SOURCE, EXTENT, AND DEGRADATION OF HERBICIDES IN A SHALLOW AQUIFER NEAR HESSTON, KANSAS

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CONVERSION FACTORS

For those readers interested in metric units (International System), the inch-pound units used in this report can be converted using the following factors:

Multiply inch-pound unit	*By*	*To obtain metric unit*
inch	25.4	millimeter
foot	0.3048	meter
mile	1.609	kilometer
pound	453.6	gram
acre-foot	1,233	cubic meter
gallon per minute	0.06308	liter per second
foot squared per day	0.09290	meter squared per day
degree Fahrenheit (°F)	°C = 5/9 x (°F-32)	degree Celsius (°C)

Sea level: In this report, sea level refers to the National Geodetic Vertical Datum of 1929--a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called "Sea Level Datum of 1929."

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ABSTRACT

Atrazine, alachlor, cyanazine, metolachlor, and metribuzin were detected in water from a domestic well completed in a shallow aquifer underlying the Harvey County Experiment Field near Hesston, Kansas. The study described in this report investigated the source, extent, and degradation of these five herbicides. Hydrogeologic analysis of the site enabled estimation of the degradation half-lives of the herbicides in the saturated zone.

The most probable source of the contamination was back-siphonage or spillage of herbicides from a sprayer tank into a trench backfilled with sand. The herbicides moved downgradient to the domestic well and then entered the aquifer via the annular space in the well. Once in the aquifer, the contamination remained nearly stationary with very little lateral movement away from the point of injection. Decreases in herbicide concentrations occurred mainly by degradation of the parent compounds and, to a lesser degree, by extensive well pumpage. Estimated herbicide degradation half-lives in the saturated environment were 1,000 days for atrazine, 400 days for alachlor, 250 days for cyanazine, 350 days for metolachlor, and 350 days for metribuzin.

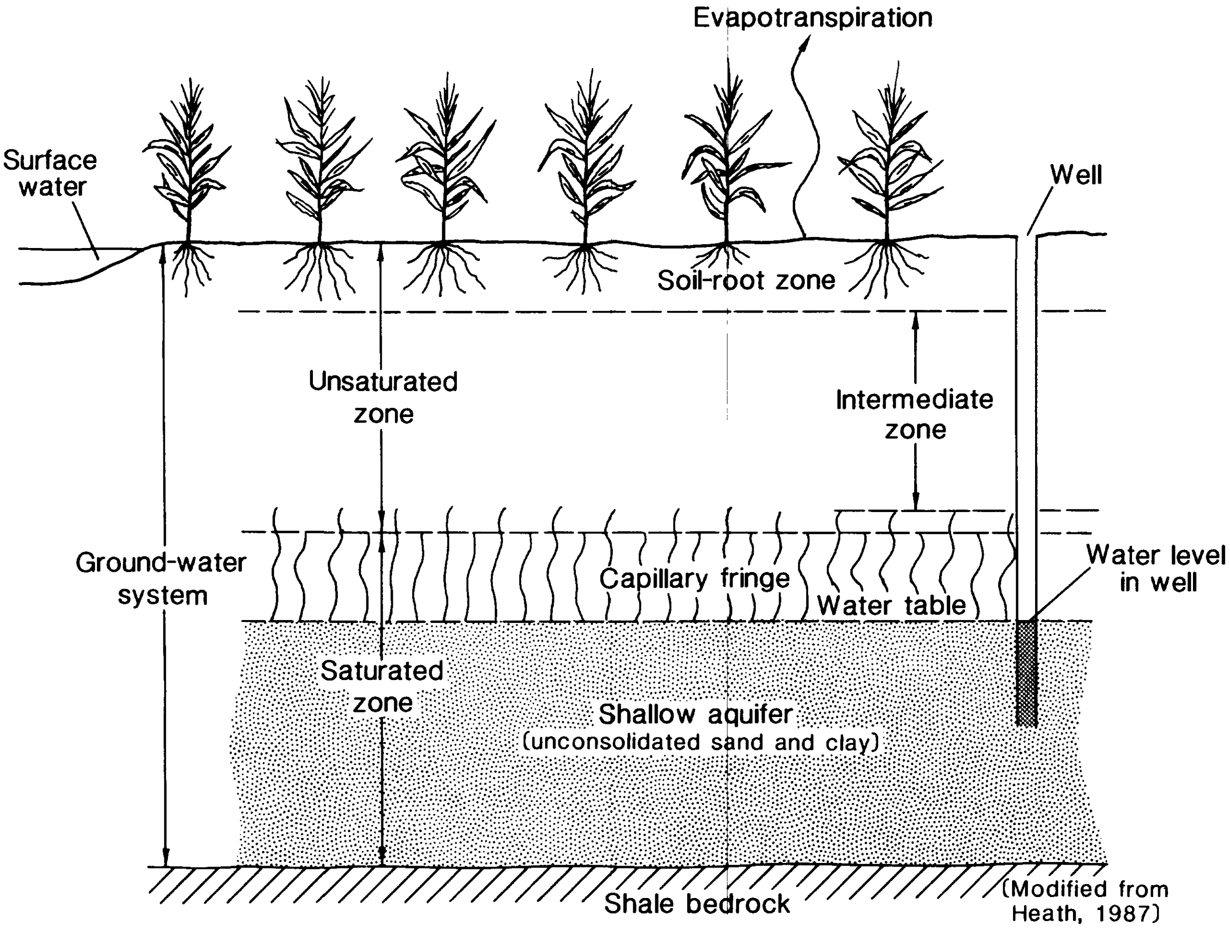
The herbicides will likely be eliminated from the soil and ground water at the experiment field by continued natural degradation at the land surface and by degradation in and continued pumping of water from the aquifer. Pumping will remove any degradation products as well as the remaining parent compounds.

INTRODUCTION

Contamination of water resources by potentially toxic organic compounds continues from nonpoint as well as point sources. Agricultural herbicides include a variety of organic compounds with greatly differing chemical properties that affect their environmental behavior and ultimate fate. During 1978, approximately 23.8 million pounds of herbicides were used in Kansas (Nilson and Johnson, 1980). With such extensive use of herbicides, intrusion of organic chemicals into the subsurface environment occurs, and residues of toxic herbicides are now being detected in shallow aquifers in many farming areas (Koelliker and others, 1987; Perry and others, 1988). In areas where the water table is near the surface and the soil and unsaturated zones consist of permeable sand, ground water may be susceptible to contamination by agricultural chemicals. Features of a shallow ground-water system are depicted in figure 1.

