

Field study of atrazine contamination of groundwater in Dane County, Wisconsin. [DNR-064] 1992

Bradbury, K. R.; McGrath, Robert W.

Madison, Wisconsin: Wisconsin Department of Natural Resources, 1992

https://digital.library.wisc.edu/1711.dl/XUFQ45WRSHJRL8S

http://rightsstatements.org/vocab/InC/1.0/

For information on re-use see: http://digital.library.wisc.edu/1711.dl/Copyright

The libraries provide public access to a wide range of material, including online exhibits, digitized collections, archival finding aids, our catalog, online articles, and a growing range of materials in many media.

When possible, we provide rights information in catalog records, finding aids, and other metadata that accompanies collections or items. However, it is always the user's obligation to evaluate copyright and rights issues in light of their own use.

140748 c.2

140748Field Study of Atrazinec.1Contamination of Groundwater
in Dane County, Wisconsin



FIELD STUDY OF ATRAZINE CONTAMINATION OF GROUNDWATER IN DANE COUNTY, WISCONSIN

by

Kenneth R. Bradbury Robert W. McGrath

.....

Wisconsin Geological and Natural History Survey

Final Administrative Report to

Wisconsin Department of Agriculture, Trade, and Consumer Protection and Wisconsin Department of Natural Resources in fulfillment of contract No.133-P531

> Water Resources Conter University of Wescardes Attist 1972 Wescard Conter New York

VICENT RESERVED CONTRACT VICENT CONTRACTORISTICS VICENT CONTRACTORISTICS Hauses, Wi 53708,

July, 1992

CONTENTS

INTRODUCTION Background Objectives	2 2 3
SECTION I: A SURVEY OF ATRAZINE IN BEDROCK AQUIFERS IN FIVE SMALL BASINS IN WESTERN DANE COUNTY, WISCONSIN Methodology Basin selection Water sampling Basin characteristics Geography and climate Geology Hydrogeology Soils Land use Well construction	5 5 6 9 9 9 12 12 13
Well construction Sampling results Atrazine Other indicator parameters Discussion Groundwater chemistry Effect of well construction and local geologic setting	14 15 15 19 20 20 21
SECTION II: ATRAZINE CONTAMINATION OF GROUNDWATER IN THE FRYES FEEDER BASIN, NEAR MT HOREB, WISCONSIN Purpose Study area description Location Land use Methodology Borehole and piezometer installation Slug tests Streamflow monitoring Water sampling Soil sampling Geology Aquifer lithologies Hydrogeology Distribution of hydraulic head Hydraulic conductivity Groundwater velocity	24 24 26 26 29 29 29 30 30 30 32 32 35 36

Page

Pesticide concentrations and groundwater chemistry Pesticides Results of soil sampling Major ions in groundwater Environmental isotopes and groundwater age Numerical modeling and particle tracking Particle tracking Discussion Conceptual model of groundwater flow General distribution of atrazine in groundwater Sources of atrazine	37 37 43 45 46 49 54 55 55 57 58
CONCLUSIONS Five basin survey Fryes Feeder basin study	60 60 61
IMPLICATIONS AND RECOMMENDATIONS	62
REFERENCES	64
APPENDIX	66

FIGURES

		Page
1.	Location and bedrock geology of the five study basins in	
	western Dane County, Wisconsin	7
2.	Stratigraphic column for western Dane County, Wisconsin	10
3.	Representative geologic cross sections showing general bedrock	
	stratigraphy in basins A through F	11
4.	Soil Contamination Attenuation Potential (SCAM) map for basin D	13
5.	Histogram summarizing atrazine results for the 5-basin survey	15
6.	Location of the Fryes Feeder basin	25
7.	Land use in the study subarea	27
8.	Map of the small study area, showing monitoring points	28
9.	Natural gamma logs for six bedrock wells	31
10.	Caliper logs from six boreholes in the Fryes Feeder basin	33
11.	Water table in the Fryes Feeder basin	54
12.	Maximum concentrations of atrazine plus desethylated atrazine	
10	in the study area without regard for well depth or sampling date	38
13.	Soil sampling sites in the small study area	44
14.	Concentration of del ²⁰ (SMOW) in precipitation collected	10
15	at Blue mounds, wi	48
15.	Finite element mid for the sumarical model employ to the	49
10.	Finite element grid for the numerical model applied to the	51
17	Model generated hydraulic heads	53
17. 18	$C_{\text{apply}} = z_{\text{oppl}} \text{ for domestic well } \Delta O_{\text{s}}^{\text{oppl}}$	56
10.	Capture zone for domestic well AO806	57
20	Conceptual cross section of the Fryes feeder hasin	58
$\Delta 1$	Man of Basin A County KP/Otto Kerl Road near Cross Plains	50
111.	Wisconsin	67
A?	Man of Basin B. Union Valley, near Cross Plains, Wisconsin	68
A3	Map of Basin C, near Pine Bluff, Wisconsin	69
A4.	Map of Basin D. Fryes Feeder, near Mt Horeb. Wisconsin	70
A5.	Map of Basin E. Milum Creek, near Montrose, Wisconsin	71

A5. Map of Basin E, Milum Creek, near Montrose, Wisconsin

TABLES

,

		Page
1	Characteristics of the five study groundwater basins in	
. .	western Dane County	6
2	Analytes recoverable through the Neutral Extractable Method	8
 3	Well construction characteristics by basin	14
5. 4	Summary of results of groundwater sampling of domestic wells	
	in Dane County during the five basin study	16
5	Comparison of samples with and without atrazine	20
6	Soil attenuation potential ratings for various areas near	
0.	sampled wells	- 22
7.	Comparison of well construction details for wells with and	
	without atrazine detections	23
8	Results of piezometer (slug) tests in the Fryes Feeder basin	35
9.	Summary of results of groundwater sampling of domestic wells,	
2.	piezometers, and springs in the Fryes Feeder basin	40
10	Results of soil analyses for atrazine in the Fryes Feeder basin	43
11	Summary of geochemical results, grouped by position in	
. . .	oroundwater flow system	46
12.	Isotope results	47
13.	Input parameters used in the parameter estimation model	52

INTRODUCTION

This report examines the occurrence of atrazine, an agricultural herbicide, and other herbicides and pesticides in groundwater in western Dane County, Wisconsin. Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is currently the most widely used herbicide in Wisconsin and the United States (Wehtje and others, 1983). In Wisconsin, atrazine is used to control annual broadleaf and grassy weeds in corn and sorghum, and, in 1985, was applied to 77% of all Wisconsin corn fields (Chesters and others, 1991). In soils and groundwater the parent atrazine compound degrades to two toxicologically significant metabolites, desisoproplyated atrazine and desethylated atrazine. Chesters and others (1991) summarize the chemistry of these two compounds. The current drinking water standards for atrazine in Wisconsin are an enforcement standard (ES) of 3.0 μ g/l and a preventive action limit (PAL) of 0.3 μ g/l (Chapter NR 140, Wisconsin Administrative Code). These two standards are based on the sum of the parent atrazine concentration plus the concentrations of the two atrazine metabolites.

1.12

Background

This study, and the study by Chesters and others (1991), were outgrowths of concerns about groundwater contamination by atrazine, and followed several years of regulatory monitoring by the Wisconsin Department of Agriculture, Trade, and Consumer Protection (WDATCP) and the Wisconsin Department of Natural Resources (DNR). Preliminary monitoring programs in the lower Wisconsin River valley showed detectable atrazine in shallow wells installed immediately downgradient from agricultural fields having sandy soils, shallow groundwater, and irrigation (Postle, 1987). The WDATCP conducted the Grade A Dairy Farm Well Water Quality Survey in 1988 to provide information that would determine the need for atrazine and alachlor rules (LeMasters and Doyle, 1989). The study sampled randomly-chosen wells on Grade A dairy farms and concluded that between 10 and 16 percent of wells on Grade A dairy farms in Wisconsin contained detectable levels of pesticides. Between 9 and 15 percent of the wells had detectable amounts of 44 atrazine. In Dane County, over 50 percent of the wells sampled contained detectable atrazine. This result was surprising because most domestic wells in Dane County are completed in bedrock aquifers and cased a minimum of 40 ft below ground surface.

As a follow-up to the Grade A Dairy Farm Well Water Quality Survey, WDATCP, WDNR, and Ciba-Geigy, an atrazine manufacturer, developed a rural well sampling program in which 2100 home owners across Wisconsin sent a sample of their well water to WDATCP and Ciba-Geigy for analysis. Over 32 percent of the wells sampled in through this program in Dane County contained detectable levels of atrazine, based on a low-cost immunoassay test (LeMasters, oral comm., 1991).

2

These pesticide detections raised concerns over the susceptibility of groundwater beneath agricultural fields, especially in Dane County, and the potential health risks associated with contaminated drinking water. In response to these concerns, the Wisconsin Legislature approved the Atrazine Rule, Chapter Ag 30, Wis. Adm. Code, which became effective April 15, 1991. This rule authorized the establishment of "atrazine management areas" and "prohibition areas" in which the use of atrazine is restricted or prohibited.

The sampling programs undertaken by WDATCP and WDNR identified the presence of atrazine in groundwater. However, these previous studies were primarily based on randomly-chosen wells without regard for such hydrogeologic controls as well depth, casing depth, aquifer type, position in a groundwater flow system, well condition, and so forth. More information was needed to assess the susceptibility of bedrock aquifers to atrazine contamination and determine whether the contamination results from point (pesticide spills or backsiphoning) or non-point (field application) sources. In particular, the WDATCP required better information on possible relationships between the occurrence of atrazine in groundwater and hydrogeologic controls on groundwater movement in order to develop a rational procedure for delineating certain areas as atrazine management or moratorium areas. This project and the parallel project of Chesters and others (1991) were designed to begin to answer these questions.

Objectives

In July, 1989, the Wisconsin Geological & Natural History Survey initiated a research project, with joint funding from the Wisconsin Department of Agriculture, Trade, and Consumer Protection (WDATCP) and the Wisconsin Department of Natural Resources (WDNR). Goals of the overall project were as follows:

- 1. to determine the extent of groundwater contamination by agricultural pesticides in bedrock aquifers in part of Dane County, Wisconsin, and to delineate the distribution of contaminants in the aquifers,
- 2. to determine whether the concentrations of contaminants vary with time, season, or precipitation,
- 3. to determine the rates and directions of movement of contaminated groundwater, and, if possible, to determine the sources of contamination.

The project was conducted in two phases, with differing objectives, and this report follows the same organization. Phase I of the project consisted of a survey of

pesticide concentrations in water produced by domestic wells in five small groundwater basins in the unglaciated part of western Dane County. The object of this phase of the project was to characterize regional pesticide concentrations in groundwater at a greater sampling density than was available from previous atrazine surveys, to attempt to relate pesticide concentrations to physical basin characteristics, and to identify one basin for more extensive study.

Phase II of the project consisted of a detailed hydrogeologic investigation of a single small groundwater basin where atrazine was present in several domestic wells. The objectives of phase II were to attempt to identify the source of the atrazine and to characterize the local groundwater flow system in the basin.

The material in this report is condensed and slightly modified from a M.S. thesis by McGrath (1991), and the reader is referred to this thesis for more details about the work discussed here. During the same time as the research described here was carried out Chesters and others (1991) undertook a similar study in the glaciated part of Dane County. The work of Chesters and others focused on the presence and movement of atrazine in relatively shallow unlithified materials (till), while the work reported here focuses on the presence and movement of atrazine in deeper bedrock aquifers.

SECTION I: A SURVEY OF ATRAZINE IN BEDROCK AQUIFERS IN FIVE SMALL BASINS IN WESTERN DANE COUNTY, WISCONSIN

Methodology

Basin Selection

Five small basins in western Dane County were selected for groundwater sampling. For the purposes of this report, a groundwater basin is defined as an area containing a local groundwater flow system and surrounded by potentiometric divides. In southwestern Wisconsin groundwater basins often coincide with topographic surface water basins. Within these basins, dairy farms, cropped fields (primarily corn), and residential developments coexist. The five basins fit the following criteria:

- 1) All basins were located in the unglaciated part, or driftless area, of Dane County. The Driftless Area refers to the southwestern portion of Wisconsin that was not covered by the continental ice sheet during the Pleistocene Epoch. This area contains relatively steep topography, thin upland soils, and high relief. Most domestic wells in the Driftless Area produce water from bedrock aquifers.
- 2) Each basin contained well-defined topographic boundaries producing local groundwater flow systems.
- 3) Each basin contained several Grade A dairy farms and corn fields.
- 4) An adequate collection of well construction reports, containing information such as casing depth and stratigraphy, was available for existing wells in each basin.

The study basins were distributed throughout the driftless area of Dane County in order to represent various soil types and bedrock lithologies. The five basins selected are outlined and labeled A - E in figure 1. Table 1 summarizes the basin characteristics. Basin areas ranged from 1.7 to 5.9 mi², and the number of wells sampled per basin ranged from 6 to 17, giving sampling densities of between 2.0 and 3.7 wells/mi². All basins sampled in this survey reflect typical driftless area physiography and land use patterns. In order to limit sampling bias, representative sampling locations were selected with the same criteria in each basin. Sites with potential point sources near the wellhead were avoided. Brief discussions with farmers in each basin indicated pesticide use in the areas was similar.



Basin	Location	Area (mi ²)	# wells sampled	wells per mi ²
А	County KP/Otto Kerl Rd, near Cross Plains	5.9	12	2.0
В	Union Valley, near Cross Plains	1.7	4	2.4
С	Pine Bluff	2.4	6	2.5
D	Fryes Feeder, near Mt Horeb	4.6	17	3.7
E	Milum Creek, near Montrose	3.5	9	2.6

Table 1. Characteristics of the five study groundwater basins in western Dane County. See figure 1 for basin locations.

