Field studies generally report times for 50 percent disappearance of the applied atrazine of a few weeks to 2 or 3 months after spring or summer applications (Tafuri et al., 1978; Walker and Zimdahl, 1981; Wu, 1980; Khan et al., 1981; Gaynor and Volk, 1981; Bauman and Ross, 1983; Kells et al., 1980). Atrazine may be much more persistent in soil during the winter months.

Atrazine is not only persistent in soil but is also mobile. The Office of Pesticide Programs has data showing atrazine, after application to the surface at normal agricultural rates, migrating with the soil-pore water through the unsaturated zone to a depth of six inches at a concentration in the water drawn by lysimeters of 1 to 2 ppb. Levels found in the ground water ca. 20 feet below the soil surface at this site were 0.3 ppb by several weeks after application. Once in this aquifer, atrazine was found to be extremely stable (Perry and Eiden, 1987; cf. Table 1).

ATRAZINE CHEMICAL CHARACTERISTICS AND ENVIRONMENTAL BEHAVIOR RELATIVE TO OTHER PESTICIDES FOUND TO LEACH TO GROUND WATER

Parameters related to the leaching potential of atrazine are summarized in Table 4 as compared to the standard for these parameters set by Cohen et al. (1984) as indicative of pesticides with high leaching potential. Adsorption of atrazine is somewhat stronger than that typical of the leaching pesticides considered by Cohen et al., the hydrolysis and photolysis rates may or may not be within their standard depending on the conditions of the test (Cohen et al., also noted higher variability for photolysis data and the difficulty of establishing a level indicative of leaching potential under particular conditions), the criteria for K_{oc} and water-solubility are met by a slight margin, and the criteria for Henry's Law constant, soil persistence, and speciation are clearly met. These criteria were empirically set on the basis of evidence of ground water contamination for atrazine and other pesticides; as additional environmental fate data become available modeling the complex relationships between these pesticide characteristics and actual degree of leaching and ground water contamination found in the environment should become possible.

In general, we can conclude that because atrazine is under at least some ambient conditions highly persistent in soil and water and is not entirely adsorbed to soil organic matter or clay, the potential for leaching to ground water exists. Furthermore, as discussed in the following section, atrazine residues already have been reported in ground water in a number of states. The available data strongly suggest that once atrazine does reach ground water it is likely to be quite persistent in most ground water environments.

Table 4. Environmental Fate-Related Characteristics for Atrazine Compared with those of Typical Leaching Pesticides as Determined by Cohen et al. (1984).

	Atrazine Characteristics[a]	Cohen et al. Standards for Leaching Pesticides
K_d	0.4 to 91.8, < 10 for most soils.	< 5, usually less than 1 or 2
K_{oc}	5.3 to 300, most values between 15 and 200.	< 300 to 500
Water Solubility, ug/mL	33	> 30
Hydrolysis rate; half-life, days	Nonsterile buffer sltn.: 42 to > 1000 (pH 5 to 10, 25-30 °C)	> 175
Henry's Law Constant (atmos-L/mol)	2.5×10^{-5}	< 10
Photolysis; half-life, days	In water: a) 1 (pH 6.8, 15 °C) b) Direct photoly. very low c) 8% degradation in 135 min. (50 °C)	> 7 (preferably meas. on soil surf. or in water)
Soil persistence half-life, days	27 to > 365 days (natural soils, 14 to 25 °C)	> 14 or 21
Speciation	Ring N atoms have partial negative charge, pKa = 1.68	Fully or partially negatively charged at ambient pH.

[a]Values are based upon data discussed previously in the text with an emphasis on data collected under typical environmental conditions, except that: (1) photolysis data not discussed previously are from: (a) Burkhard and Guth (1976), (b) Wolfe et al. (1976), and (c) Khan (1978); and (2) speciation information is taken directly from the discussion by Cohen et al. (1984).