Very little is known about the movement and long-term pollution potential of agricultural herbicides in use today (1990). One of the most critical factors in evaluating the extent of contamination of ground-water resources by herbicides is the lack of information on the rate of degradation of herbicides in the saturated environment. Virtually all the research on degradation half-lives of herbicides has been conducted in the uppermost soil-root zone (fig. 1).

Determination of a herbicide's degradation half-life in the soil is one of the requirements for registration of the chemical by the U.S. Environmental Protection Agency. Herbicide degradation half-lives depend on many different soil properties, such as particle size, organic matter, pH, temperature, soil moisture, biotic activity, and ionic characteristics. Conditions in the soil-root zone vary considerably in both space and time. The chemical manufacturer is responsible for conducting, to the U.S. Environmental



(Modified from Heath, 1987)

Figure 1. Schematic diagram of a shallow ground-water system.

Protection Agency's satisfaction (U.S. Environmental Protection Agency, 1978), the experiments that will determine the registered herbicide half-life under anticipated soil conditions. These soil conditions usually are considerably different from conditions that occur in the underlying ground-water system. The lack of biotic activity and organic carbon, constant temperature and moisture conditions, and the reduction of oxygen are several factors that are known to retard the degradation of any organic chemical (McGlamery and Slife, 1966; Skipper and others, 1967; Gibson and Suflita, 1986). If an agricultural herbicide enters an environment in which any of the above factors are present, its degradation half-life would be expected to increase.

However, data are required to prove the hypothesis that herbicide degradation half-lives increase from a surface soil environment to a saturated environment. The construction of such an experiment would necessitate the actual contamination of an aquifer with the herbicides in question to a level that could be monitored by standard sampling and analytical procedures. Fortunately for this type of experiment, a field site was discovered where a shallow aquifer inadvertently had been contaminated by several herbicides from a single point source.

During August 1985, water was sampled from a well located on the Harvey County Experiment Field near Hesston, Kansas. This sampling was part of a cooperative effort between the Kansas Department of Health and Environment and the U.S. Geological Survey to assess the potential for contamination of ground water by herbicides. Analysis of the initial ground-water sample indicated the possibility of aquifer contamination by atrazine, alachlor, and metolachlor, which are herbicides commonly used on crops in the area. Two subsequent samples obtained in November 1985 and March 1986 confirmed herbicide concentrations of 46 µg/L (micrograms per liter) for atrazine, 1.9 µg/L for alachlor, 3.7 µg/L for cyanazine, 43 µg/L for metolachlor, and 14 µg/L for metribuzin. These values were substantially greater than the detection limits of the analytical procedure for each herbicide. The detection limit for any analytical procedure is the smallest concentration that can be reported with reliability. Smaller concentrations may be present in the sample but cannot be evaluated quantitatively. The finding of this preliminary sampling and analyses resulted in initiation of a cooperative investigation of the local ground-water system at the Experiment Field by the Kansas State University Agronomy Department, the Kansas Department of Health and Environment, and the U.S. Geological Survey.

Purpose and Scope

The purpose of this investigation was to: (1) Determine the source of the ground-water contamination and map its areal extent, and (2) estimate the future movement, dispersal, or degradation of the contamination. The objectives were to: (1) Identify the source and entry point of contamination, (2) determine the extent of the contamination plume to facilitate cleanup, and to advise nearby ground-water users, (3) perform a hydrologic analysis of the site involving local water-level mapping and aquifer-property estimations to determine future movement of the contaminants, and (4) assess herbicide dispersal and degradation in soil and ground water.

A case study of a point-source contamination by herbicides of the shallow aquifer at the Experimental Field resulted from the accomplishment of the investigation objectives. The herbicides investigated were atrazine, alachlor, cyanazine, metolachlor, and metribuzin. Herbicide concentrations were monitored for 4 years (1985-89). Originally, only the parent compounds were monitored. However, when reliable analytical procedures became available in 1988, the degradation products, deisopropylatrazine and deethylatrazine, were added to the analysis. A procedure for the other major degradation product of atrazine, hydroxyatrazine, was not available.

Site Description

The Harvey County Experiment Field is a part of the Kansas State University Agronomy Department's experimental-field system and is used to perform scientific agricultural research. This research includes crop-production, fertilizer-, herbicide-, and insecticide-application and tillage studies. The Harvey County Experiment Field is located in north-central Harvey County, approximately 0.5 mile west of Hesston, Kansas (fig. 2). Hesston is approximately 10 miles northwest of Newton and 35 miles north-northwest of Wichita in south-central Kansas.

The climate of the area is characterized by moderate precipitation, a wide range of temperatures, and moderately high average wind velocity. Mean annual precipitation at the site is 30.96 inches, and coupled with high summer temperatures and ample wind, evapotranspiration can deplete soil moisture during the growing season (April through September). However, short-term precipitation can exceed evapotranspiration requirements, resulting in periodic ground-water recharge (Farnsworth and Thompson, 1982).

The soil at the Harvey County Experiment Field is Ladysmith silty clay loam (Claassen and Fjell, 1985), and the land surface has very little relief. Typical field slopes usually are less than 2 percent. The soil has a surface layer of silty clay loam about 10 inches thick. The intermediate zone is silty clay that is not easily penetrated by roots, water, and air. The permeability of this soil commonly ranges from 0.20 to 0.63 inch per hour at the surface to less than 0.06 inch per hour in the deeper silty clay. The entire soil profile has a moderate to high shrink-swell potential and a pH range of 5.6 to 7.3 (Hoffman and Dowd, 1974).