Water Sampling

Groundwater samples were collected from 48 domestic and public wells and springs in the five basins during December, 1989, and many wells were resampled in June, 1991. Samples were analyzed for pesticides, nitrate-nitrogen, and chloride. Specific conductance and temperature were measured *in situ* at each sampling location. The 48 sampling locations included 10 dairy farms, 5 public buildings, 10 non-dairy farmhouses, 19 private homes on non-agricultural land, and 4 springs. Sampling points were chosen to reflect representative locations throughout each basin. Samples were collected from wells located on ridges (probable groundwater recharge areas) and in valley bottoms (probable groundwater discharge areas). Sites with obvious surficial contaminant sources were avoided. A Wisconsin Unique Well Identification Number (WUWN) supplied by the WDNR was assigned to all wells sampled. Well locations are identified on basin maps in Appendix A.

Sampling techniques followed approved WDNR guidelines (WDNR, 1987). Where possible, samples were taken from a sampling tap located between the well and the pressure tank. Alternatively, a cold water faucet was used for sample collection if the pressure tank was inaccessible. At all locations, the water flowed for at least 5 minutes prior to sampling. Pesticide samples were collected in washed and capped one-liter amber glass bottles with Teflon lined caps provided by the laboratory. Nitrate-nitrogen and chloride samples were collected in 250-ml polypropylene bottles.



Figure 1. Location and bedrock geology of the five study basins in western Dane County, Wisconsin.

7

Pesticide samples were analyzed by the WDATCP Laboratory using the Neutral Extractable Method of the State Lab of Hygiene Organics Section, Method 1200 (Wis. Lab. of Hygiene, 1988). The analytes detectable with this method are

Analvte	Analyte
•	
Alachlor	Lindane
Aldrin	Linuron
Atrazine	Malathion
Benefin	Methamidaphos
HC	Metolachlor
Bladex	Methoxychlor
Casoron	Methyl Parathion
Chlordane	Parthion
Chlordene	PCB
Chlorothalonil	PCNB
Chlorpyrifos	Pendamethlin
Dacthal	Phorate
DDT	Phorate-Oxygen analogue
Diazinon	Phthalates
Dieldrin	Prometone
Dimethoate	Sencor
Disulfoton	Simazine
Endosulfan	Sutan
Endrin	Terbufos
Eptam	Trifluralin
Fonofos	
HCB	
Heptachlor	
Heptachlor Epoxide	

Table 2. Analytes recoverable through the Neutral Extractable Method

Neutral Extractable Method, Method 1200, State of Wisconsin Hygiene Laboratory, Organics Section

listed in Table 2. Nitrate-nitrogen and chloride samples were analyzed by the Soil and Plant Analysis Lab, University of Wisconsin-Extension. In addition to the compounds listed in Table 2, samples taken during 1991 were tested for deisoproplyated atrazine and desethylated atrazine, the two toxicologically significant atrazine metabolites. Accurate laboratory methods for determination of these metabolites were not available during the initial 1989 sampling round.

Basin Characteristics

Geography and Climate

The Driftless Area of Wisconsin was not covered by continental glaciation during the Pleistocene. Topography of the groundwater basins is characterized by undulating to rolling ridges, steep valley walls, and narrow valley bottoms. Maximum relief in the basins ranges from 370 ft in basin A to 180 ft in basin E.

Average air temperature in Dane County ranges from 16.7° F in January to 71.4° F in July. Approximately 30 inches of precipitation falls annually. Over 60 percent of the annual precipitation falls during the growing season, which extends from late April to early October.

Geology

Sandstones, dolomites, and shales of Cambrian and Ordovician age underlie the soil mantle in the driftless area of western Dane County (fig. 2) (Cline, 1965). Thin layers of alluvial sediments derived from fluvial and slope wash origin are found in the valley bottoms.

The two northern basins (A and B) have similar geologic settings (fig. 3). Dolomite of the Prairie du Chien Group of lower Ordovician age caps ridges in this area. Along the northeast ridge of basin A, moraines composed of sandy till represent the farthest extent of Pleistocene glaciation and overlie the Prairie du Chien Group. Till deposits are up to 75 ft thick. Sandstones of the Jordan Formation, St. Lawrence Formation, and Tunnel City Group underlie the dolomite and form the valley walls and bottom. The sandstones serve as the primary bedrock aquifer for domestic wells in the area.

The three southern basins (C, D, and E) developed higher in the stratigraphic section (fig. 3). Dolomites and limestones of the Sinnipee Group (Upper Ordovician) cap ridges in this area. Sandstone and shale of the Middle Ordovician St. Peter Formation underlie the Sinnipee Group and commonly form valley walls. Dolomite of the Prairie du Chien Group, found in the valley bottom, serves as the primary aquifer in most of the region. The contact between the Prairie du Chien and St. Peter is an unconformity which exhibits large local relief and creates large variations in the Prairie du Chien thickness. For example, the Prairie du Chien Group is approximately 150 ft thick within basin D, and may be only 20 ft thick within basin E. Locally, domestic wells withdraw groundwater from bedrock formations other than the Prairie du Chien due to variable thickness. In both basins C and E, domestic wells also withdraw groundwater from sandstones of the Cambrian Jordan Formation, St. Lawrence Formation, and Tunnel City Group.

9







Northern Basins (A & B)



Southern Basins (C, D, E)

Figure 3. Representative geologic cross sections showing general bedrock stratigraphy in basins A and B (top) and C, D, E and F (bottom).

11

Hvdrogeology

Topography and surface hydrology suggest that local groundwater flow systems exist within each basin. Recharge to the local flow systems probably occurs primarily along the broad undulating ridges which are also surface water divides. Springs and wetlands found in the valley bottoms are locations of local groundwater discharge.

The local hydrogeologic systems depend on basin stratigraphy. In the northern basins, recharge along the ridges flows through an unsaturated zone which may consist of till (up to 75 ft thick), Prairie du Chien dolomite (10 - 80 ft), and the Jordan sandstone (20 - 40 ft). The St. Lawrence sandstone (30 ft thick) and the Tunnel City Group sandstone (50 ft) compose the primary aquifers for domestic wells in the basin.

In the southern basins till is absent and recharge moves through the Sinnipee Group dolomites and limestones (up to 120 ft thick), St. Peter Formation sandstone and shale (30 - 60 ft), and the upper part of the Prairie du Chien dolomite (10 ft). The Prairie du Chien dolomite (up to 150 ft thick) is the principal aquifer.

The lithologic differences of these units (fig. 3) suggest that recharge in the northern basins may be less rapid than recharge in the southern basins. Recharge in the northern basins is primarily through interconnected pore spaces in sandstone. Recharge in the southern basins flows through joints, fractures, and solution channels in the Sinnipee and Prairie du Chien Groups. Such lithologic and flow path differences may influence the amount of contaminants reaching the water table.

Soils

Soil characteristics in the five basins reflect the bedrock beneath the soil horizon. Soils found in the small basins formed primarily from loess, dolomite, and sandstone (USDA, 1978). Most of the soils on the broad undulating ridges formed partly in loess. Along valley slopes and drainage channels where the loess eroded, soils formed in the weathered dolomite and sandstone. Along the glaciated north ridge of basin A, the soils are moderately to well drained silt loams with thicknesses of five to ten ft. On the valley slopes of basin B, moderately to somewhat excessively well drained sandy loams are underlain by sandstone. The soils found in the two northern basins have a lower pH range (5.1 to 6.5) than soils found in the southern basins. Moderately well drained, shallow silt loams on the ridges in basins C and D are underlain by fractured dolomite. The soils in these southern basins are neutral to mildly alkaline (6.6 to 7.8).



Figure 4. Soil Contamination Attenuation Potential (SCAM) map for basin D.

Soil associations based on seven physical and chemical characteristics are used to evaluate soil contaminant attenuation-potential according to the method described in Cates and Madison (1990). Four soil attenuation potential classifications - *best*, *good, marginal*, and *least* - reflect a soil solum's ability to attenuate contaminants. The distribution of soils in a particular basin can be used to map potential contaminant attenuation, as illustrated in figure 4 for basin D. Soil attenuation-potential maps for the other basins are found in McGrath (1991).

Land Use

Approximately 80 percent of the total land area in Dane County is used for ricultural purposes (Wisconsin Blue Book, 1990), and dairy farms are the major erprise in western Dane County. Within the five study basins, agricultural fields

occur both on the ridges and in the valley bottoms. Grazing areas often occur on the valley slopes or at the base of the valley walls.

In Wisconsin, farmers commonly apply one or more pesticides to corn fields. Common herbicides applied include atrazine (Aatrex), alachlor (Lasso), cyanazine (Bladex), dicamba (Banvel), metolachlor (Dual), and pendimethalin (Prowl). In 1985, a total of 5.2 million pounds of atrazine was applied to 77 percent of the acres planted with corn (WDATCP, 1986). Alachlor was applied to 41 percent of the corn and soybean acreage planted in 1985.

Well Construction

Well construction reports were available at the WGNHS for all wells sampled. Data from these well construction reports are compiled in McGrath (1991). According to the construction reports, all wells sampled complied with construction requirements for potable wells set forth in the Wisconsin Well Code (WDNR, 1989). Prior to sampling a well, observations at each site confirmed that the well appeared to meet requirements. However, this study could not conclusively verify that each well fully complied with the Code.

Basin	No of wells	Depth to rock (ft)		Casing depth (ft)		Depth (to water (t)	Total well depth (ft)	
		Mean	Range	Mean	Range	Mean	Range	Mean	Range
А	10	32	3-107	97	42-185	130	17-235	208	90-230
В	4	35	1-120	69	41-130	18	14-20	112	85-158
С	6	7	2-17	66	40-139	105	57-170	185	140-220
D	15	6	0-31	59	31-219	77	13-180	144	66-230
E	9	5	0-12	53	29-102	42	18-75	108	75-132

Table 3. Well construction characteristics by basin.

Well construction characteristics, such as the depth of the well or the depth of the casing, influence the susceptibility of groundwater to contamination. Well construction characteristics compiled by basin are presented in Table 3. In general, well construction reflects the hydrogeologic setting. In basin A, the average depth to groundwater is 130 ft, and wells average 208 ft depth with 130 ft of casing. In contrast, average depth to groundwater in basin E is 55 ft. Wells sampled in basin E average 53 ft of casing and are 120 ft deep. Wells in the two northern basins (A and B) averaged over 30 ft to bedrock, while wells in the southern three basins averaged less than 10 ft to rock.

Sampling Results

Atrazine

Of the 44 analytes tested, only atrazine or its metabolites were present at detectable concentrations in groundwater during the 5 basin survey. Figure 5 summarizes the results and individual well results are tabulated by basin in Table 4. Atrazine was detected in 17 of 80 water samples, and desethylated atrazine was detected in 6 of 33 water samples at concentrations above the detection limit of 0.15 micrograms per liter (μ g/l). Overall, atrazine or desethylated atrazine, or both, were found in 26% of the samples tested. In 6 of the 80 samples the concentration of atrazine was above the PAL of 0.3 μ g/l based on parent alone, and in 14 of the 80 samples the sum of atrazine plus metabolites exceeded the PAL. One sample exceeded the atrazine ES of 3.0 μ g/l; this was a concentration of 3.14 μ g/l. Desethylated atrazine was detected in four samples where the parent compound was not detected; deisoproplyated atrazine was not detected in any sample.





15

Table 4. Summary of results of groundwater sampling of domestic wells in Dane County during the five basin study. Shading indicates wells where atrazine or its metabolites were detected.

Wisconsin Unique Well Number	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Deisoprop lyated Atrazine (µg/l)	Atrazine plus metabolites (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25 °C)	Cl (mg/l)
AQ781	12/02/89	0.00			0.00	1.5	9.0	579.6	3.5
AQ781	06/21/91	0.00	0.00	0.00	0.00				
AQ782	12/02/89	0.00			0.00	0.0	8.0	603.6	4.5
AQ784	12/04/89	0.00			0.00	3.5	9.0		5.5
AQ784	06/21/91	0.00	0.00	0.00	0.00				
AQ785	12/04/89	0.00			0.00	5.0	8.0	686.6	7.0
AQ785	06/26/91	0.00	0.00	0.00	0.00				
AQ786	12/04/89	0.00			0.00	2.0	7.5	650.5	13.5
AQ790	12/04/89	0.00			0.00	5.0	10.0	614.1	6.5
AQ790	06/21/91	0.00	0.00	0.00	0.00				
AQ791	12/04/89	0.00			0.00	0.5	8.5	572.8	1.0
AQ792	12/05/89	0.00			0.00	0.0	12.0	576.1	0.5
AQ792	06/26/91	0.00	0.00	0.00	0.00				
AQ793	12/05/89	0.00			0.00	0.5	8.0	580.9	3.5
AQ793	06/26/91	0.00	0.00	0.00	0.00				
AQ814	12/12/89	0.00			0.00	1.0	7.0	551.3	1.5
AQ814	06/21/91	0.00	0.00	0.00	0.00				
SPRING	12/12/89	0.00			0.00	1.0	5.0	585.3	4.5
SPRING	12/14/89	0.00			0.00	0.0	5.0	544.1	0.0

Basin A: County KP/Otto Kerl Road near Cross Plains

Basin B: Union Valley, near Cross Plains

Wisconsin Unique Well Number	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Deisoprop lyated Atrazine (µg/l)	Atrazine plus metabolites (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25 °C)	Cl (mg/l)
AQ787	12/05/89	0.00			0.00	3.0	9.0	579.6	8.5
AQ787	06/21/91	0.00	0.00	0.00	0.00				
AQ794G	12/05/89	0.00			0.00	0.0	12.0	447.3	1.5
AQ795	12/05/89	0.00			0.00	5.0	9.0	807.1	23.5

Ì

AQ811	12/11/89	0.00			0.00	1.5	9.0	425.6	4.0
AO811	06/21/91	0.00	0.00	0.00	0.00				

Basin C: Pine Bluff

Wisconsin Unique Well Number	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Deisoprop lyated Atrazine (µg/l)	Atrazine plus metabolites (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25 °C)	Cl (mg/l)
AQ796	12/05/89	0.00			0.00	5.5	9.0	660.4	13.5
AQ802	12/09/89	0.00			0.00	3.5	7.0	590.1	5.0
AQ803	12/09/89	0.17			0.17	3.5	8.0	573.4	6.5
AQ803	06/28/91	0.00	0.36	0.00	0.36				
AQ815	12/12/89	0.52	ger Maria - Star Balanda Star Balanda - Star Balanda Star Balanda - Star Balanda		0.52	14.0	10.0	999.7	53.5
AQ816	12/12/89	0.44			0.44	11.0	9.0	484.3	14.5
AQ817	12/12/89	0.30	an la chuir ann an 1999. Tha ann an 1999 ann an 199 Tha ann an 1999		0.30	27.0	4.0	1361.2	61.0