REPORTS OF ATRAZINE RESIDUES IN GROUND WATER

The occurrence of atrazine residues in ground water has been documented in at least 18 States including over 1200 of at least 4300 samples containing 0.1 up to 550 ppb (ng/mL) (point source) or up to 33 ppb of atrazine when the source appeared to be nonpoint (Table 5). Specific discussion of the significance of some of these data follows.

The maximum residue concentration of 550 ppb occurred in a sample from a private well near Green Bay, Wisconsin. Concentrations exceeding 100 ppb (the proposed 10-day health advisory is 100 ppb) have also been found in ground water in other locations in Wisconsin and in Michigan and North Carolina. Residues at such levels in Wisconsin are clearly associated with point sources, primarily pesticide storage facilities in agricultural communities (David A. Belluck, Wisconsin Department of Health and Social Services, Madison; 1987, personal communication). Such point sources are of special concern to the Office of Pesticide Programs because they are associated with registered agricultural uses in that they represent the sales distribution centers for the agricultural uses of pesticides. The high residues found in some samples from private wells in Hillside and St. Joseph counties, Michigan (Ciba-Geigy, 1987a) remain unexplained; in many samples taken from the same wells a few weeks apart, no atrazine was detected. High residues found in Greensboro, North Carolina (Ciba-Geigy, 1987f) were associated with leaking fuel oil from underground storage tanks.

Several of the available ground water monitoring studies provide evidence for nonpoint source contamination of wells with atrazine. The Big Spring Basin study in Clayton County, Iowa (Hallberg et al. 1983; Table 5) assessed atrazine residues in karst-carbonate aquifers in northeastern Iowa. About 11 percent of the basin drains entirely to sinkholes. Therefore, hydrogeology of this study area makes the ground water quite vulnerable to contamination by agricultural chemicals applied to the surface. All 54 samples in this survey were taken in 1982; of the 41 samples taken in June or July after normal agricultural applications of atrazine 21 contained detectable residues of 0.06 to 0.64 ppb with a mean positive concentration of 0.16 ppb. By contrast, Big Spring was sampled on a weekly to biweekly basis from October 1981 to January 1984 (Hallberg et al. 1984); of 108 samples 103 contained detectable residues of 0.1 to 5.1 ppb. For the 1983 water year, the flow-weighted mean concentration in Big Spring ground water was 0.28 ppb, while the mean of all analyses was 0.72 ppb.

In a survey of existing domestic water supply wells in Floyd and Mitchell counties, Iowa, samples were taken approximately monthly from February to December 1983 from each of the 19 wells. Atrazine was not detected in 13 deep bedrock (> 50 ft depth) region samples, occurred at 0.1 to 0.85 ppm in 17 of 29 shallow bedrock (< 50 ft depth) region samples, occurred at 0.1 to 0.25 ppm in 5 of 23 karst region samples, and at 0.1 ppm in 1 of 20

Table 5. Monitoring Data for Atrazine in Ground Water[a]

Location State/County or City	Total Wells #/samples/+	Conc., ppb range/mean[b]	Well Information	Comments (Reference)
Arkansas Jefferson Desha	31/>520/0	ND (DL = 5)	well depth > 100 ft; depth to water 40-70 ft; irrigation wells	soils from well-drained to poorly drained; cotton, soybeans, corn, milo (Lavy et al. 1985)
California a) 30 counties	912/1067/74	Up to 10	Wells either in agric. regions or selected because of perceived potent. for contam.	Nonpoint source Brown et al. (1986)
b) Tulare	120/120/11	.02-8.5/.91	No data	Troiano and Segawa (1987)
c) Near L.A.	15/NA/15 (w)	ND-3.4/NA	"Annual Report on Results of Water Qual. Monitoring; 85-86"	Ciba-Geigy (1987g)
Colorado Weld	4/38/18	1.1-2.3/1.4	Well depth 10 to 18 ft	Sandy loam, loamy sand soils; test area with atrazine use in corn for 10 yrs (Wilson et al. 1987)
Florida Suwanne	2/2/2	Low	No data	Inman (1987)
Hawaii	81/83/33	.05-4.1	drinking water, all positives were for spring-derived sources	All values > 1.0 ppb were reported for tap water (Peterson, 1987)
Illinois a) Mason	8/79/12	1.07-7.3	USGS monitor wells; locate down-grd. from corn and soybeans	Well-drained sandy soil; water level 0-15 ft (McKenna and Sheng-Ful, 1987)
b) Statewide	400/400/3	0.3-2.5/1.3	All community water supply wells.	All 3 pos. occurred in wells near agric. chem. commercial operat. (Cobb and Sinnott, 1987)