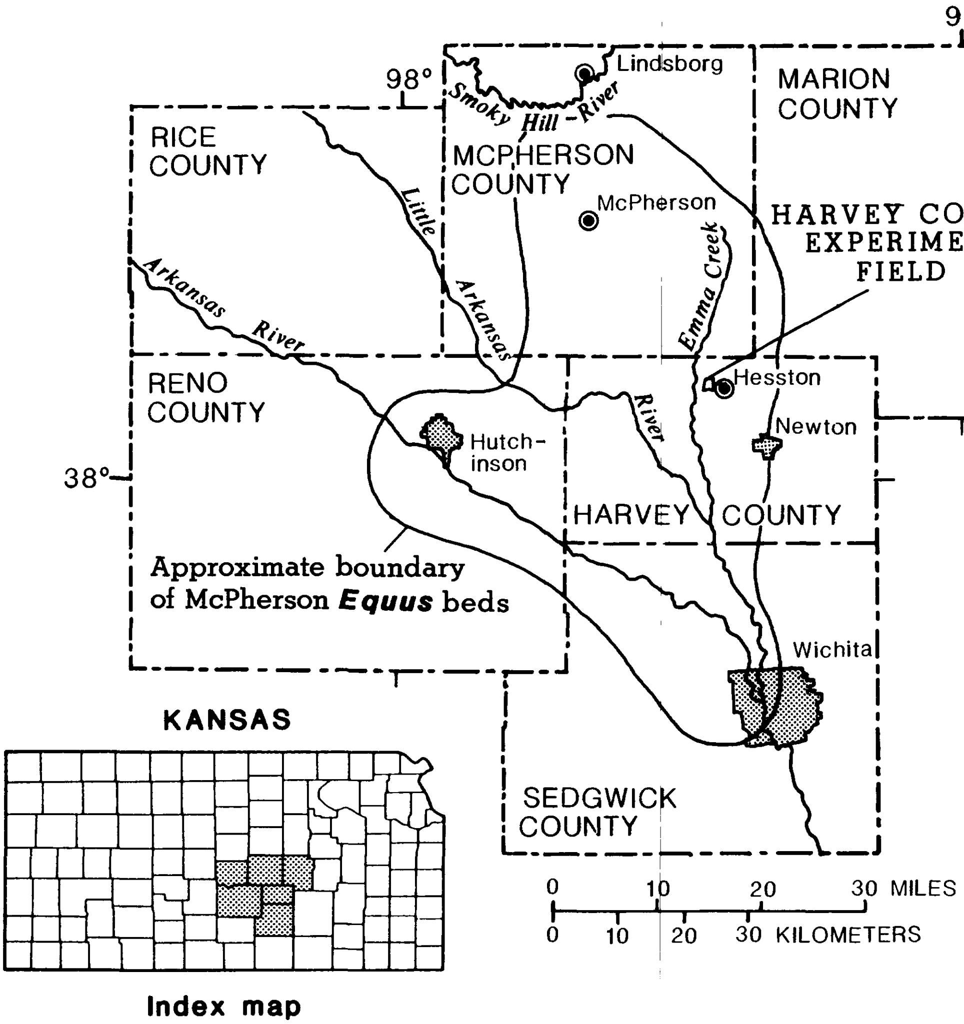


Figure 2. Location of Harvey County Experiment Field near Hesston.

The experiment field is located in the eastern part of the McPherson *Equus* beds (Williams and Lohman, 1949). These deposits (fig. 2), consisting of thin lenses of fine-to-medium sand, in places mixed with clay, generally yield less than 10 gallons per minute to domestic wells in this area. The water table is approximately 15 to 20 feet below land surface, and shale bedrock is another 10 to 25 feet deeper, as indicated by logs from nearby wells (on file with the Kansas Geological Survey, Lawrence).

Potential Sources of Herbicide Contamination

All the herbicides that were detected in the initial water samples had been used at the experiment field at one time or another. There were five potential sources from which the shallow aquifer could have been contaminated: (1) Leaching from concentrated surface contamination (sprayer-washout area) to the aquifer; (2) leaching from a septic-tank lateral field; (3) back-siphonage from a sprayer tank through water-supply lines and the well casing to the aquifer; (4) leaching from the surrounding agricultural fields to the aquifer; and (5) flow from a sprayer tank through the water-supply-line trench to the aquifer via the annular space of the domestic well.

At first observation, the most conspicuous of the potential sources was a low-lying area where water used to clean the herbicide sprayer had collected. Although sprayer cleaning at this location had been curtailed prior to the discovery of herbicides in the ground water, there was no vegetation growing in the low-lying area, indicating that a persistent herbicide residue was present. This "grass-kill" area was located approximately 75 feet southeast of the contaminated domestic well (fig. 3). The method of transport of the herbicides would be unsaturated flow downward through silty clay to the shallow aquifer and lateral saturated flow to the domestic well. The unsaturated flow could be enhanced by the formation of deep cracks in the clay during periods of little precipitation.

The second potential source was the lateral leach field for the septic-tank system serving the office and shop. Small quantities of herbicides could have entered the septic-tank system from a sink in the shop used for the cleaning of sprayer parts. The lateral field reportedly had been installed at a depth of 6 feet, placing the septic leachate about 10 feet above the water table.

The third potential source of contamination was back-siphonage from the herbicide-sprayer tank through the water-supply lines, through the pump, and down the domestic-well casing (fig. 4A). This potential source requires a scenerio of events. First, the end of the water-supply hose must be below the fluid level in the herbicide tank. Next, the water-supply pump would have had to fail, and simultaneously, the foot valve of the jet pump would have had to remain open to allow the water to siphon from the herbicide tank into the well casing and thence into the aquifer.

A fourth potential source of contamination could be that the herbicides found in the ground water may have leached from the agricultural fields surrounding the area. This would be a case of nonpoint-source contamination, whereas all the other potential sources would be considered point sources.

The fifth potential source of contamination was siphonage from the herbicide tank through the freeze-proof hydrant to the trench containing the water-supply line. This siphonage occurs when the valve of the hydrant is closed and water is released through the weep hole (fig. 4B). The only requirement is that the end of the water-supply hose remain below the fluid level in the herbicide-sprayer tank. Once in the trench, the contamination moves toward the domestic well through the disturbed soil and sand used for trench fill and then down the annular space of the well to the aquifer.