Basin D: Fryes Feeder, near Mt Horeb

Wisconsin Unique Well Number	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Deisoprop lyated Atrazine (µg/l)	Atrazine plus metabolites (µg/l)	NO ₃ -N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25 °C)	Cl (mg/l)
AQ788	12/11/89	0.00			0.00	4.5	8.0	671.5	15.0
AQ788	05/03/90	0.00	0.00	0.00	0.00	4.0	11.8	783.4	16.0
AQ788	06/28/91	0.00	0.00	0.00	0.00				
AQ797	12/06/89	0.00			0.00	3.0	10.5	613.0	7.0
AQ797	05/03/90	0.00	0.00	0.00	0.00	3.0	11.5	617.9	7.0
AQ797	06/28/91	0.00	0.00	0.00	0.00			u ku	
AQ798	12/06/89	0.52	د. مانعات مدان کار کروهم		0.52	5.0	8.0	845.0	39.5
AQ798	04/26/90	0.28	0.37	0.00	0.65	5.0	12.2	944.1	32.5
AQ798	12/10/90	0.26	0.00	0.00	0.26		8.5	818.4	
AQ798	06/11/91	0.20	0.00	0.00	0.20				
AQ799	12/07/89	0.28			0:28	4.5	11.0	834.6	41.5
AQ799	04/30/90	0.00	0.00	0.00	0.00	3.5	12.5	903.5	42.0
AQ799	06/28/91	0.00	0.61	0.00	0.61				
AQ800	12/07/89	0.26			0.26	4.0	9.0	616.3	9.0
AQ800	04/26/90	0.00	0.20	0.00	0.20	4.0	14.5	586.3	75
AQ801	12/07/89	0.19			0.19	14.0	8.0	1282.6	69 <i>.</i> 5
AQ801	04/26/90	0.00	0.17	0.00	0.17	3.0	12.6	1335.2	85.0
AQ801	12/20/90	0.58	0.69	0.00	1.27		9.0	953.8	

61.00	The second s	NAMES AND ADDRESS AND ADDRES		(2) S. M. A. K. S. S. M. M. M. M. S. M.	 A second state of the second stat	1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	An alaba and a share of the	a state de set de la companya de la		
	AQ801	06/14/91	0.23	0.00	0.00	0.23				÷
	AQ804	12/07/89	0.00	0.00	0.00	0.00	2.5	12.0	616.8	12.5
	AQ805	12/09/89	0.00			0.00	3.0	9.0	616.3	3.5
	AQ805	05/12/90	0.00	0.00	0.00	0.00	2.5	11.5	590.4	2.5
	AQ806	12/09/89	0.37			0.37	7.0	8.0	905.4	15.0
	AQ806	05/12/90	0.00	0.00	0.00	0.00	7.5	10.4	883.2	17.0
	AQ806	06/11/91	0.17	0.00	0.00	0.17				
	AQ812	12/11/89	0.00			0.00	1.0	9.0	198.1	4.5
	AQ812	05/12/90	0.00	0.00	0.00	0.00	2.0	11.0	250.4	5.0
	AQ813	12/11/89	0.00			0.00	3.5	12.0	813.4	20.5
	AQ818	12/12/89	0.00			0.00	3.5	7.0	590.1	5.0
	AQ819	12/12/89	0.00			0.00	3.5	7.0	543.5	16.0
	AQ824	12/15/89	0.00	0.00	0.00	0.00	4.5	8.0	603.6	12.0
	AQ825	12/15/89	0.00			0.00	2.0	10.0	621.3	5.5
	AQ825	05/15/90	0.00	0.00	0.00	0.00	3.5	13.0	594.9	9.5
	AQ826	04/30/90	0.00	0.00	0.00	0.00	7.0	10.6	653.6	6.0
	SPRING	12/09/89	0.00			0.00	2.0	4.0	646.6	7.5
	SPRING	12/11/89	0.00			0.00	2.0	8.0	535.7	3.5

Basin E: Milum Creek, near Montrose

Wisconsin Unique Well Number	n Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Deisoprop lyated Atrazine (µg/l)	Atrazine plus metabolites (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25 °C)	Cl (mg/l)
AQ789	12/02/89	0.00		an an in the state of the state of the	0.00	1.5	8.0	498.0	3.5
AQ807	12/09/89	3.14			3.14	17.5	10.0	1023.3	42.5
AQ808	12/09/89	0.00			0.00	4.5	9.0	587.0	11.5
AQ809	12/09/89	0.00			0.00	19.5	8.0	475.3	49.0
AQ810	12/09/89	0.00			0.00	4.0	10.0	242.8	20.5
AQ820	12/13/89	0.00			0.00	3.5	9.0	498.9	6.5
AQ821	12/13/89	0.19			0.19	8.5	7.0	357.2	12.5
AQ822	12/13/89	0.00			0.00	2.0	7.0	900.7	29.5
AQ823	12/13/89	0.00			0.00	5.5	7.0	590.1	9.0

The frequency of atrazine detection varied by basin. Neither atrazine nor its metabolites were detected in any of the 25 samples from the 16 wells in the two northern basins (Basins A and B; see Table 4). In the three southern basins, detectable atrazine was present in 17 of 52 samples from 32 wells or springs. The types of locations having atrazine detections included Grade A dairy farms, non-dairy farm houses, two private homes on non-agricultural land, a church, and a town hall.

The detection of atrazine in a given well was generally repeatable with time, although several exceptions occurred and absolute levels differed. In basins A and B no atrazine was detected in either the 1989 or 1991 samplings. In basin D most wells with a non-detect in 1989 were also negative in 1991, and all wells having detections in 1989 were also positive in 1991. However, two wells in which atrazine was detected in 1989 and 1991 did not test positive for atrazine in an intermediate sampling in 1990.

Other Indicator Parameters

Nitrate-nitrogen, chloride, and specific conductance are commonly used as indicator parameters of groundwater contamination in agricultural regions. Nitrogen and chloride occur naturally at only very low levels (on the order of 1 mg/l) in shallow bedrock aquifers in south-central Wisconsin, but often occur at elevated levels where groundwater contamination from surface processes has occurred. Likely potential sources of nitrate-nitrogen in western Dane County include fertilizers and human and animal waste. Likely sources of chloride include human and animal waste and highway deicing salts. Specific conductance is the ability of water to conduct an electric current, and is a general measure of the total ionic strength of the water. Elevated values of specific conductance can be an indicator of groundwater contamination.

Nitrate-nitrogen concentrations were generally higher in wells with atrazine detections (Table 5). Nitrate-N concentrations ranged from less than 0.5 to 27 mg/l. In 6 of the 47 nitrate samples (13 percent), the concentration of nitrate-N was greater than the ES of 10 mg/l. At locations with detectable atrazine, seven of the eight highest nitrate concentrations (7 to 27 mg/l) were reported. Nitrate concentrations exceeding the ES were found at three Grade A dairy farms, a non-dairy farm, a private home, and a church.

Groundwater from wells with detectable atrazine contained an average chloride concentration of 33.2 mg/l compared to an overall average chloride concentration of 14.9 mg/l (Table 5). Chloride concentrations ranged from less than 0.5 to 69.5 mg/l. Six of the seven highest chloride concentrations (39.5 to 69.5 mg/l) reported occurred at wells with detectable atrazine.

	Samples with Atrazine			Samples without Atrazine			
Parameter	n	Mean	Range	n	Mean	Range	
Nitrate-N (mg/l)	11	10.6	3.5-27	36	3.1	0-19.5	
Chloride (mg/l)	11	33.2	6.5-69.5	36	9.7	0-49	
Specific Conductance (µmho/cm)	11	563	230-850	37	380	135-600	

 Table 5. Comparison of samples with and without atrazine.

Specific conductance measurements ranged from 170 to 800 (μ mho/cm). The average conductivity measurement for all samples was 430 μ mho/cm. At wells with detectable atrazine, conductivity measurements averaged 560 μ mho/cm. Seven of the eight highest conductivity measurements (560 to 850 μ mho/cm) were found at wells with detectable atrazine.

Discussion

Groundwater Chemistry

In spite of limited data, the locations of the atrazine detections suggest that contamination is not limited to individual farms or agricultural fields. In basin D, four consecutive wells along a three-quarter mile section of road contained detectable atrazine. In basin C, four detections were scattered over an area of one square mile. Atrazine contamination in wells located on land with no prior record of atrazine use suggests that atrazine and its metabolites are mobile in the subsurface.

Because of variability in soil types in the area sampled, soil composition and permeability are not basin attributes suitable for determining a region's susceptibility to groundwater contamination. However, the extent of pesticide detections in basins with shallow soil profiles indicates that soil depth, an attribute more easily measured and mapped than permeability, influences groundwater susceptibility.

Soil associations immediately adjacent to wells sampled were compiled to consider the relationship between atrazine detections and soil attenuation-potential ratings (McGrath, 1991). All wells without atrazine detections in basins A, B, and C are located in areas with soils rated *good* or *best*. However, over 60 percent of wells with atrazine in basins C, D, and E are also located in areas with soils of *good* or *best* potential to attenuate contaminants. In basins C and D, most wells located in areas with soils rated *marginal* or *least* did not have atrazine detections.

Since contamination might not occur immediately adjacent to a well, soil associations for land upgradient and within one-half mile of each well were compiled. Table 6 lists the percentage of wells with a particular soil rating that is found upgradient of the well. For example, soil rated as marginal is found upgradient of 36.4 percent of the wells in basin D. In basins C, D, and E, soils rated least are found upgradient of less than 55 percent of wells with atrazine detections. Over 50 percent of the wells without atrazine detections in basins D and E have soil of marginal or least attenuation potential upgradient. These results are inconclusive because the soil attenuation potential maps were not directly compared to the zones of contribution for individual wells. (An ongoing study by Bohn and others (1991) is attempting to compare atrazine detections with soils data and land use within the zones of contribution of individual wells.)

The absence of atrazine detections in the two northern basins may be due to geology. Shallow groundwater flow in the northern basins (A and B) occurs mostly through Cambrian sandstone units (see figures 1 and 3) where primary porosity dominates. In the southern basins, groundwater flow is mostly through dolomite and limestone of the Prairie du Chien Group, where fracture porosity may be more dominant. Groundwater in this fractured environment might move rapidly through fracture conduits, with little or no attenuation of contaminants. Nine of eleven wells with detectable atrazine were finished in dolomite of the Prairie du Chien Group.

Effect of Well Construction and Local Geologic Setting

Well construction factors may increase the probability that a well will yield water contaminated by pesticides or barnyard runoff. For instance, wells with shallow casings or faulty annular seals could provide conduits from the land surface to the aquifers. Shallow wells are generally more susceptible to contamination than are deeper wells. In addition, local hydrogeologic factors, such as shallow bedrock or shallow water table, might contribute to a well being highly susceptible to contamination. In order to determine whether well characteristics and local hydrogeologic setting were related to the presence of atrazine in water produced by the well, wells were grouped according to the absence and presence of atrazine. Mean values of casing depth, water depth, bedrock depth, and total well depth are compiled in Table 7. In this study, atrazine was detected more frequently in wells with shorter average casing depths and shallower average total depths. In addition, wells with atrazine detections had shallower average bedrock depths and shallower depths to groundwater. However, McGrath (1991) concluded that the number of wells sampled in each basin was too small to prove a statistically valid relationship

Soil Rating Adjacent to Wells Sampled Wells with Atrazine Detections								
BASIN	% Best	% Good	% Marginal	% Least				
А	0.0	0.0	0.0	0.0				
B	0.0	0.0	0.0	0.0				
C	25.0	50.0	0.0	25.0				
D	20.0	60.0	0.0	20.0				
Ē	0.0	66.7	33.0	0.0				

Table 6. Soil attenuation potential ratings for various areas near sampled wells.

Note: As an example. 25% of wells with atrazine detection in Basin C are located in area of best rating.

Soil Rating Adjacent to Wells Sampled Wells without Atrazine Detections

BASIN	% Best	% Good	% Marginal	% Least
А	27.3	72.7	0.0	0.0
В	75.0	25.0	0.0	0.0
c	25.0	50.0	0.0	0.0
D	20.0	42.9	14.3	28.6
E	0.0	33.3	50.0	16.7

Soil Rating Upgradient of Wells Sampled Wells with Atrazine Detections

BASIN	% Best	% Good	% Marginal	% Least
А	0.0	0.0	0.0	0.0
в	0.0	0.0	0.0	0.0
Ċ	25.0	100.0	50.0	25.0
D	18.2	96.0	36.4	54.6
Ē	66.7	100.0	33.3	0.0

Note: As an example, 25% of wells with atrazine detections in Basin C have soil rated best upgradient of wellhead.

Soil Rating Upgradient of Wells Sampled Wells without Atrazine Detections

BASIN	% Best	% Good	% Marginal	% Least
А	18.2	100.0	9.0	72.8
В	66.7	66.7	22.2	44.4
С	66.7	100.0	0.0	0.0
D	16.6	66.7	50.0	66.7
E	0.0	54.6	90.1	54.6

÷.•.

Well	Wells with atrazine			Wells without atrazine			
characteristic	<u>n</u>	Mean	Range	<u>n</u>	Mean	Range	
Casing depth (ft)	11	52	31-139	33	74	29-219	
Bedrock depth (ft)	11	9	2-31	33	16	0-120	
Water depth (ft)	11	64	13-170	33	86	14-235	
Total depth (ft)	11	136	66-220	33	160	75-320	

Table 7. Comparison of well construction details for wells with and without atrazine detections.

between well construction factors and the presence of atrazine in a particular well.