Table 5. Monitoring Data for Atrazine in Ground Water[a] (Cont'd)

Location State/County or City	Total Wells #/samples/+	Conc., ppb range/mean[b]	Well Information	Comments (Reference)
Iowa				
a) Clayton	19/54/24	0.05-0.64	Wells were to Karst-carbonate aquifers	Corn grown in much of the study area. Hallberg et al. (1983)
b) Clayton	1/108/103	.1-5.1	All samples were from a spring	Hallberg et al. (1984)
c) Floyd-Mitchell	19/181/22	.10-0.85	Domestic water supply wells, many shallow (< 50 ft) includes Karst regions	Libra et al. (1984)
d) Statewide	70/70/24	1.4-3.0	Existing public water supply wells	Selected sites close to industry, hazardous waste, or with high nitrate levels. 19 of 24 wells were alluvial (shallow); other 5 bedrock (Kelley, 1985)
e) Little Sioux River	25/29/3	2.0-4.4	NA	12 of 25 wells shallow alluvial, others deep (Kelley and Wnuk, 1986)
Kansas				
Statewide	104/104/3	1.5-7.4	Randomly selected by county on the basis of farmstead well density. All sites with current agric. activity and wells used for drinking, include many shallow wells (< 50 ft)	Atrazine used by 70% of farmers (Steichen et al. 1986)

Table 5. Monitoring Data for Atrazine in Ground Water[a] (Cont'd)

Location State/County or City	Total Wells #/samples/+	Conc., ppb range/mean[b]	Well Information	Comments (Reference)
Maryland				
Statewide	30/36/3	.4-.9/NA	Private & public drinking water wells, selected for shallow depth, agrics. activity, and evid. of nitrate contam.	Tolman (1986)
Michigan				
Hillside	8/45/14	DL-210/15	30-200 ft	Ciba-Geigy (1987a)
St. Joseph	17/30/6	DL-107/7.9	20-87 ft	
Kalamazoo	9/9/0	--	20-96 ft	
Minnesota				
a) Mainly central & SE part of MN	105/420/36	.05-42.4/.58[c]	mostly USGS monitoring	Selected sites where the soils and hydrogeologic conditions made the ground water especially vulnerable; study in progress (Klauseus, 1986)
	157/157/77	.01-13.9/.09[c]	public drin.	
	25/200/23	.01-31.4/.18[c]	private drin.	
	214/214/42	.02-5.2/.08[c]	public drin.	
b) Todd	NA/NA/1	6.7	NA	Ciba-Geigy (1987f), contin. program, 40 samples to date in 4 States
Nebraska				
a) Richardson Pawnee	30/30/18	TR-3.3/NA	Monitoring	EPA-USGS IAG in-house (Eiden and Cohen, 1986)
b) Southeast	47/47/13	ND-1.1/.46	Drinking water	Poor well construction cited as cause (Exner & Spalding, 1985)
c) Hall Holt	NA/NA/5	.35-1.4	NA	Ciba-Geigy (1987f), contin. program, 40 samples to date in 4 States

Table 5. Monitoring Data for Atrazine in Ground Water[a] (Cont'd)