HYDROGEOLOGIC ANALYSIS

Observation-Well Installation

The local ground-water system was analyzed by installing a series of observation wells in the vicinity of the contaminated well located on the Harvey County Experiment Field (fig. 3). Nine observation wells were installed using techniques that prevented contamination during hollow-stem augering (Perry and Hart, 1985). Well casings were 2-inch polyvinyl-chloride pipe with 5-foot screens. The annular space between the screen and the borehole wall were packed with clean, coarse sand and the remaining borehole sealed with bentonite (fig. 4C). The top 10 feet of the well casings were protected with a concrete plug. The bottom of the well screen was placed from 5 to 10 feet below the water table.

A log of the auger cuttings was made at each observation well. In addition, a gamma log was taken both before and after the well was packed with sand and sealed with bentonite. These procedures enabled a good description of the lithology for each well site. The two types of logs indicated that there is significant variability between each well site with respect to depths of clay and sand lenses and the thickness of the water-bearing materials, which suggests a series of thin interbedded sand lenses. There was a trend, however, of increasing thickness of saturated sand in a southeast direction across the site. A three-dimensional layout of the site and the location of sand lenses in the lithology at each well site are shown in figure 5A.

Each well in the observation-well field, including the domestic well, had the altitude of its measuring point (MP) established by a set of levels run using an arbitrary datum. Water-table altitudes in all the wells were measured to

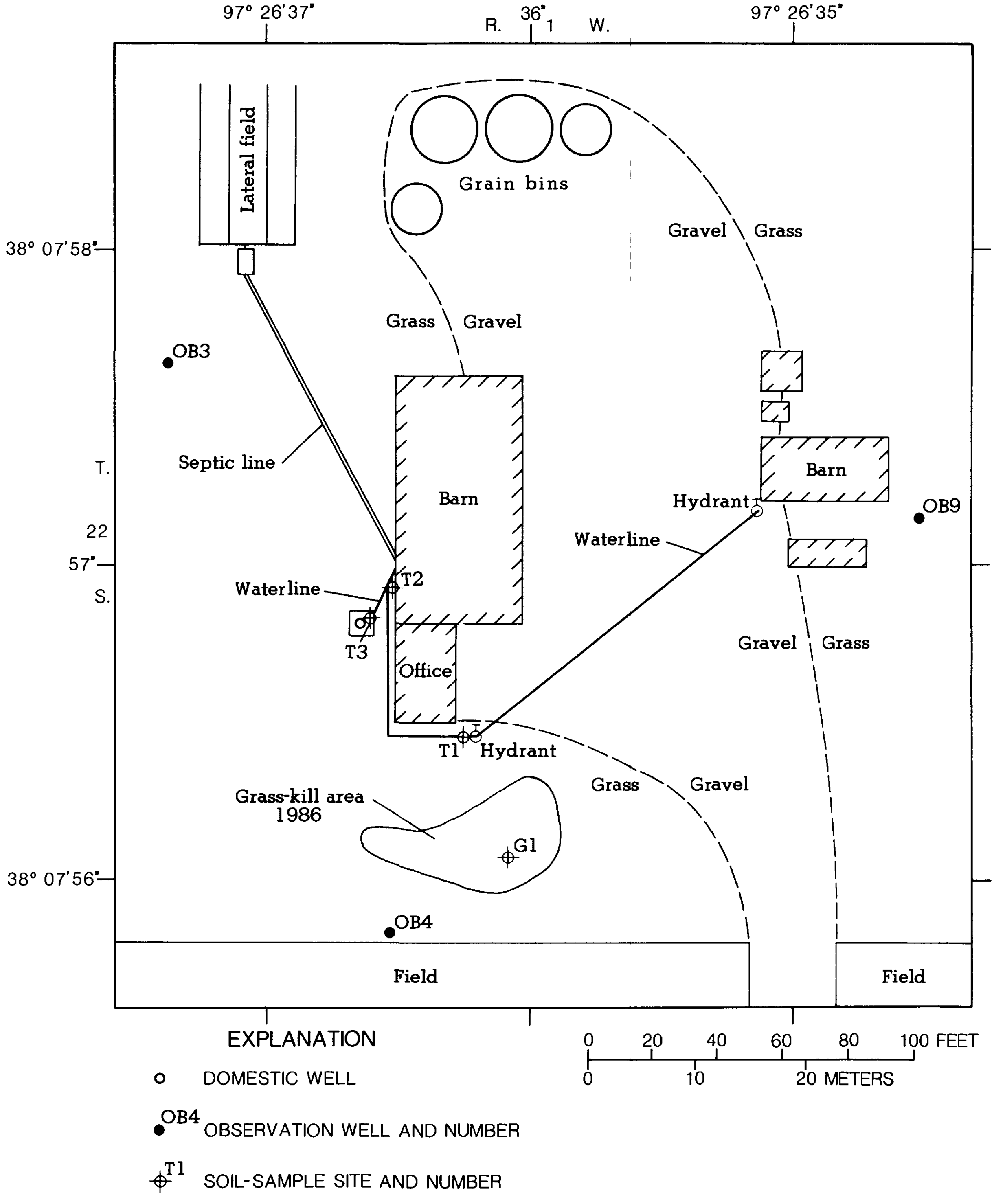


Figure 3. Location of Harvey County Experiment Field office and barns and adjacent site features.