Bedrock aquifers in south-central Wisconsin are susceptible to atrazine contamination. Atrazine and/or its metabolites were detected in groundwater samples collected from wells and springs in three of five basins in western Dane County. Contamination was not limited to farms or agricultural fields; wells supplying public buildings and private homes also contained detectable atrazine. Most detections were at concentrations less than 0.5 μ g/l. Wells with atrazine commonly contained elevated nitrate, chloride, and specific conductance.

Soil thickness and bedrock lithology seem to be the most important basin attributes in determining the susceptibility of groundwater in the basin to contamination. Soil attenuation-potential ratings for land adjacent or upgradient to wells cannot be used exclusively to accurately predict the location of atrazine contamination. Areas with thin soil horizons underlain by carbonate bedrock appear to be most susceptible to contamination. Basins where groundwater flow was mainly through dolomite contained more atrazine detections than basins where groundwater flow was mainly through sandstone.

Absence of atrazine detections in basins A and B may be attributed to the combination of soil with good and best attenuation-potential ratings, a greater average depth to groundwater, and thinner dolomite layers. Atrazine detections in basins C, D, and E may occur because of thicker dolomite layers and a shallower average depth to groundwater.

SECTION II: ATRAZINE CONTAMINATION OF GROUNDWATER IN THE FRYES FEEDER BASIN, NEAR MT HOREB, WISCONSIN

Purpose

A detailed examination of pesticide concentrations, hydrogeology, and land use was carried out in a small groundwater basin southwest of the village of Mt. Horeb, Wisconsin. Specific purposes of the research efforts in this groundwater basin were as follows:

-to assess the occurrence and distribution of atrazine and other pesticides in groundwater in bedrock aquifers in a small basin in the driftless area of Dane County, Wisconsin,

-to establish a conceptual model for groundwater flow within the study area and to relate the distribution of pesticides to the groundwater flow system,

 \mathbb{R}^{2}

-to determine aquifer parameters, such as hydraulic conductivity and recharge rates, within the basin,

-to estimate groundwater flow rates and groundwater age within the basin,

-to determine the contributing areas for domestic wells in the basin,

-to attempt to determine the source of atrazine in groundwater in the basin.

Study Area Description

Location

The study area consisted of part of the Fryes Feeder basin (basin D in Section I of this report), located about one mile southeast of Mt Horeb, Wisconsin (fig. 6). This basin was selected for intensive study because it contained several bedrock wells where atrazine was detected in the five-basin survey discussed in Section I, it had easily-defined topographic and hydrogeologic boundaries, land use was typical of much of the driftless area of southwest Wisconsin, and several landowners in the basin expressed a willingness to participate in the research. The area of the entire basin was 4.6 mi². After choosing this basin we focused the study on a smaller subarea of about one mi² at the junction of sections 20, 21, 28, and 29, T 6 N, R 7 E. Figure 7 shows details of this subarea, which extends from the ridge crest on the west to Fryes Feeder creek. The area contained parts of three farms and three non-farm residences.



Figure 6. Location of the Fryes Feeder basin.

25

Land use

Land use in the subarea is typical of the basin as a whole. Agricultural fields, pastures, and barns are identified in fig. 7. A dairy farm (domestic well AQ801), with approximately 50 cows, is located in the middle of the subarea. Fields to the north (domestic well AQ798) were cultivated until 1988 when the property was enrolled in the Conservation Resource Program (CRP). Fields south of AQ801 are usually planted with corn, oats and alfalfa.

The fields along the ridge and valley slopes follow a rotation consisting of one to three years of corn followed by two to four years of alfalfa. Fields in the valley bottom have been continuously planted with corn for nearly 15 years. Atrazine was probably applied once to a field when a new rotation of corn was planted or yearly depending on the farmer's preference and the extent of weed growth. Most fields in the basin had not had an atrazine application for at least five years prior to this study. Atrazine was applied to approximately 15 acres of land on the west side of the ridge in May, 1990 (fig. 7). Fields to the north of AQ801 received annual atrazine applications prior to CRP enrollment in 1989. When atrazine was applied to fields in the basin, the reported application rate was between 1.5 and 2 pounds per acre except for the northern fields. Atrazine may have been applied at a rate of 3 to 4 pounds per acre in the northern fields. The atrazine survey in Section I of this report detected atrazine in domestic wells AQ798, AQ801, and AQ806 within the subarea.

Methodology

Borehole and piezometer installation

A series of piezometers were installed in boreholes throughout the small study area (fig. 8). In the bedrock, six boreholes were drilled by air-rotary techniques. These bedrock boreholes ranged in depth from 100 to 200 ft. Bedrock cutting samples were collected at 5-ft intervals throughout the drilling, described in the field, and transported to the WGNHS subsurface laboratory for additional analysis. All bedrock boreholes were cased to 20 ft with six inch diameter steel casing. In alluvial sediments in the valley bottom, eight piezometers were installed using solid stem augers. Soil and sediment samples were taken directly off the augers at five foot intervals. In three locations, nests of two piezometers at different depths were installed. Drilling logs are compiled in McGrath (1991).

After the completion of drilling, a borehole geophysical survey collected additional subsurface data in the six bedrock holes. Four logs, natural gamma, resistivity, spontaneous potential, and caliper, were run in each borehole. Comparison of geophysical logs aided in determining geologic correlations and formation thickness. Complete geophysical logs are included in McGrath (1991).







Figure 8. Map of the small study area, showing monitoring points.

Three piezometers of two-inch threaded polyvinyl chloride (PVC) pipe were installed in each bedrock borehole after completion of geophysical logging. In general, piezometers were positioned at the bottom of the borehole (labelled piezometer A), at an intermediate point (B), and at the water table (C). In three wells, the third piezometer (C) was installed above the water table to capture water moving through the unsaturated zone. These unsaturated piezometers were designed with a short section of unslotted casing below the piezometer screen which served as a reservoir to collect a sample of infiltrating water in the unsaturated zone. A sand pack was placed around each five foot length of piezometer screen and bentonite filled the annulus between screens to seal the borehole.

In the unlithified materials in the valley bottom, piezometers consisted of two-inch PVC pipe with either a three or five foot length of well screen. A sand pack was installed around the piezometer screen. Above the sand pack, the annulus was sealed with bentonite. In three locations, a two- piezometer nest was constructed to determine vertical hydraulic gradients in the sediment. At these locations, piezometers were positioned at the water table and just above the bedrock.

Slug Tests

Slug tests were conducted in 13 of the piezometers. The response of the water level to the introduction and removal of a three foot PVC slug was recorded using a pressure transducer and data logger. Data were plotted and analyzed using the Hvorslev method (Hvorslev, 1951).

Streamflow Monitoring

Streamflow monitoring was undertaken to determine the amount of groundwater discharging into the stream. Staff gages were installed in the stream at three locations (Fig 8). Stream level measurements recorded the water elevation in the stream. Streamflow was calculated from measurements of water velocity and channel cross sectional area. Flow velocities were measured at each stream gage with a current meter.

Water Sampling

Groundwater samples were collected for pesticide analysis during December, 1989, May, August, and December, 1990, and May, 1991. Sampling and analytical procedures were as described in Section I of this report. Samples from domestic wells and springs were analyzed for major ions and isotopes in May, 1990. Piezometers installed specifically for this project were sampled in August, 1990, for major ion and isotope analyses. Major ion analyses were checked with a
charge-balance equation to determine analytical accuracy. A charge-balance error of greater than five percent was considered unacceptable.

Precipitation samples were collected by a weather observer located in the Village of Mt. Horeb approximately 5 miles northwest of the study area. After precipitation events which exceeded 0.5 inches, rain or melted snow was collected in polypropylene bottles. Samples were analyzed for the isotopes oxygen-18 and tritium.

Soil Sampling

In order to determine whether soils in the study area could be a continuing contaminant source, soil samples were collected and analyzed for atrazine. Composite soil samples were obtained at ten sample areas. Within each of these ten sample areas we obtained soil samples at five locations using a hand-driven core sampler. Samples were collected from a depth of one foot at each location, and the five samples were mixed to create a singe composite sample for each sample area. The samples were stored in glass jars and transported to the DATCP laboratory where they were tested for atrazine content.

Geology

Aquifer lithologies

Most domestic wells within the study area withdraw groundwater from sandstones or dolomites of Ordovician age. High capacity Mt. Horeb municipal wells and a few domestic wells extend to deeper Cambrian sandstones. In the valley bottoms, monitoring wells penetrate alluvial sediments. Lithologies present in the study area are identified in the stratigraphic column in fig. 2 and on a bedrock map of the basin (fig. 1). Cross sections displaying basin stratigraphy are presented in figure 3. McGrath (1991) presents more detail on local geology.

Natural gamma logs from six boreholes in the basin (fig. 9) show the horizontal continuity of lithologic units in the subsurface and aid in identifying the units (see figure 7 for borehole locations). The upper part of the bedrock section (above 1040 ft elevation) consists of interbedded sandy dolomites, limestones, and shale partings of the Sinnipee Group. The St. Peter Formation (elevation 1010 to 1040 ft) has a very distinctive gamma signature. The upper Tonti member, a mature quartz sandstone, has very little gamma radiation, while high levels of natural gamma radiation are detected in the Reedstown member, a basal shale just below the St. Peter.

The gamma logs suggest that the Sinnipee Group is more heterogeneous than the lower Prairie du Chien Group. Below elevation 980 ft, gamma intensities





are fairly constant and low. These gamma intensities correspond to an interval of sandy dolomite in the lower Prairie du Chien. Varied natural gamma radiation levels in the upper Prairie du Chien (elevation 980 to 1010 ft) indicate shale partings are more common in this interval. In the Sinnipee Group (elevation 1040 to 1160 ft), gamma intensities vary greatly.

Caliper logs detected fractures or openings in each lithology (fig. 10). The 3-arm caliper tool measured borehole diameter, and the tool responded to fractures by indicating a slight increase in borehole diameter over a short vertical interval. This instrument can detect only near-horizontal fractures having significant aperture thickness; very narrow fractures, dipping fractures, or vertical fractures would not have been detected. Dolomites of the Prairie du Chien Group (below elevation 1020 ft on fig 10) contained the most frequent fractures, although no single fracture or fracture zone was traceable between boreholes. Increased hole diameters in the St. Peter Formation were detected in every borehole that penetrated the group. These openings may be the result of the caving of the loosely cemented sandstone and shale.

150

Hydrogeology

Distribution of hydraulic head

A water table map of the study area was constructed using head measurements from piezometers and domestic wells taken between October 13 and 20, 1990 (fig. 11). Along the ridge, the water table occurred in sandstone of the St. Peter Formation. During the drilling, groundwater in the St. Peter was believed to be perched above the basal shale layer. However, hydraulic head measurements in DN 1341 and 1342 (located along the ridge) indicated that the entire thickness of the underlying Prairie du Chien Group was saturated. The water table had a horizontal gradient of 0.04 ft/ft toward the east in the Prairie du Chien Group beneath the broad ridge. In piezometers located along the valley slope (DN 1343 and 1345) the water table was deeper than anticipated. In the valley bottom, the water table was in the alluvial sediments and had a horizontal gradient of about 0.0075 ft/ft.

The vertical component of groundwater movement was downward over much of the study area, but was upward in the valley bottom. Significant downward vertical hydraulic gradients occurred at each of the bedrock piezometer nests (DN1341-DN1346). Measurements collected from piezometer nests in the alluvial deposits confirmed upward flow in the valley bottom. The presence of springs and wetlands also suggested upward flow in the valley. Upward gradients measured in the alluvial deposits ranged from 0.08 in MW 2 and 3 to 0.02 in MW 4 and 5. The magnitude of the vertical hydraulic gradients increased near the ground surface.



Figure 10. Caliper logs from six boreholes in the Fryes Feeder basin. See fig. 8 for locations.



Figure 11. Water table in the Fryes Feeder basin, based on measurements taken in October, 1990.

Hydraulic heads in the basin varied little over time. Hydraulic heads in most bedrock piezometers varied less than four feet during 1990 - 1991. The maximum variation in head was 3.9 ft in DN 1341B. In both DN 1341A and DN 1341C, heads varied less than 2 ft. The small fluctuations observed in DN 1341 are similar to those observed in other bedrock piezometers. The response of bedrock piezometers to specific recharge events was not discernible from these data.

Greater head variations were observed in the alluvial piezometers, especially immediately following a recharge event. In the water table piezometers MW 3 and MW 5, a four foot change occurred after a thunderstorm. The rapid response to recharge events occurred due to the shallow water table and the high hydraulic conductivity of alluvial sediments.

Piezometer	Number of Tests	Hydraulic Conductivity (ft/sec)	Comments
Bedrock			
DN 1341B DN 1342A DN 1342B DN 1342C DN 1344A	2 1 1 2 3	3.5 x 10 ⁻⁴ 1.8 x 10 ⁻⁴ 3.9 x 10 ⁻⁴ 3.6 x 10 ⁻⁴ 7.7 x 10 ⁻⁵	St.Peter Fm.
DN 1344B DN 1344C DN 1346A DN 1346B	2 1 2 2	6.6 x 10 ⁻³ 3.9 x 10 ⁻⁴ 7.1 x 10 ⁻⁵ 1.6 x 10 ⁻⁴	Fracture Zone
Alluvial Sediments	5		
MW 1 MW 2 MW 4 MW 8	1 2 2 3	3.7 x 10 ⁻⁶ 7.2 x 10 ⁻⁶ 8.0 x 10 ⁻⁶ 2.9 x 10 ⁻⁴	

Table 8. Results of piezometer (slug) tests in the Fryes Feeder basin.

Hydraulic Conductivity

Hydraulic conductivities determined from the slug tests are presented in table 8. The average measured hydraulic conductivity for the Prairie du Chien dolomite was 2.3×10^{-4} ft/sec. The average hydraulic conductivity for the alluvial sediments was 7.7 x 10^{-5} ft/sec.