Location State/County or City	Total Wells #/samples/+	Conc., ppb[b] range/mean	Well Information	Comments (Reference)
New York				
Eagle Bridge	11/41/41	.12-9.12/2.29	Private drin. < 30 ft	Point source near agric. chem. distrib. ctr. in rural town (Neubeck, 1986)
North Carolina				
Greensboro	2/3/2	20.-190./105.	NA	Ciba-Geigy (1987h), point source
Pennsylvania				
a) Berks	4/7/2	.30-.8/.55	USGS obs.	All wells located in the Sussq./Potomac river basin (Buchanan et. al. 1983)
Lancaster	42/79/23	.20-3.0/.61	USGS obs.	
Berks	3/3/2	.30-.40/.35	USGS obs. well	Same, only 1984 (Loper et. al.)
Lancaster	38/38/12	.20-1.2/.42	USGS obs. well	
Berks	1/2/2	.82-20.0/10.4	NA	Ciba-Geigy (1987c)
b) Mahantango Creek Wtshed	20/20/14	.013-1.11/NA	NA	Ciba-Geigy (1987e).
c) Berks	NA/NA/3	.13-2.3/.9	NA	Ciba-Geigy (1987f) continuing program; 40 samples reported in 4 States.
South Dakota				
Union	1/1/1	1.7	NA	Shade (1986)
Brookings	1/1/1	5.8-7.1 (?)		
Vermont	165/230/5	1.0-24.0/NA	Of 5 pos: 4 < 30 ft - 1 260 ft	Allbee (1987)
Wisconsin				
a) many cities	NA/349/50	NA/max = 140	"Worst-case" areas	Wisc. Dept. of Natur. Resou. sampling reported by Holden (1986)

Table 5. Monitoring Data for Atrazine in Ground Water[a] (Cont'd)

Location State/County or City	Total Wells #/samples/+	Conc., ppb range/mean[b]	Well Information	Comments (Reference)
b) 9 cities	39/147/63	0.1-33.0/5.3	"Research" wells	Ground wtr sampled beneath worst-case fields with known previous use (Postle, 1987).
c) Iowa City	5/6/6	29.-109./58.	NA	Ciba-Geigy (1987d).
d) Walworth	NA/NA/1	.13	NA	Ciba-Geigy (1987f); contin. prog., 40 samp. in 5 States.
e) Green Bay	1/1/1	550	Private well	Ciba-Geigy (1987b), finding of Wis. DHSS; point source likely.
TOTAL U.S. (estimates) 18 States)	> 1800 wells > 4300 samples > 1200 positives	Nonpoint: .1-33..0 ppb point: 20 to >100 ppb Max = 550 ppb		
STORET[d] 19 States inc. AL, MA, MT, OH, TN, UT, VA which are not in EAB's files	2123 "Stations" 2750 samples 366 positives.	Maximum = 1400 ppb 85th Percentile = 1.90 ppb		

[a]NA = Not available.
[b]ND = Nondetectable, DL = Detection Limit, TR = Trace.
[c]Median of positive values..
[d]These data are from an internal document dated February, 1987 by C.A. Hoheisel and L.L. Kutney (Exposure Assessment Branch, Haz. Eval. Div., Of. Pestic. Progr.). The STORET data are summarized here for informational purposes but are not discussed in detail as they largely duplicate the data already presented above and the STORET data base is considered less reliable.

incipient karst region samples. Land use information gathered for this survey indicates that these sites represent areas where only nonpoint sources are available for leaching to ground water.

Postle (1987) reported on atrazine residues in monitoring wells installed in sandy outwash soils along the lower Wisconsin River and the Central sands area in Wisconsin, both regions with ground water considered susceptible to contamination by pesticides. The data summarized in Table 5 are from 13 agricultural fields where ground water was sampled from three wells each drawing water at different increments below the water table; the depth to ground water in these fields was 5 to 12 feet.

Klauseus (1986) found significant contamination (up to 31 ppb atrazine) of wells they surveyed throughout Minnesota which were selected for sampling primarily based upon relatively high hydrogeologic vulnerability.