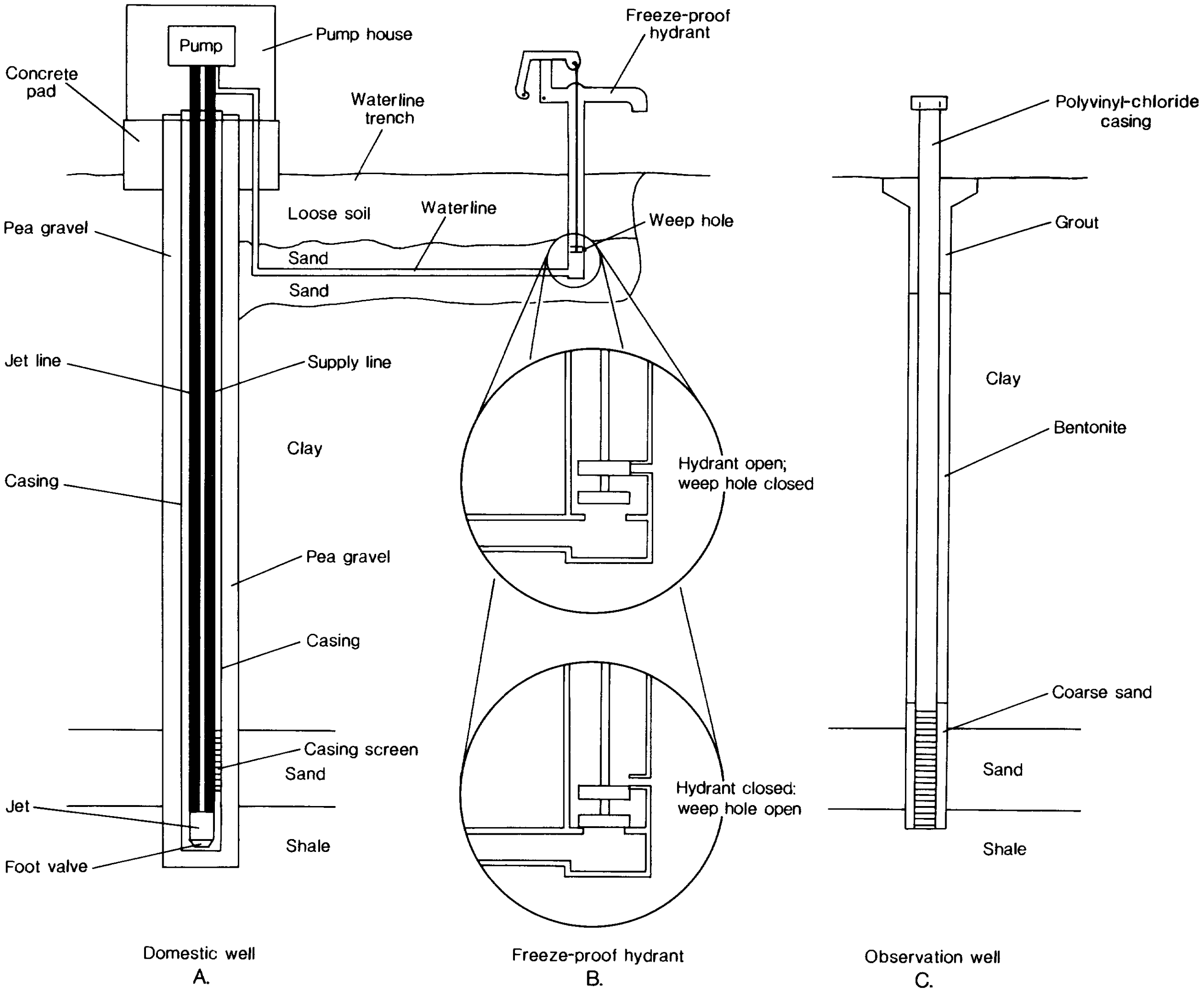


Figure 4. (A) domestic-well installation at Harvey County Experiment Field, (B) freeze-proof hydrant weep-hole function, and (C) observation-well construction.

an accuracy of 0.01 foot, and a map of the water-table surface on June 10, 1987, was developed (fig. 6). The water-table gradient was to the south-southeast and had a slope of about 0.004. The domestic well did not create any detectable change in the water-table surface because of its minimal usage.

Aquifer Test

As part of an evaluation of possible methods for removing the herbicides and their degradation products from the aquifer, an aquifer test was made using the domestic well and the nine observation wells. The domestic well was pumped continuously for more than 3 months, beginning on July 17, 1987, at an average rate of 3.3 gallons per minute using the existing jet pump. Water levels in the observation wells were measured frequently during the first 2 days of the test and intermittently thereafter until pumping was curtailed just before the first hard freeze in the fall. The computer program THEIS.VARQ (Butt and McElwee, 1984) was used to calculate transmissivity and storage coefficients by fitting the Theis equation to observed aquifer-test data. The calculated results for six of the nine observation wells are listed in table 1 (wells OB7 and OB8 were unaffected by pumping, and the computations for well OB5 did not converge to a solution).

The average transmissivity for six of the observation wells was 1.14 feet squared per day, with a range of 0.30 to 2.23 feet squared per day.