Groundwater velocity

The average velocity of groundwater helps control the extent of pesticide contamination. As a means to estimate groundwater velocity, the average linear velocity v, is calculated from:

$$v = (-K/n) \times (dh/dl)$$

where K is hydraulic conductivity (ft/sec), n is effective porosity, and dh/dl is the hydraulic gradient.

Based on the range of estimates for porosity and hydraulic conductivity, McGrath (1991) estimated the travel time for a conservative tracer from the ridge (recharge area) to stream (discharge area) in the saturated zone to range from 2.2 to 16.2 years. He calculated average linear velocities and corresponding travel times using hydraulic conductivities ranging from 2.3 x 10^{-4} to 2.3 x 10^{-5} ft/sec and effective porosities ranging from 0.05 to 0.10.

Such estimates require a number of assumptions. The average linear velocity calculation assumes flow through a continuous porous medium. Secondary porosity, fractures, or solution channels could decrease the actual travel times by channeling flow through discrete zones. The calculation also depends on the accuracy of the effective porosity estimate. Little information was available on the porosity of the Prairie du Chien Group, and a range was chosen to reflect uncertainty. Finally, the velocity calculations ignore the effect of vertical groundwater flow. As observed in piezometer measurements, a strong downward gradient was present along the ridge. A downward gradient could increase the actual groundwater travel times by increasing the length of flow paths. Thus, the estimated travel times are minimum travel times because they ignore the vertical component of flow.

Groundwater recharge

The conceptual model of groundwater flow in the basin assumes that groundwater discharge along the valley of Fryes Feeder is about equal to recharge on the ridges along the valley. The field data support this assumption. Mean stream discharge increased by 0.9 cubic foot per second in the 1.5 mile reach of Fryes Feeder between SG-1 and SG-3, and this increase was attributed to baseflow resulting from groundwater discharge (McGrath, 1991). Assuming one-half of the increase resulted from groundwater discharge from the west side of Fryes Feeder, groundwater

(1)

discharge was equivalent to 9.7 in/yr. Surface runoff does not contribute to streamflow except during periods of heavy precipitation and snowmelt. Regional recharge estimates range from 9 to 11 in/yr. These recharge estimates were calculated by dividing the quantity of streamflow in nearby Mt. Vernon Creek during low flow periods by total basin area. A water stage recorder in Mt. Vernon Creek (USGS Water-Stage Recorder 05436000) approximately three miles southeast of the study area recorded eleven years of stream discharge data used in the calculation. McGrath (1991) gives additional details about the water balance for the basin.

Pesticide Concentrations and Groundwater Chemistry

Pesticides

Overall detections--Of the 44 compounds detectable with the WDATCP technique, only atrazine, desethylated atrazine, alachlor, metolachlor, and metribuzin were detected in groundwater samples collected from the study area (Table 9). Atrazine was detected in 23 of 105 samples analyzed (22%) and desethylated atrazine was detected in 26 of 69 samples analyzed (38%). The overall average concentration of atrazine in wells where it was detected was 0.38 μ g/l, and the average concentration of desethylated atrazine was 0.68 μ g/l. The overall average of atrazine plus desethylated atrazine was 0.76 μ g/l. Although 21 percent of the samples with detectable atrazine contained concentrations of atrazine or atrazine plus metabolite greater than the PAL of 0.30 μ g/l, no samples contained concentrations greater than the ES of 3.0 μ g/l. The maximum concentration of atrazine plus metabolites was 2.45 μ g/l. Alachlor was detected in two samples and metribuzin and metolachlor were each detected in one sample.

The concentration of atrazine in groundwater varied greatly over short distances in the study area. There was no obvious areal trend to the distribution of atrazine concentrations. Figure 12 shows maximum concentrations of atrazine plus desethylated atrazine in the study area without regard for sampling date or well depth.

Domestic wells--Atrazine was detected in 5 of 16 (31%) domestic wells sampled in the Fryes Feeder basin. The mean detectable concentrations were 0.30 μ g/l atrazine, 0.41 μ g/l desethylated atrazine, and 0.41 μ g/l total atrazine. Atrazine concentrations varied with time in domestic wells. In AQ801, atrazine concentrations increased from 0.20 μ g/l in December, 1989, to 0.67 μ g/l in December, 1990. In contrast, atrazine concentrations over the same time interval decreased in both AQ798 and AQ806. Desethylated atrazine was detected in three domestic wells analyzed (Table 9). Similar to the relationship found in piezometer samples, desethylated atrazine



Figure 12. Maximum concentrations of atrazine plus desethylated atrazine $(\mu g/l)$ in the study area without regard for well depth or sampling date.

concentrations were greater than atrazine concentrations in December, 1990. In May, 1991, desethylated atrazine was not detected in the domestic wells.

Monitoring wells and piezometers--Atrazine or desethylated atrazine was detected in 14 of the 24 piezometers installed for this project, for a detection percentage of 58%. The average detectable atrazine in piezometers and monitoring wells was 0.46 μ g/l for atrazine, 0.76 μ g/l for desethylated atrazine, and 0.98 μ g/l for atrazine plus desethylated atrazine. Atrazine occurred in a variety of locations, including bedrock piezometers beneath the ridge (DN 1341A and DN 1342C), in bedrock below the valley bottom (DN 1344A and C), and in alluvial deposits in the valley bottom (MW 1-7). In the bedrock aquifer, atrazine was detected in the unsaturated zone (DN 1343C), at the water table (DN 1342C and DN 1344C), and up to 70 ft below the water table (DN 1341A and DN 1344A). In the alluvium, atrazine was found both at the water table and up to 20 ft below the water table (MW 4).

Atrazine concentrations varied with time in the monitoring wells. Atrazine increased from 0.37 μ g/l in May 1990 to 0.87 μ g/l in December 1990 at MW 6. In five piezometers, atrazine was detected in an initial sampling round in May 1990 and not detected in subsequent analyses. At DN 1342C and MW 3, atrazine concentrations remained nearly constant at 0.44 μ g/l and 0.19 μ g/l, respectively, until May, 1991. Alachlor, metolachlor, and metribuzin were each detected in only one sampling round. Alachlor was detected in the valley bottom (MW 2, MW 3) in August, 1990. Metolachlor and metribuzin were detected at the water table beneath the ridge (DN 1341C and DN 1342C) in December, 1990.

Wisconsin Unique Well Number	Project ID	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Atrazine plus Desethylated Atrazine (µg/l)	No ₃ -N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25°C)	Cl (mg/l)
AQ788	AQ788	12/11/89	< 0.15			4.5	. 8.0	671.5	15.0
AQ788	AQ788	05/03/90	< 0.15	< 0.15	< 0.15	4.0	11.8	783.4	16.0
AQ788	AQ788	06/28/91	< 0.15	< 0.15	< 0.15				
AQ797	AQ797	12/06/89	< 0.15			3.0	10.5	613.0	7.0
AQ797	AQ797	05/03/90	< 0.15	< 0.15	< 0.15	3.0	11.5	617.9	7.0
AQ797	AQ797	06/28/91	< 0.15	< 0.15	< 0.15				
AQ798	AQ798	12/06/89	0.52			5.0	8.0	845.0	39 <i>.5</i>
AQ798	AQ798	06/11/91	0.20	< 0.15	0.20				
AQ798	AQ798	04/26/90	0.28	0.37	0.65	5.0	12.2	944.1	32.5
AQ798	AQ798	12/10/90	0.26	< 0.15	0.26		8.5	818.4	
AQ799	AQ799	12/07/89	0.28			4.5	11.0	834.6	41.5
AQ799	AQ799	04/30/90	< 0.15	< 0.15	< 0.15	3.5	12.5	903.5	42.0
AQ799	AQ799	06/28/91	< 0.15	0.61	0.61				
AQ800	AQ800	12/07/89	0.26			4.0	9.0	616.3	9.0
AQ800	AQ800	04/26/90	< 0.15	0.20	0.20	4.0	14.5	586.3	7.5
AQ801	AQ801	12/07/89	0.19			14.0	8.0	1282.6	69.5
AQ801	AQ801	06/14/91	0.23	< 0.15	0.23				
AQ801	AQ801	04/26/90	< 0.15	0.17	0.17	3.0	12.6	1335.2	85.0
AQ801	AQ801	12/20/90	0.58	0.69	1.27		9.0	953.8	
AQ804	AQ804	12/07/89	< 0.15	< 0.15	< 0.15	2.5	12.0	616.8	12.5
AQ805	AQ805	12/09/89	< 0.15			3.0	9.0	616.3	3.5
AQ805	AQ805	05/12/90	< 0.15	< 0.15	< 0.15	2.5	11.5	590.4	2.5
AQ806	AQ806	12/09/89	0.37			7.0	8.0	905.4	15.0
AQ806	AQ806	05/12/90	< 0.15	< 0.15	< 0.15	7.5	10.4	883.2	17.0
AQ806	AQ806	06/11/91	0.17	< 0.15	0.17				
AQ812	AQ812	12/11/89	< 0.15			1.0	9.0	198.1	4.5
AQ812	AQ812	05/12/90	< 0.15	< 0.15	< 0.15	2.0	11.0	250.4	5.0
AQ813	AQ813	12/11/89	< 0.15			3.5	12.0	813.4	20.5
AQ818	AQ818	12/12/89	< 0.15	•		3.5	7.0	590.1	5.0
AQ819	AQ819	12/12/89	< 0.15			3.5	7.0	543 <i>.5</i>	16.0
AQ824	AQ824	12/15/89	< 0.15	< 0.15	< 0.15	4.5	8.0	603.6	12.0
AQ825	AQ825	12/15/89	< 0.15			2.0	10.0	621.3	5.5
AQ825	AQ825	05/15/90	< 0.15	< 0.15	< 0.15	3.5	13.0	594.9	9.5
AQ826	AQ826	04/30/90	< 0.15	< 0.15	< 0.15	7.0	10.6	653.6	6.0
AQ827	DN1341A	08/01/90	< 0.15			7.0			7.5
AQ827	DN1341A	12/19/90	0.35	0.70	1.04				
AQ827	DN1341A	06/01/91	< 0.15	0.75	0.75	9.0			

Table 9. Summary of results of groundwater sampling of domestic wells, piezometers, and springs in the Fryes Feeder basin.

Table 9, continued.

.

,

Wisconsin Unique Well Number	Project ID	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Atrazine plus Desethylated Atrazine (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25°C)	Cl (mg/l)
40828	DN1341B	08/01/90	< 0.15			6.5			7.5
A0828	DN1341B	12/19/90	< 0.15	0.63	0.63				
AQ828	DN1341B	06/01/91	< 0.15	0.75	0.75	8.0			
AQ829	DN1341C	08/01/90	< 0.15			5.5			6.5
AO829	DN1341C	12/19/90	< 0.15	< 0.15	< 0.15				
A0829	DN1341C	06/01/91	< 0.15	< 0.15	< 0.15	7.0			
A0830	DN1342A	08/01/90	< 0.15			5.0			8.5
A0830	DN1342A	12/18/90	< 0.15	0.40	0.40		5.5	698.2	
AO830	DN1342A	06/01/91	< 0.15	< 0.15	< 0.15	8.0			
AO831	DN1342B	08/01/90	< 0.15			6.0			8.5
AO831	DN1342B	12/18/90	< 0.15	0.67	0.67		5.0	709.0	
A0831	DN1342B	06/01/91	< 0.15	< 0.15	< 0.15	11.0			_
A0832	DN1342C	08/01/90	0.42			8.0			11.5
A0832	DN1342C	12/18/90	0.46	0.49	0.95		6.0	759.7	
A0832	DN1342C	06/01/91	< 0.15	< 0.15	< 0.15	11.0			
	DN1343B	05/14/91	0.25	2.20	2.45	16.5			21.0
	DN1343C	05/11/91	< 0.15	1.32	1.32	10.5			27.0
A0833	DN1344A	08/01/90	0.19			3.5			8.0
A0833	DN1344A	12/01/90	< 0.15	< 0.15	< 0.15		8 <i>.5</i>	654.7	
A0833	DN1344A	06/01/91	< 0.15	< 0.15	< 0.15	5.0			
A0834	DN1344B	08/01/90	< 0.15			4.0			7.0
40834	DN1344B	12/01/90	< 0.15	< 0.15	< 0.15		7.5	658.2	
A0834	DN1344B	06/01/91	< 0.15	< 0.15	< 0.15	5.0			
A0835	DN1344C	08/01/90	< 0.15			9.5			18.0
A0835	DN1344C	12/01/90	0.29	0.59	0.88		9.0	865.8	
A0835	DN1344C	05/11/91	< 0.15	< 0.15	< 0.15	22.0			
AQ536	DN1345A	08/01/90	< 0.15			7.5			8.0
AQ536	DN1345A	12/17/90	< 0.15	< 0.15	< 0.15		6.0	719.7	
AQ536	DN1345A	05/14/91	< 0.15	< 0.15	< 0.15	7.0			
A0837	DN1345B	08/01/90	< 0.15			7.0			9.0
A0837	DN1345B	12/17/90	< 0.15	0.33	0.33		6.0	695.8	
A0837	DN1345B	05/14/91	1.20	0.77	1.97	7.0			
A0839	DN1346A	08/01/90	< 0.15			11.0			34.5
A0839	DN1346A	12/06/90	< 0.15	0.49	0.49		9.0	1100.6	
A0839	DN1346A	05/06/91	< 0.15	< 0.15	< 0.15	6.0			
A0839	DN1346A	05/06/91	< 0.15	< 0.15	< 0.15	6.0			
A0840	DN1346B	08/01/90	< 0.15			9.0			22.0
AO840	DN1346B	12/06/90	< 0.15	< 0.15	< 0.15		8.0	943.1	
AO840	DN1346B	05/06/91	< 0.15	< 0.15	< 0.15	9.0			
	DN1346C	05/06/91	< 0.15	0.41	0.41	6.0			14.0
A0842	MW1	08/01/90	< 0.15			1.0			<i>5</i> 6
AO842	MW1	12/01/90	< 0.15	< 0.15	< 0.15		9.5	709.3	
A0842	MW1	05/11/91	< 0.15	< 0.15	< 0.15	1.5			