The California Well Inventory Data Base (Brown et al. 1986) provides some insight into the extent of contamination in the state. For many of the nearly 1000 wells sampled in 30 counties included in this data base it was apparently determined that any atrazine residues which occurred were from a nonpoint agricultural source. The maximum confirmed concentration of atrazine in ground water from any of these wells was 10 ppb. Only 8 percent of the wells in four counties had detectable residues in the samples collected, however, typical detection limits were not specified in their report. Although suggesting that normal agricultural use has resulted in the contamination of ground water at a level up to a few ppb in four California counties, this data base, like the others discussed previously, is not representative of state-wide contamination since sampling was clustered around densely populated areas and data were collected by different agencies with different subjective criteria for determining where to take their samples.

Only the Kansas and Vermont studies listed in Table 5 were truly statewide studies and appear to be fairly representative of the extent of contamination of wells used for drinking water and in active agricultural areas of their respective states. Although the percentage of sites with atrazine application is not at present available for the Vermont survey, it presumably is large since this survey included only sites planted to corn, a crop for which atrazine is a major herbicide. In Kansas, 70 percent of the farmers reported using atrazine. Only for 3 percent of the wells in each state did any of the collected samples bear detectable atrazine residues (more than $\approx$ 1 ppb).

The proposed lifetime health advisory for atrazine in drinking water, 3 ppb, is exceeded in numerous samples from 14 of the 18 states for which ground water monitoring data are currently available. The available ground water data were, for the most part, gathered by systematic selection processes for sites more likely to yield high levels of ground water contamination by atrazine, therefore, no definitive conclusions can be made at this time

about the extent of occurrence of atrazine residues in ground water nationwide. Nevertheless, the data do indicate widespread contamination of ground water with atrazine and do imply that it is possible that a substantial number of people might be exposed to levels exceeding the proposed lifetime health advisory of 3 ppb. With some drinking water wells with atrazine levels exceeding 100 ppb, it is certain that at least some individuals are receiving an exposure to atrazine through drinking water that exceeds the proposed 10-day health advisory (currently the proposed 1-day health advisory, in the absence of appropriate data, is also 100 ppb).

CONCLUSIONS

The available data indicate that atrazine is sufficiently persistent in nearly all, if not all, mineral soils so that the lack of occurrence of measurable residues in ground water resulting from normal agricultural practices cannot be assumed a priori regardless of the hydrogeologic setting. Furthermore, the water solubility is sufficiently high, the octanol-water partition coefficient is sufficiently low, the vapor pressure is sufficiently low, and the soil adsorption constants are sufficiently low (for most soils) such that the potential for leaching of measurable residues to ground water should be considered. Based upon the available hydrolysis data, including limited data on hydrolytic stability in actual ground water, it is evident that once atrazine enters ground water, this chemical could persist for many years. In areas where there is a continual addition of atrazine to the soil surface and leaching to ground water occurs to any significant extent, the possibility of a buildup of the concentration of atrazine in ground water after many years of use must be considered.

The irregular nature of the data base on occurrence of atrazine residues in ground water nationwide precludes any possibility of making conclusions about the extent and magnitude of atrazine residues in United States ground waters. There is evidence that atrazine in ground water can reach a very high level with point sources; more needs to be done to prevent leaching of excessively high levels of atrazine to ground water from sites such as agricultural chemical commercial facilities as has already been demonstrated to be a widespread problem in Wisconsin (D.A. Belluck, 1987, personal communication; Holden, 1986; Ciba-Geigy, 1987b). To date, most of the occurrences of atrazine residues in ground water exceeding a few ppb, if not associated with point sources, can be attributed to normal agricultural application of atrazine in an exceptionally vulnerable hydrogeological setting. Additional data are needed to define more clearly the circumstances under which atrazine can be expected to contaminate ground water at such levels. Should these levels be considered an unacceptable risk to humans based upon the toxicological issues such as the cancer potency factor for atrazine, restriction of atrazine use to hydrogeologically less vulnerable areas might be needed to reduce the risk to the general population

below a 10^{-6}-level. We recommend that the registrant conduct a large-scale retrospective ground-water monitoring study to assess the true extent of contamination by atrazine nationwide.

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