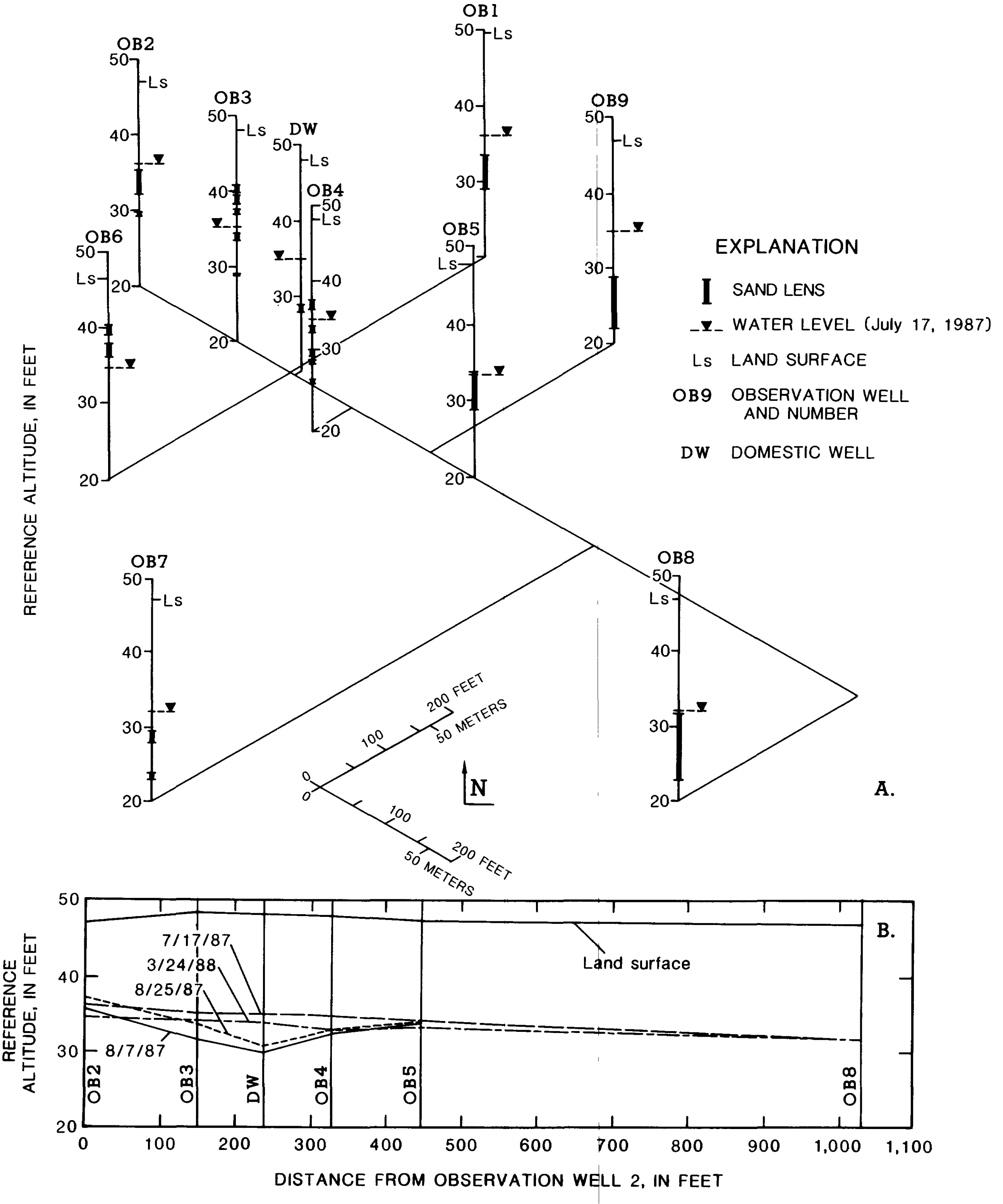


Figure 5. (A) Observation-well layout and relative position of sand lenses and (B) water-table altitudes for cross section at various times during study.

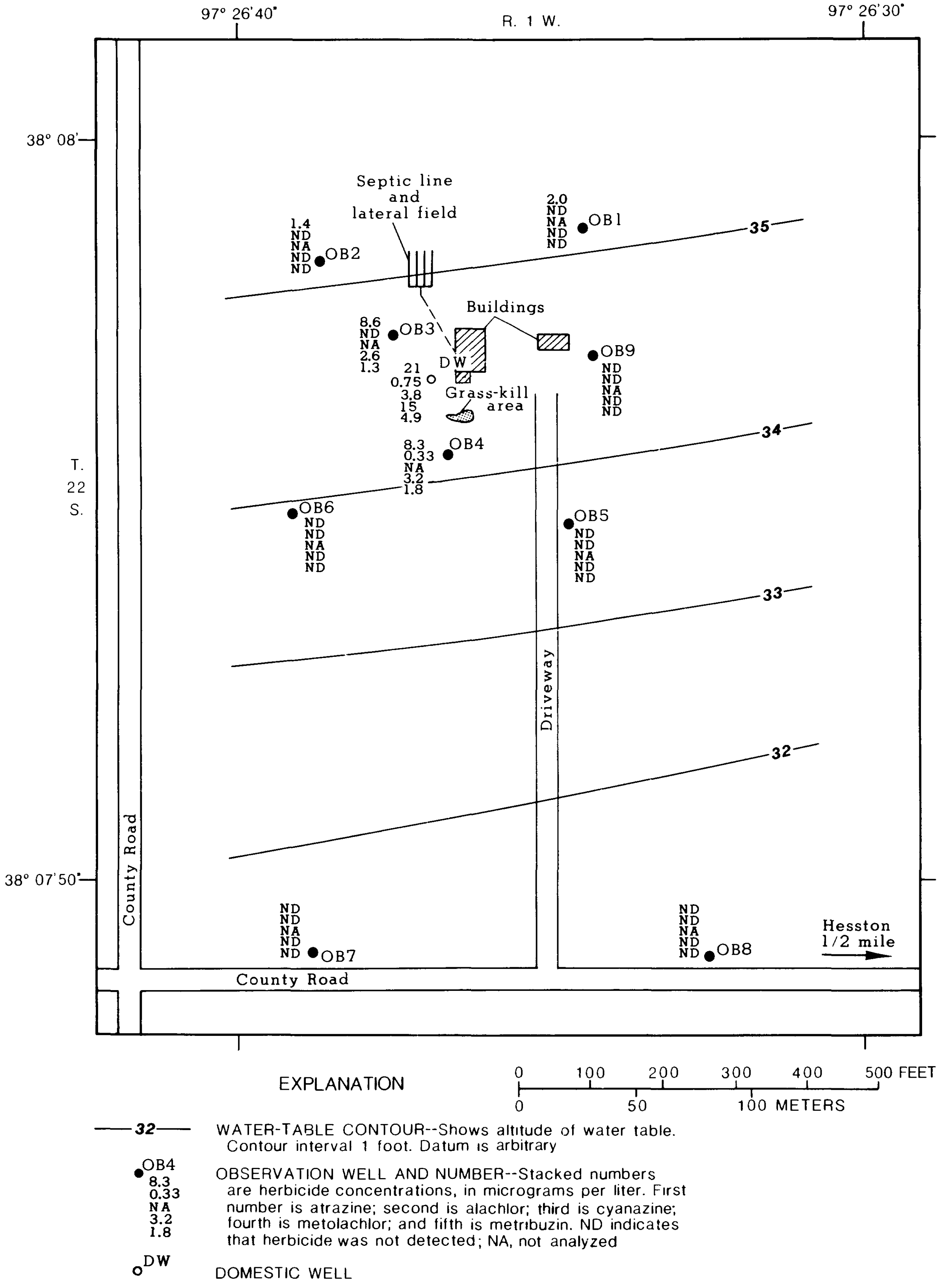


Figure 6. Water-table altitudes and herbicide concentrations, June 10, 1987.