41

ey. Gyr

Wisconsin Unique Well Number	Project ID	Date	Atrazine (µg/l)	Desethylated Atrazine (µg/l)	Atrazine plus Desethylated Atrazine (µg/l)	NO3-N (mg/l)	Temp (°C)	Cond (µmho/cm @ 25°C)	Cl (mg/l)
AQ843	MW2"	08/01/90	< 0.15	· · · · · · · · · · · · · · · · · · ·		1.5			25.5
AQ843	MW2	12/01/90	< 0.15	< 0.15	< 0.15		8.5	520.8	
AQ843	MW2	05/11/91	< 0.15	< 0.15	< 0.15	3.5			
AQ844	MW3 ⁻	08/01/90	0.21			6.5			15.5
AQ844	MW3	12/01/90	0.17	0.31	0.48		8.0	550.8	
AQ844	MW3	05/11/91	< 0.15	< 0.15	< 0.15	7.5			
AQ845	MW4	08/01/90	< 0.15			6.0			14.0
AQ845	MW4	12/01/90	< 0.15	< 0.15	< 0.15		10.5	916.1	
AQ845	MW4	05/11/91	< 0.15	< 0.15	< 0.15	1.5			
AQ846	MW5	08/01/90	< 0.15			1.0			14.5
AQ846	MW5	12/01/90	< 0.15	< 0.15	< 0.15		11.0	904.1	
AQ846	MW5	05/11/91	< 0.15	< 0.15	< 0.15	1.0			
AQ847	MW6	08/01/90	0.67			18.0			12.0
AQ847	MW6	12/01/90	0.87	1.41	2.28		10.0	999.7	
AQ847	MW6	05/11/91	< 0.15	< 0.15	< 0.15	17.0			
AQ848	MW7	08/01/90	< 0.15			4.0			8.0
AQ848	MW7	12/01/90	< 0.15	< 0.15	< 0.15		10.0	599.8	
AQ848	MW7	05/11/91	< 0.15	< 0.15	< 0.15	4.5			
AQ849	MW8	12/01/90	< 0.15	< 0.15	< 0.15		12.0	657 <i>.5</i>	
AQ849	MW8	05/11/91	< 0.15	< 0.15	< 0.15	5.5			
SPRING	SPR01	12/09/89	< 0.15			2.0	4.0	646.6	75
	SPR01	05/03/90	0.28	< 0.15	0.28	3.0	10.5	422.8	15.5
SPRING	SPR02	12/11/89	< 0.15			2.0	8.0	535.7	3.5
	SPR03	05/03/90	< 0.15						
	SPR03	05/03/90	< 0.15	< 0.15	< 0.15	4.5	9.5	608.0	16.0
				Summary St	atistics				
	Minimum o	detected	0.17	0.17	0.17	1	4.0	422.8	25
	Maximum	detected	1.20	2.20	2.45	22	14.5	1335.2	85.0
	Mean dete	cted	0.38	0.68	0.76	5.94	8.8	682.3	16.3
	No of anal	yses	105	69	69	75	53	53	53
	No of dete	ctions	23	21	26		,		

Table 9. continued.

Other pesticides detected: <u>Metolachlor</u>. DN1341C, 12/19/90, 0.51 μ g/l; <u>Metribuzin</u>. DN1342C, 12/18/90, 0.05 μ g/l; <u>Alachlor</u>. MW2 and MW3, 8/1/90, 0.30 and 0.32 μ g/l.

Results of soil sampling

Atrazine in soil was detected at two sites, S1 and S5 (fig 13), and was not present at any other sites above the detection limit of 0.1 ppm (Table 10). The presence of atrazine in the soil at these two sites was unexpected because neither site was an area of known recent atrazine use. Site S1 is the woodlot/grazing yard. This area was never cultivated and had no known history of atrazine application. Site S5 is a pasture currently in the CRP program. Atrazine probably has not been applied in this area for at least three years. Neither area contains the sites of any known atrazine spills, mixing, loading, or container disposal. One potential source of atrazine at site S1 is through runoff water and sediment transport from cultivated fields immediately to the west of the site. The woodlot/grazing yard is at the foot of a sloping field where atrazine was applied in past years.

The absence of detectable atrazine in soil at the other sites where atrazine was applied (areas S2, S3, S4, and S10) is somewhat surprising. Either atrazine in soil has been completely leached or degraded at these sites or the composite sampling procedure diluted any atrazine present to levels below detection.

Sampling Site	Sample Date	Atrazine (ppm)
S1 S2 S3 S4 S5 S6 S7 S8 S9 S10	5/14/91 5/14/91 5/14/91 5/14/91 5/14/91 5/14/91 5/14/91 5/14/91 5/14/91 5/14/91	$\begin{array}{r} 0.17 \\ < 0.08 \\ < 0.08 \\ < 0.08 \\ 1.24 \\ < 0.08 \\ < 0.08 \\ < 0.08 \\ < 0.08 \\ < 0.08 \\ < 0.08 \\ < 0.08 \end{array}$

Table 10. Results of soil analyses for atrazine in the Fryes Feeder basin. Detection limit is 0.08 ppm.



Figure 13. Soil sampling sites in the small study area.

Major ions in groundwater

Major ion concentrations are one means to interpret the chemical evolution of groundwater. Groundwater in the study area is classified as calcium magnesium bicarbonate type based on definitions by Back (1961) and Morgan and Winner (1962). Groundwater samples were grouped by location into three categories - ridge, valley slope, and valley bottom - that represent distinct regions along a groundwater flow path. Major ion analyses averaged by groups are presented in Table 11. Water in the aquifer beneath the ridge and in the valley bottom are geochemically similar.

Agricultural activities in the basin have clearly affected groundwater chemistry, especially in wells along the valley slope. Nitrate, chloride, and sodium are found in appreciable concentrations in animal wastes, and their presence in groundwater could indicate that agricultural activities (e.g, manure spreading and waste management) on the ground surface are affecting groundwater chemistry. In this region, background concentrations for nitrate, chloride, and sodium are approximately 3.0, 7.0, and 3.0 mg/l, respectively. Background concentrations were determined by calculating the mean of the samples with concentrations less than the median. Nitrate concentrations were greater than the Enforcement Standard of 10 mg/l in three samples. In 78 percent of the samples, nitrate concentrations exceeded 3.0 mg/l. Chloride concentrations exceeded 7 mg/l in 78 percent of the samples. In 68 percent of the samples, sodium concentrations were greater than 3.0 mg/l.

Specific conductance, dissolved oxygen, pH, and temperature were measured *in* situ during each sampling round. Specific conductance at 25°C ranged from 350 to $800 \ \mu mho/cm$ in the piezometers Dissolved oxygen measurements ranged from 3.1 mg/l in alluvium in the valley bottom (MW 2, MW 3) to 13.2 mg/l at the water table near the ridge (DN 1345B). The low dissolved oxygen in MW 2 and MW 3 might be the result of depletion of oxygen by organic material in the valley bottom sediments. High dissolved oxygen concentration in DN 1345B is expected due to its location in a recharge area. The pH of the groundwater ranged from 7.0 to 7.6. Only six percent of the samples had a pH value greater than 7.6. The uniformity of pH measurements reflects the uniform groundwater chemistry.

In general, groundwater was slightly undersaturated with respect to calcite and dolomite. McGrath (1991) calculated mineral saturation indices for all water samples using the geochemical speciation program PHREEQE (Parkhurst and others, 1980). Groundwater samples from four piezometers (DN 1342A, DN 1344C, MW 2, MW 4) were slightly oversaturated with respect to calcite. Groundwater beneath the ridge (DN 1341 and DN 1342) was slightly less saturated with calcite and dolomite than groundwater from the valley bottom (DN 1344 and MW 1-7), supporting the conceptual model of flow from the ridge to the valley.

				Positi	on in flov	v system			
Parameter		Ridge			Middle			Valley	
	Mean	Std Dev	Ν	Mean	Std Dev	N	Mean	Std Dev	N
Temp.°C	9.4	2.7	28	10.6	2.3	25	12.4	2.5	20
Cond.µmho/cm	n 722	102	28	879	231	25	703	167	20
pH	7.33	0.25	28	7.17	0.34	24	7.46	0.21	19
D.O.	8.6	2.3	25	8.7	1.5	22	6.2	2.7	1S
Ca	78.2	5.4	9	87.5	12.1	7	78.5	9.2	7
Mg	42.8	3.7	9	46.0	7.1	7	37.6	8.7	7
Na	6.4	8.0	9	26.3	28.2	7	10.3	9.4	7
ĸ	0.9	0.5	8	1.4	1.2	7	4.8	8.5	7
HCO.	394.9	26.9	9	415.1	63.8	10	400.6	90.7	7
Cl	8.3	1.3	9	28.9	24.3	11	13.8	6.6	8
SO.	16.5	5.4	9	21.9	6.2	7	19.0	8.9	7
NO ₂	7.2	1.8	18	9.9	5.6	17	4.0	2.6	14
SI.	-0.23	0.14	9	-0.12	0.12	7	-0.48	1.09	7
SL	-0.59	0.30	9	-0.39	0.24	7	-1.05	2.20	7
	-2.09	0.16	9	-2.09	0.16	7	-2.67	1.04	7
³ H T.U.	19.2	18.0	9	22.1	13.8	8	15.4	11.9	10
¹⁸ O, permil	-9.3	0.6	9	-9.4	1.0	11	-9.0	0.2	10

Table 11. Summary of geochemical results, grouped by position in groundwater flow system. All analyses in mg/L except as indicated.

Environmental isotopes and groundwater age

Tritium and oxygen-18 (¹⁸O) analyses were completed on domestic wells, piezometers, and springs in the basin (Table 12). Precipitation samples analyzed for ¹⁸O were composite samples of two precipitation events occurring within the same month. Oxygen-18 composition is temperature dependent, and there are strong seasonal variations in the isotopic composition at a given location. Isotopic composition of precipitation can also vary during individual precipitation events. ¹⁸O concentrations ranged from -8.3 to -11.3 permil in the piezometers and from -8.4 to -9.2 permil in domestic wells. Oxygen-18 in rain samples from March, 1990 to May, 1991, ranged from -17.9 permil in May, 1991, to -4.0 permil in July, 1990 (fig. 14).

Tritium concentrations were measured in a selection of groundwater samples (Table 12). Tritium concentrations ranged from 6 TU (tritium units) in MW 6 to 44 TU in DN 1341B. Domestic wells exhibited a smaller range of tritium concentrations (16.1 to 38.9 TU). Precipitation samples collected from March to May, 1990

Table 12. Isotope Results

		180	377	Estimated
Project	Date	·•0	² H	Estimated
ID	Sampled	(permil)	(TU)	age (yr)
Domestic	wells and	springs		
2011000		1 3		
AQ788	May-90	-8.7	26	8
AQ797	May-90	-9.2	25	8
AQ798	May-90	-8.6	28	8
AQ799	May-90	-8.4	23	7
AQ800	May-90	-9.0	24	8
AQ801	May-90	-8.9	29	8
AQ805	May-90	-9.0	16	7
AQ806	May-90	-9.1	27	8
AQ812	May-90	-9.2	39	9
AQ825	May-90	-8.6	25	8
AQ826	May-90	-8.4	29	8
SPR01	May-90	-8.6	24	8
SPR03	May-90	-9.5	29	8
Piezon	neters			
			•	0
DN1341A	Aug-90	-9.1	30	8 10
DN1341B	Aug-90	-9.2	44	18
DN1341C	Aug-90	-9.5	40	18
DN1342A	Aug-90	-9.1	30	9
DN1342B	Aug-90	-9.2	0 4	24
DN1342C	Aug-90	-8.7	24	24
DN1343B	May-91	-8.3		
DN1343C	May-91	-8.5	20	0
DN1344A	Aug-90	-9.2	38	9
DN1344B	Aug-90	-9.5	28	0
DN1344C	Aug-90	-9.0	20	0
DNI345A	Aug-90	-8.9		
DN1345B	Aug-90	-0.9		
DN1346A	Aug-90	-9.0	40	18
DN1340B	Aug-90	-0.9	-0	10
DINI346C	May-91	-9.5	22	7
	Aug 00	-0.9	مدمد	1
	May-90	-0.9	22	7
	Aug-90	-9.1	36	ģ
MW2	May 00	-9.2	16	5
IVI W S	Aug. 90	-9.4	10	3
MUVA	Aug-90	-0.0	21	7
NAXX75	Δ110-00	-9.1	41	,
MWA	$\Delta u \sigma_0 0$	-9.0 _11 3	6	1
NTX/6	May_01	_11 2	12	5
MW7	Δ110-90	-10.8		2
NATXIQ	$\Delta 110-00$	_2.0		
TAT AN O	Aug-90	·0•/		



contained between 14.1 and 16.5 TU.

Groundwater ages based on the tritium content of groundwater provide independent estimates of groundwater ages and travel times. Groundwater in the study area is hydrogeologically young, with estimated ages ranging from one to nine years (Table 12). A tritium input history for the basin was developed as described by Bradbury (1991). The tritium input history was constructed using precipitation tritium measured at Madison, Wisconsin and elsewhere. Figure 15 presents the tritium input for the basin corrected for radioactive decay to 1989 and 1990. These curves represent the theoretical amount of tritium remaining in the groundwater flow system in 1989 and 1990. Tritium concentrations in groundwater samples may be compared to figure 13 to estimate minimum groundwater ages. According to the tritium interpretations, none of the groundwater sampled in the study area recharged prior to 1972. Groundwater ages derived from the tritium concentrations agree with





-



Figure 15. Tritium input curves for tritium in groundwater in Dane County. Curves indicate tritium remaining in groundwater allowing for radioactive decay prior to the indicated sample dates.

age estimates determined with the average linear velocity calculations presented earlier. Those calculations estimated travel times from the ridge to Fryes Feeder ranging from 4.2 to 24 years.

Numerical Modeling and Particle Tracking

A numerical groundwater flow model was used to simulate the advective movement of groundwater and pesticides in the Fryes Feeder basin. We simulated groundwater flow in the basin using the parameter estimation groundwater flow model of Cooley (1977), commonly referred to as the Cooley model. The Cooley model includes a two-dimensional finite-element groundwater flow code linked to a nonlinear regression routine designed to calculate estimates of various aquifer parameters such as hydraulic conductivity and recharge rates. Such computer codes are generally called inverse models because they vary aquifer parameters until the model reaches a best-fit solution matching hydraulic heads measured at monitoring wells. Prior information, such as means and standard errors of various parameter estimates, are used to constrain the solution. Cooley and Naff (1990) give a detailed explanation of the theory and assumptions of this type of modeling.

The Cooley model was used to simulate horizontal groundwater flow in the bedrock in part of the Fryes Feeder basin. The two-dimensional model was chosen because of lack of sufficient data to calibrate a three-dimensional model, and the inverse approach was chosen because of uncertainty about the appropriate recharge rates and hydraulic conductivity to use for the bedrock system. It is important to note that the model only simulates the deep bedrock system and ignores flow in the upper sandstones and flow in alluvium along Fryes Feeder. The purpose of the model was to examine potential pathways for pesticide transport within the lower bedrock Figure 16 shows the model grid. The study area was divided into a finite element mesh consisting of 130 nodes and 146 elements. The model solves for hydraulic head at every model node, and twelve of the nodes were coincident with the locations of monitoring wells.

Model boundary conditions included constant heads along the eastern boundary where groundwater discharges into Fryes Feeder and a zero-flux boundary coincident with the groundwater divide along the western side of the model and along a flow line on the north side of the model. Recharge was added to the model in three zones. Recharge zone 1 consisted of relatively level upland fields along the ridge crest, recharge zone 2 consisted of the steep, vegetated slopes below the ridge crest, and recharge zone 3 consisted of the relatively level floodplain between the ridge slope and Fryes Feeder. A single value of hydraulic conductivity was applied to the entire model, and the aquifer was treated as isotropic in the horizontal plane. The base of the aquifer was treated as impermeable. Pumping wells were simulated at the locations of domestic wells in the basin.

Table 13 summarizes input parameters and model results. Initial parameter estimates (hydraulic conductivity, recharge rates) were taken from data developed by McGrath (1991). The parameter estimation model was then used to calculate improved estimates of three parameters and a hydraulic head distribution. The parameters estimated were hydraulic conductivity and recharge rates in zones one and three. The model proved insensitive to recharge in zone two, and it was set to a constant value of 0.4 in/yr.

The model produced an acceptable reproduction of hydraulic heads measured in the field. Figure 17 shows the model-generated head distribution. The deviations



Figure 16. Finite-element grid for the numerical model applied to the Fryes Feeder basin.

Portion of study area	Model Zone	Initial Parameters	Final Parameters
ridgetop fields steep slopes valley bottom ridgetop fields steep slopes	K zone 1 (ft/sec) K zone 2 (ft/sec) K zone 3 (ft/sec) recharge zone 1 (in/yr) recharge zone 2	3.0e-04 3.0e-04 3.0e-04 9.8	1.2E-5 1.2E-5 1.2E-5 3.5 0.4
valley bottom	(in/yr) recharge zone 3 (in/yr)	3.8	-2.4
Statistical Parameters Error Variance (ft) Sum of squared err No of observations	rors (ft2)	8.2 294.3 36	3.3 121.4 36

Table 13. Input parameters used in the parameter estimation model.

between field-measured and model-simulated heads ranged from 6.6 ft at well 1345A to 0.4 ft at well 1341A. More exact reproduction of field-measured heads would probably not be possible without adding additional zones of recharge or hydraulic conductivity to the model, and field data were insufficient to justify any such additions.

The model-estimated value for hydraulic conductivity $(1.2 \times 10^{-5} \text{ ft/sec})$ was considerable smaller than the field estimated value of $3.0 \times 10^{-4} \text{ ft/sec}$ but is within the range of uncertainty possible in this geological setting. The upland recharge rate of 3.4 in/yr is also smaller than estimated from field data. However, the model only simulated the lower part of the bedrock system. It seems very likely that a shallower groundwater flow system occurs in the upper part of the section, and that some groundwater discharges from this system into the alluvium along the floodplain of Fryes Feeder. The model was not designed to simulate this flow.



Figure 17. Model-generated hydraulic heads.



Particle Tracking

Particle tracking delineated the capture zone of domestic wells and piezometers which contained detectable atrazine. Particle tracking also determined areas likely to be affected by agricultural practices in specific fields, pastures, and barnyards.

The US EPA WHPA Model (Blandford and Huyakorn, 1991), a modular code for the delineation of wellhead protection areas, was used in this study. The WHPA model, an outgrowth of an EPA document "Guidelines for Delineation of Wellhead Protection Areas", is recommended by the EPA for wellhead protection studies. GPTRAC, the general particle tracking module of WHPA, delineated pathlines and capture zones. Input data for GPTRAC include the hydraulic head field generated by the numerical model, aquifer thickness and hydraulic conductivity, porosity, and the locations of pumping wells. An effective porosity estimate of the aquifer was based on lithologic information discussed above. The bedrock was assigned an effective porosity of 0.08 which is about the middle of the estimated range.

Two particle tracking simulations were performed. In the first simulation, well capture zones were delineated by backward tracking of particles placed at a well. In the second simulation, particles representing agricultural chemicals were placed on specific plots in corn fields where atrazine applications have occurred, in the pasture, and in the barn yard, Particles were tracked forward until they reached Fryes Feeder.

Delineation of Pathlines and Capture Zones for Specific Wells

Forward particle tracking from fields along the ridge clearly showed the susceptibility of wells in the valley bottom to conservative agricultural contaminants originating on the ridge. Travel times indicate contaminants applied to fields on the ridge could reach Fryes Feeder within two to five years. According to these simulations, flow from the pasture and barnyard could affect three domestic wells and three piezometer nests in the basin. Contaminants originating in the barnyard could affect AQ801, AQ806, MW 1, and MW 2. Similarly, animal waste management practices in the pasture may affect groundwater withdrawn from AQ797, DN 1346, MW 1, and MW 2. Elevated nitrate and chloride concentrations were detected in groundwater samples collected from four of the six well locations (AQ801, AQ806, DN 1344, and DN 1346). Travel times calculated by this model range from three to five years for flow from the source areas to Fryes Feeder.

A capture zone is defined as the map or land surface area surrounding a pumping well that supplies water to the well. Capture zones for two particular wells identify potential source areas for the atrazine, nitrate, and chloride concentrations found in these wells. In AQ801, a farm well, atrazine and nitrate concentrations ranged up to 0.58 μ g/l and 14 mg/l, respectively. As shown on figure 18, the capture zone for AQ801 extends almost 3/4 mile to the northwest of the well and is over 500 ft wide. The predicted capture zone covers areas in the CRP program but also an area of active crop production. The maximum horizontal travel time to AQ801 is about two years. The well capture zone for AQ801 includes both fallow fields on the ridge adjacent to DN 1341 and the barnyard. Elevated nitrate concentrations in AQ801 may result from both potential source areas. Well AQ806 is a domestic well on non-agricultural land. This well produced water having atrazine detections of up to 0.37 μ g/l. The capture zone for AQ806 is wider than for AQ801 (fig. 19) but extends about the same distance upgradient, with a maximum horizontal travel time of about 2.5 yr.

Capture zones (not shown) were also delineated for various monitoring wells, however these very slender capture zones were not influenced by pumping rates and are more accurately called pathlines which intersect the well location. Particle tracking results show contaminants originating in the pasture could reach DN 1346 within two years. Elevated nitrate and chloride concentrations detected in this piezometer nest probably result from inadequate animal waste management practices in the pasture.

Agricultural chemicals applied to fields on the ridge could reach AQ801 and MW 6 within three years. The location and orientation of the reverse pathlines originating from MW 6 suggested that atrazine detected there results from field application. Atrazine mixing or storage is not known to have occurred in the capture zone for MW 6. Particle tracking indicated that flow paths intersecting MW 2 and DN 1344 originate in fallow fields currently under CRP rules. Atrazine was detected at each of these well locations. Travel times from fields along the ridge to these wells and piezometers range from two to seven years.

Discussion

Conceptual model of groundwater flow

Groundwater flow in the Fryes Feeder basin is probably typical of flow in hundreds of other small basins in the driftless area of southwestern Wisconsin. Figure 20 illustrates a conceptual diagram of the groundwater flow system along a representative cross section from the ridge to the valley. The system consists of three distinct groundwater and land use zones. Much of the agricultural production in the basin occurs on the broad, relatively level, uplands along and flanking the ridge. In the Fryes Feeder basin this is an area of thin soils over carbonate bedrock and the water table lies nearly 150 ft below the land surface. Groundwater recharge occurs through diffuse infiltration, macropores, and fractures, but the travel time from the



Figure 18. Capture zone for domestic well AQ801.

land surface to the water table can be several months or years.

A second groundwater and land use zone occurs along the steep valley walls. Most of the landscape in this zone is too steep for either cultivation or farm and dwelling structures, and the land is either wooded or is grassed for grazing areas. Where wooded, this zone might be an important area for groundwater recharge if the vegetation is thick enough to hold runoff. However in unwooded areas runoff is rapid, and little recharge probably occurs. Groundwater flow in this zone is mostly horizontal.

The third groundwater and land use zone occurs in the valley bottom along Fryes Feeder. In this zone the landscape is relatively level and soils are thicker than on the ridge or valley walls. Land use in the valley bottom is a mix of cultivated fields, farm buildings, and residences. The water table occurs only a few feet below the surface, however, vertical component of groundwater movement is upward to discharge into



Figure 19. Capture zone for domestic well AQ806.

the surface stream, and consequently little or no groundwater recharge occurs in the valley zone. The stream (Fryes Feeder) represents a flow system divide.

General distribution of atrazine in groundwater

Atrazine and desethylated atrazine were detected in the study area despite the lack of recent applications on the east side of the ridge. Although atrazine and desethylated atrazine most commonly were found at the water table, the contaminants were also present far below the water table. Atrazine and desethylated atrazine were detected in the recharge area at DN 1341A (200 ft below ground surface) and DN 1342C (130 ft below ground surface). Atrazine was detected 70 ft below the water table in DN 1341A and DN 1344A. Atrazine was also detected below the water table in AQ798 and AQ806, two domestic wells cased 20 ft below the water table.



10

Figure 20. Conceptual cross section of the Fryes Feeder basin.

Spatial and temporal variations in atrazine concentrations were observed between sampling rounds. In 6 of 18 bedrock piezometers, atrazine was detected in only one of the three sampling rounds. At piezometers MW 2 and MW 3, atrazine was twice detected in MW 3 (screened interval 4 - 9 ft below the surface) without being detected in MW 2 (screened interval 11.5 to 14.5 ft below the surface). Atrazine was always detected in samples from AQ801 and AQ806, but never detected in groundwater samples from AQ797, less than one-quarter of a mile from AQ801.

Sources of atrazine

Except for one location described below, atrazine contamination in the bedrock and alluvial aquifers of the study area probably is the result of pesticide application to fields and post-application leaching to the groundwater. The occurrence of atrazine contamination in each region of the bedrock and alluvial aquifers (recharge and discharge areas, shallow and deep depths) suggests the source is largely non-point leaching of surface applied atrazine. Occurrence of atrazine in the aquifer beneath active fields, fallow fields, and areas with no pesticide use history suggest atrazine is persistent and transported with groundwater flow. Although it is impossible to rule out unreported spillage and mishandling as possible atrazine sources, the widespread detection of atrazine in the study area is more consistent with a source related to field application. According to the landowners, atrazine mixing, storage, or spillage have not occurred on the properties.

The thick unsaturated zone beneath the ridge appears to act as a reservoir and continuing source for atrazine contamination of groundwater. Even though atrazine was not applied along the ridge for at least one, and possibly two, years prior to monitoring, we detected atrazine and/or desethylated atrazine at sites DN1341 and DN1342 near the top of the saturated zone but up to 200 ft below the land surface. According to the conceptual model of flow in the basin, these sites are on or near the groundwater divide, and should not be receiving any horizontal flow. Any atrazine in these piezometers probably originated on the land surface directly above. A second line of evidence suggesting that atrazine resides in the unsaturated zone is the occurrence of atrazine in piezometers DN1343C and DN1346C in May, 1991. These monitoring points were constructed as "dry wells" situated about 50 ft above the permanent water table, and consisted of a screened interval above a section of unscreened, or "blank", casing. These wells were designed to capture water moving downward through the unsaturated zone during major recharge events, and were dry throughout most of the project period. Following rains in the spring of 1991, both piezometers filled with water containing desethylated atrazine. This atrazine must have originated above the water table, but atrazine was not applied during the spring of 1991. The most likely source for the atrazine in these piezometers is residual atrazine in the thick zone of unsaturated dolomite beneath the ridge.

Our data also suggest that atrazine can be transported by soil erosion. The presence of atrazine at soil sampling sites S1 and S5 was surprising because atrazine had not been applied near S5 for at least three years and had never been applied near S1. However, site S1 is below the base of a sloping cultivated field with a history of atrazine use. It is possible that soil containing atrazine residuals might erode from the field and be deposited near S1, where it could act as a continuing atrazine source to groundwater.

Atrazine detections at one site, MW 6, may be the result of atrazine applied at the maximum allowable rate. According to one local resident, a previous owner of the land around MW 6 may have applied atrazine in 1988 at a rate of 3 to 4 pounds per acre. The normal application rate for atrazine is 2 pounds per acre. However, this possible application of atrazine probably has not affected other piezometers or domestic wells in the region. Bedrock piezometers are located upgradient of the area affected.

CONCLUSIONS

Five-Basin Survey

Pesticide contamination of groundwater has occurred in bedrock aquifers in the unglaciated part of western Dane County, Wisconsin, where water samples were collected from wells in five small groundwater basins. Detectable amounts of atrazine, a herbicide applied to corn fields to control broadleaf weeds and grasses, were found in samples collected from three of the five basins at an average concentration of 0.58 μ g/l. No other pesticides or herbicides were found in groundwater in this five-basin survey. Contamination was not limited to individual farms or agricultural fields. Wells with atrazine contamination were found on sites of various land uses, including dairy farms, private homes, and public buildings. In addition to the parent compound, desethylated atrazine, an atrazine metabolite, was detected in 18% of the samples tested, and was found in four samples where the parent compound was not detected.