Table 1. *Calculated transmissivity and storage coefficient for selected observation wells at the Harvey County Experiment Field*

Observation-well number (fig. 5)	Transmissivity (feet squared per day)	Storage coefficient (dimensionless)
OB1	1.65	0.000020
OB2	1.17	.000140
OB3	.30	.000019
OB4	.52	.000200
OB6	1.00	.000064
OB9	2.23	.000072
Average	1.14	0.000086

The relatively small values are reflected in the water-table altitudes observed in the observation wells on August 7, 1987, after 506 hours of constant pumping at 3.3 gallons per minute (fig. 5). These small values for transmissivity are caused by the thin interbedded layers of fine sand. The abundance of silt and clay causes the storage coefficients to be small, averaging 0.000086 for the six wells (table 1). The shallow aquifer is considered to be unconfined. By October 21, 1987, a well-established cone of depression had developed in the water table (fig. 7).

The first month of the aquifer test occurred during a period of slightly less-than-average rainfall, which totaled 2.49 inches. However, rainfall during the last three-fourths of the month of August was exceptional, totaling more than 7 inches. The water levels measured on August 25 indicated that some recharge to the aquifer had occurred (fig. 5). All meteorological factors were collected routinely and automatically by instruments installed at the experiment field. Water levels in the wells decreased slightly from August 25 to October 21, during which average pumping rates were 3.2 gallons per minute. The total volume of water pumped from July 17 until October 21 was approximately 1.4 acre-feet. The water was applied to nearby fields using several lawn sprinklers. The water was consumed by a late-maturing crop of soybeans.

Soil and Water Analyses

Various soil and water samples were collected at specific locations and times to determine the original source of the herbicide contamination, the extent of the contamination plume, and the effect of pumping. Both physical and chemical measurements were made throughout the investigation.

Soil Analyses

The permeability of the soil near the area where the grass had been killed by herbicide residues was measured using an in-situ permeameter. Measurements were taken at 2.1 and 4.1 feet. The 2.1-foot measurement resulted in a permeability of 3.3 inches per day, and the 4.1-foot measurement was about 0.25 inch per day. These permeability values indicated that vertical movement of contaminants through the soil would be very slow. However, the Ladysmith soil is subject to shrinkage during moisture-deficient periods, enabling water and solids to move downward through the macropores (Hoffman and Dowd, 1974).

In addition to the permeability test, the soil was analyzed for particle-size distribution, pH, and organic-carbon matter at various locations and through various depths. The particle-size distribution confirmed the homogeneity of the soil over the part of the

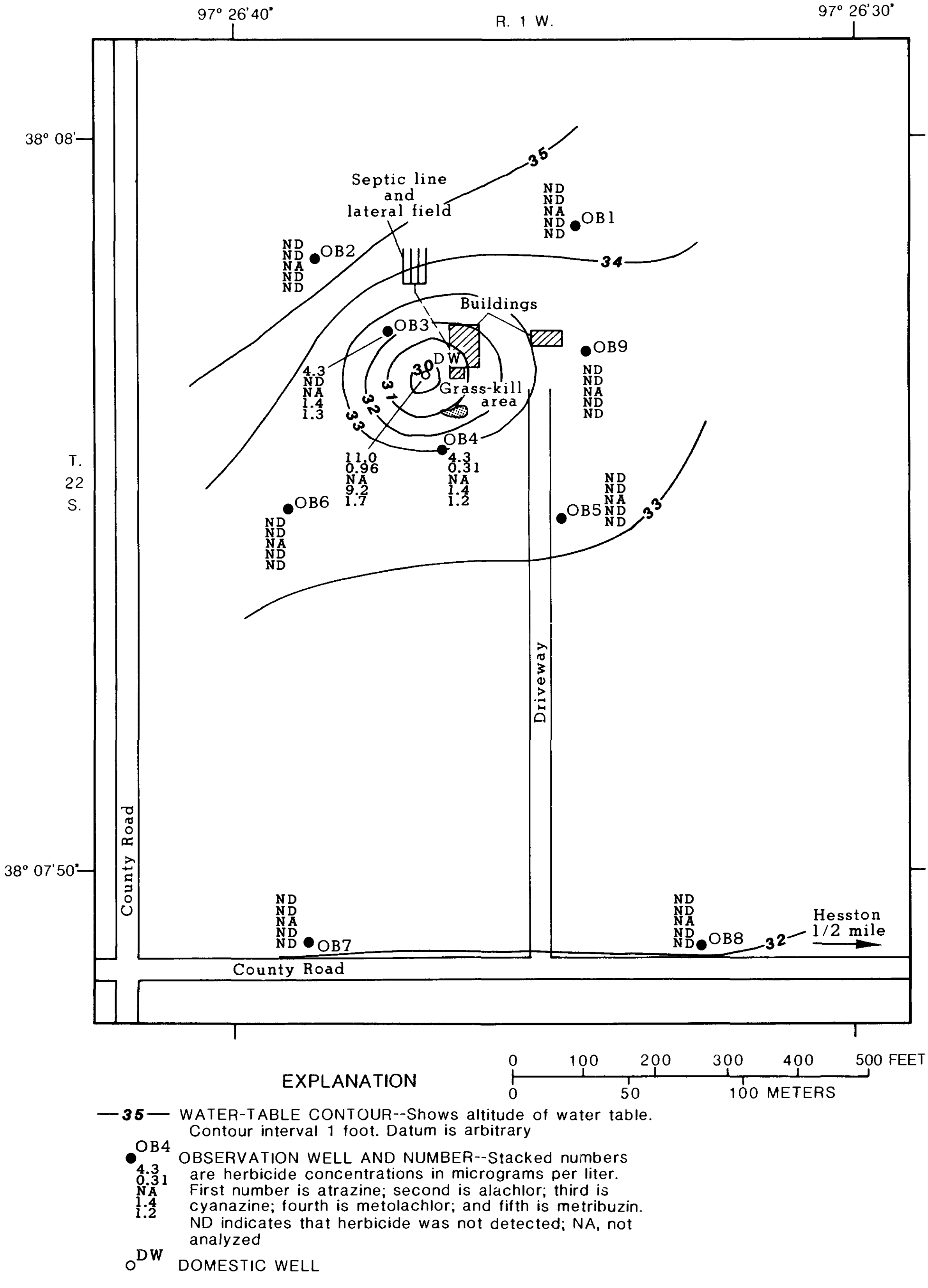


Figure 7. Water-table altitudes and herbicide concentrations, October 21, 1987.