The susceptibility of groundwater in western Dane County to contamination by atrazine cannot be attributed to any one particular physiographic or geologic characteristic, but may be related to combinations of such characteristics. Characteristics of each basin were examined to determine attributes that increase or decrease the susceptibility of groundwater to atrazine contamination. Atrazine was not detected in two northern basins having greater average depth to groundwater, thinner dolomite layers, and better soil contaminant attenuation characteristics than in three southern basins. The predominance of atrazine detections in aquifers composed of dolomite, a carbonate rock prone to fracturing, suggests that areas with dolomite layers in the unsaturated and/or saturated zone are very susceptible to contamination. In addition, the higher frequency of atrazine detections in basins with shallow soil profiles indicates that soil thickness might be an important control on the susceptibility to atrazine contamination.

Results of the five-basin survey are consistent with, and reinforce, results of previous DATCP and DNR atrazine surveys. These previous surveys of atrazine in groundwater in Wisconsin relied on random samples from domestic wells of generally unknown or poorly-known construction, and were open to the criticism that any contamination of these wells might be related to poor well construction practices or damaged or defective well casings or seals. Our study sampled only wells in good repair and of known construction conforming to Wisconsin well construction codes. In this study, 26% of wells sampled contained detectable atrazine. This overall result compares very favorable with results from the southwest district of the DATCP Grade A Dairy Farm Survey (LeMasters and Doyle, 1989), where 29% of the wells sampled in the south central agricultural reporting district contained detectable atrazine. Such agreement implies that ignoring well construction details in the statewide surveys probably does not bias the DATCP results.

Fryes Feeder Basin Study

In a detailed examination of a small groundwater basin, the Fryes Feeder basin, near Mt Horeb, Wi., atrazine and/or desethylated atrazine were detected in 35 percent of 26 bedrock and alluvial wells and piezometers sampled. The average concentration of atrazine in samples where it was detected was 0.38 $\mu g/l$, and the average concentration of desethylated atrazine in samples where it was detected was 0.68 μ g/l. The average concentration of atrazine plus desethylated atrazine was 0.76 μ g/l, which exceed the PAL of 0.30 μ g/l. The presence of atrazine was not confined to a single stratigraphic horizon, depth, or geologic unit. Atrazine was detected both in recharge and in discharge areas. In the bedrock aquifer, atrazine was detected both at the water table and up to 70 feet below the water table. In the alluvium, atrazine was found both at the water table and up to 20 feet below the water table. Atrazine was found in aquifers composed of dolomite, sandstone, and sand and gravel. Desethylated atrazine, a metabolite of atrazine, was detected in 50 percent of the 26 piezometers. The average concentration of desethylated atrazine in samples where it was detected was 0.74 μ g/l. All groundwater samples with atrazine also contained desethylated atrazine, but not all samples containing desethylated atrazine also contained the parent compound at concentrations above the 0.15 μ g/l analytical detection limit.

Atrazine concentrations in the basin varied with time and in space. At one piezometer constructed in alluvium, atrazine increased from 0.37 μ g/l to 0.87 μ g/l over a six-month period. At other piezometers, atrazine was detected in an initial sampling round and not detected in subsequent analyses. In some wells, atrazine concentrations remained fairly constant. In each sampling round, atrazine occurred in groundwater samples collected from two domestic wells but not in piezometers or a domestic well one-quarter mile away. In the alluvial sediments, atrazine was detected in samples from a water table piezometer and not detected in groundwater collected from a screen five feet below the water table.

The source of atrazine in groundwater in the Fryes Feeder basin lies within the basin itself. The conceptual model of the groundwater system shows that at least the shallow groundwater in the basin moves in a flow system closed to contamination sources outside the basin. Recharge to the bedrock aquifer system occurs primarily along the ridge. Downward hydraulic gradients in the bedrock aquifer occur beneath the ridge. Upward hydraulic head gradients occur in the alluvial aquifer near Fryes Feeder. Discharge occurs from the aquifer system into the stream and wetlands in the valley bottom. Water balance calculations indicate all recharge to the water table in the study area discharges into Fryes Feeder.

Groundwater in the study area was relatively young. Environmental isotope data were consistent with the conceptual model. Tritium concentrations show that the minimum age of groundwater in the basin probably ranges from one to nine years.

determined with an average linear velocity calculation and particle tracking. Travel times from the ridge to the stream based on average linear velocity calculation range from two to sixteen years. Two-dimensional particle tracking calculated a range of minimum ridge to stream travel times from two to five years. Since both calculations ignore vertical hydraulic gradients, the travel times are minimum estimates only. Oxygen-18 data suggest most recharge originates as winter snowmelt and spring rain.

Both the relatively thin upland soils and the relatively thick unsaturated zone in the Fryes Feeder basin may act as reservoirs for atrazine leached from the soil surface, and could continue to supply atrazine to the groundwater system for some unknown time (perhaps years) after field applications have ceased. Atrazine was not applied to the upland ridge in our study area for several years prior to our study, yet bedrock piezometers below the recharge zone contained detectable atrazine. This atrazine could only have come from the unsaturated zone above the water table.

IMPLICATIONS AND RECOMMENDATIONS

The frequency of detections of atrazine and its metabolites in properly constructed wells finished in bedrock aquifers in western Dane County implies that many such wells in Dane County and in similar areas of southwestern Wisconsin are at risk from atrazine contamination. Many of the detections were at locations without a history of atrazine use or pesticide mixing around the well or even on the property, suggesting that atrazine and its metabolites are mobile in the subsurface. While it is impossible to rule out accidental and unreported pesticide spills as contaminant sources, the frequency of atrazine detections in this study strongly implies that field application of atrazine at historic rates is a source of groundwater contamination to deep bedrock aquifers.

Areas with thin soil where dolomite is the uppermost bedrock lithology appear to have a greater incidence of atrazine contamination of groundwater than areas with thicker soils or areas where sandstone is the uppermost bedrock lithology. Atrazine was consistently present in some wells in three southern basins and was consistently absent all wells sampled in two northern basins. Land use and atrazine use in the two groups of basins appears to be similar. Although many variables might be responsible for the difference in atrazine detections, one of the most obvious is a fundamental difference in Hydrogeologic setting between these two basin groups. In the northern basins the bedrock aguifer is composed mostly of sandstones, while in the southern basins the bedrock aquifer is composed mostly of dolomites and limestones. The dolomites and limestones contain fractures which allow rapid groundwater movement with little attenuation of contaminants. Such rocks compose much of the Sinnipee and Prairie du Chien Groups and occur over wide areas of southern and western Wisconsin. A detailed examination of the effect of local geology, particularly the occurrence of near-surface dolomite, on pesticide movement was beyond the scope of this five-basin survey and should be the subject of future research. Additional hydrogeologic studies are needed to Trotter et al, 1990

examine degradation and adsorption of atrazine in geologic materials besides soil. Intently, very little information is available on the fate of atrazine in bedrock aquifers.

The frequency of detection of atrazine in bedrock piezometers installed for this project was only slightly higher than the frequency of detection of atrazine in pre-existing domestic wells. The consistency of results between these two types of monitoring points suggests that the results of large-scale well water pesticide monitoring programs undertaken by DATCP and DNR are probably representative of pesticide conditions in the groundwater system. In addition, the favorable comparison of results from piezometers, which have short screens and sample discrete intervals of the aquifer, and domestic wells, which have long open intervals and sample large thicknesses of the aquifer, implies that atrazine and its metabolites are distributed through large aquifer thicknesses rather than confined to narrow plumes or slugs.

Desethylated atrazine, a toxicologically significant metabolite of atrazine, was frequently found at greater concentrations than the parent product, and was occasionally found in samples where the parent was not detected. Analyzing water samples for the parent product alone might significantly underestimate the occurrence of atrazine contamination in a given area. Future pesticide monitoring should include all atrazine metabolites as well as the parent compound. Atrazine was found in groundwater which was relatively young (less than 10 years) based on both hydraulic analyses and isotopic data. This implies that contamination of groundwater by pesticides is presently occurring or only recently occurred, and is not something that ceased 20 or 30 years ago. The presence of atrazine in soils and in the unsaturated zone suggests that these areas could be a continuing source of atrazine contamination, and that groundwater contamination might continue to occur for some years even after the use of atrazine were to be severely restricted or banned.

Relatively small surface drainage basins, such as the Fryes Feeder basin, represent closed groundwater systems, at least with respect to water produced by relatively shallow domestic wells. Because underflow across the basin boundaries appears to be small it might be possible to treat the basins as distinct and separate management units with respect to application rate: of pesticides and other agricultural chemicals. However, more work is necessary to 'est this hypothesis in other basins in the Driftless Area.

REFERENCES CITED

- Back, W. 1961. Techniques for Mapping of Hydrochemical Facies, U.S. Geol. Surv. Prof. Paper 424-D, pp.380-382.
- Blandford, T.N. and P.S. Huyakorn, 1991. WHPA 2.0 Code, a Modular Semi-analytical Model for the Delineation of Wellhead Protection Areas. Prepared for the United States Environmental Protection Agency, Office of Ground Water Protection., Washington, D.C.
- Bohn, M.F., M.A. Muldoon, F.W. Madison, K.R. Bradbury, A. Zaporozec, and J. Postle. 1991.
 Evaluation of five groundwater susceptibility systems in Dane County, Wisconsin.
 Proposal to Wisconsin Deoartment of Natural Resources and Department of Agriculture, Trade, and Consumer Protection. 13 p.
- Bradbury, K.R. 1991. Tritium as an Indicator of Ground-Water Age in Central Wisconsin, Ground Water, v.29, no.3, pp. 398-404.
- Cates, K. J. and F.W. Madison, 1990. Soil-Attenuation-Potential Map of Pepin County, Wisconsin. Wisconsin Geological & Natural History Survey Soil Map 10, scale 1:100000.
- Chesters, G., J. Levy, D.P. Gustafson, H.W. Read, G.V. Simsiman, D.C. Liposcak, and Y.Xiang. 1991. Sources and extent of atrazine contamination of groundwater at grade A dairy farms in Dane County, Wisconsin. Final Report to Wisconsin Department of Agriculture, Trade, and Consumer Protection. Water Resources Center, University of Wisconsin-Madison. 141 p.
- Cline, D.R., 1965. Geology and ground-water resources of Dane County, Wisconsin. U.S.G.S. Water Supply Paper 1779-U. 64 pp.
- Cooley, R.L., 1977. A method of estimating parameters and assessing reliability for models of steady-state groundwater flow, 2--Application of statistical analyses. Water Resources Research, v. 15, no. 3. p. 603-617.
- Cooley, R.L., and R. L. Naff. 1985. Regression modeling of ground-water flow. U.S.G.S Open-File Report 85-180. 450 p.

÷.

- Hvorslev, M.J. 1951. Time lag and soil permeability in groundwater observations. U.S Army Corps Engrs. Waterways Exp. Sta. Bull. 36, Vicksburg, MI.
- LeMasters, G. Wisconsin Department of Agriculture, Trade, and Consumer Protection, Madison, WI. Oral communication on., August 2, 1991.

- Frath, R. W., 1991. Investigation of atrazine contamination in bedrock aquifers, western Dane County, Wisconsin. Unpublished M.S. Thesis, Dept. of Geology, University of Wisconsin-Madison. 218 p.
- gan, C.O. and M.D.Winner, Jr. 1962. Hydrochemical Facies in the 400 foot and 600 foot sands of the Baton Rouge Area, Louisiana. U.S. Geol.Surv.Prof.Paper 450-B, pp. B120-121.

:

- hurst, D.L., Thorstenson, D.C., and L.N. Plummer, 1980. PHREEQE A Computer Program for Geochemical Calculations. U.S. Geol. Water-Resources Investigations 80-96, 210 pp.
- Department of Agriculture, 1978. Soil Survey of Dane County, U.S. Department of Agriculture, Washington, D.C., 193 pp.
- itje, G. R., Spalding, R. F., Burnside, O. C., Lowry, S. R., and J. R. C. Leavitt, 1983. Biological Significance and Fate of Atrazine under Aquifer Conditions. Weed Science, v. 31, pp. 610-618.
- consin Blue Book, 1990. Agricultural Statistics. Wisconsin Department of State, Madison, WI., 459 p.
- Iasters, G., and D.J. Doyle, 1989. Grade A Dairy Farm Well Water Quality Survey, Wisconsin Department of Agriculture, Trade, and Consumer Protection, Madison, WI., April, 1989.
- consin Department of Agriculture, Trade, and Consumer Protection, 1986. Wisconsin 1985 Pesticide Use Survey. Wisconsin Department of Agriculture, Trade, and Consumer Protection, Madison, WI., 32 pp.
- consin Department of Natural Resources, 1987. Groundwater Sampling Procedures Guidelines. Wisconsin Department of Natural Resources, Madison, WI., PUBL WR-153-87, 91 p.
- consin Department of Natural Resources, 1989. Wisconsin Administrative Code, Chapter NR 112. Wisconsin Department of Natural Resources, Madison, WI.
- consin Laboratory of Hygiene, 1988. Neutral Extractable Method, Method 1200, Organics Section. Wisconsin Laboratory of Hygiene, Madison, WI. Revised July 1988.
APPENDIX A

Basin Maps







- esterni

Figure A2. Map of Basin B, Union Valley, near Cross Plains, Wisconsin.



Figure A3. Map of Basin C, near Pine Bluff, Wisconsin.



Figure A4. Map of Basin D, Fryes Feeder, near Mt Horeb, Wisconsin.

70



Figure A5. Map of Basin E, Milum Creek, near Montrose, Wisconsin.



÷.

Ł



140748 c.2 Field Study of Atrazine Contamination of Groundwater in Dane County, Wisconsin

Water Resources Center University of Wisconsin - MSN 1975 Willow Drive Madison, WI 53706

DEMCO