Table 2. *Herbicide analysis of soil matrix at various locations*

[Detection limit in soil matrix for atrazine and metolachlor was 4.0 micrograms per kilogram; NA, not analyzed for; ND, not detected]

Sample location (fig. 3)	Date (month/ day/ year)	Sample depth (feet below land surface)	Material	Herbicide concentration (micrograms per kilogram)	
				Atrazine	Metolachlor
G1-A	3/27/86	1.0-1.5	Clay	6.2	NA
G1-B	3/27/86	3.0-3.5	Clay	ND	NA
G1-C	3/27/86	4.0-5.0	Clay	ND	NA
G1-D	3/27/86	9.0-10.0	Clay	ND	NA
G1-E	3/27/86	13.0-14.0	Clay	ND	NA
G1-F	3/27/86	21.0-22.0	Saturated fine sand; 0.1-foot clay lens at 21.9 feet	10.1	NA
G1-G	3/27/86	22.0-22.5	Saturated sand	0	NA
T1-A (hydrant weep hole)	3/24/88	1.5-2.5	Gravel	32.4	ND[1]
T2-A (building	3/24/88	1.0-1.5	Sand	2.9	ND
T2-B foundation)	3/24/88	2.0-3.0	Sand	ND	32.4
T3-A (pump-house	3/24/88	1.5-2.0	Pea-sized gravel	ND	ND
T3-B well casing)	3/24/88	2.0-3.0	Pea-sized gravel	ND	ND

[1] Interference in gas-chromatograph analysis.

experiment field that was under investigation. The pH and organic-carbon matter indicated that the soil was slightly acidic (pH of 6.8) at the surface and that it contained 8.3 grams per kilogram of organic carbon.

Soil from the grass-kill area (G1) was analyzed in segments down to the water table. An atrazine concentration of 6.2 µg/kg (micrograms per kilogram) was measured in the top 18 inches, indicating that washwater or a chemical spill definitely had collected in the shallow depression. However, below 18 inches, the soil samples did not yield detectable concentrations of atrazine until the aquifer was penetrated 21 feet below land surface. In addition, soil samples were obtained from the waterline trench, the building foundation, and from packing material around the domestic-well casing near the ground surface. Elevated concentrations of both atrazine and metolachlor (greater than 20 µg/kg) were detected in the waterline trench and the foundation backfill material. However, neither herbicide was detected in the well-packing material. Results of the soil analyses are listed in tables 2 and 3.

Water Analyses

Water from the domestic well on the experiment field was first analyzed from a sample collected in August 1985. Atrazine and metolachlor were detected in concentrations larger than in any previously analyzed sample of ground water from Kansas. Subsequent samples were collected to confirm the presence and concentration of the herbicides. During each sampling, specific conductance, pH, and water temperature were determined onsite. On three occasions, water samples were obtained from the domestic well and from the observation-well network. These particular samples were analyzed at the U.S. Geological Survey's laboratory in Arvada, Colorado, for specific conductance, pH, alkalinity, inorganic cations, sulfate, chloride, nitrate, ammonia, phosphate, iron, and manganese. Concentrations of these constituents for the different sampling times are listed in table 4. Concentrations of herbicide in duplicate samples obtained from the domestic well and the observation wells were determined at several different laboratories. Herbicide concentrations are listed in table 5.

Table 3. *Organic-carbon matter in soil at location G1, Harvey County Experiment Field*

Depth interval (feet)	Organic-carbon matter, in grams per kilogram as carbon	
	Total organic carbon	Inorganic carbon
Surface-1.0	8.3	0.1
1.0-2.0	4.6	.2
2.0-3.0	3.2	.7
3.0-4.0	2.9	.4

Interpretation of Water-Quality Data

All water-quality data were plotted on maps showing the location of observation wells and the potential sources of the contamination. The potential sources of the contamination were: (1) The grass-kill area, 75 feet south-southeast of the domestic well; (2) the septic-tank lateral field about 130 to 180 feet north-northwest of the domestic well; (3) back-siphonage from a sprayer tank through the water-supply lines; (4) the surrounding agricultural fields; and (5) transport down the annular space of the domestic well.

The sulfate, chloride, nitrate, and phosphate concentrations were slightly increased in samples from the observation wells closest to the lateral field. These constituents are indicators of septic-tank leachate, and evidence of leachate can be seen in the ground-water analyses. Calcium, magnesium, sodium, potassium, silica, iron, and manganese did not show any areal trends.

Herbicide concentrations did not exhibit the same pattern as the sulfate, chloride, nitrate, and phosphate concentrations. Concentrations of atrazine, alachlor, metolachlor, and metribuzin detected in the domestic and observation wells on June 10, 1987, are shown in figure 6. The largest concentrations were detected in water from the domestic well, and concentrations decreased symmetrically to water from the two closest observation wells (OB3 and OB4). Herbicide concentrations on October 21, 1987, after the domestic well had been pumped continuously at 3.3 gallons per minute since July 17, 1987, are

Table 4. *Inorganic chemical analyses of water samples from a domestic well and observation wells, Harvey County Experiment Field, 1985-87*

[Concentrations are given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C), milligrams per liter (mg/L), and micrograms per liter (µg/L), except as noted]

Well number (fig. 5)	Date of sample (month/day/year)	Specific conductance, (µS/cm at 25 °C)	pH (standard units)	Calcium, dissolved as Ca (mg/L)	Magnesium, dissolved as Mg (mg/L)	Sodium, dissolved as Na (mg/L)	Potassium, dissolved as K (mg/L)	Alkalinity, total as $CaCO_3$ (mg/L)	Sulfate, dissolved as SO_4 (mg/L)	Chloride, dissolved as Cl (mg/L)
DW	11/5/85	--	--	--	--	--	--	--	--	--
	3/27/86	--	--	--	--	--	--	--	--	--
	3/17/87	--	--	--	--	--	--	--	--	--
	6/10/87	879	7.6	72	16	84	0.7	249	47	57
	7/17/87	883	7.5	60	15	86	.6	309	49	47
	10/21/87	1,010	7.4	89	19	110	.8	350	53	84
	11/20/87	--	--	--	--	--	--	--	--	--
OB1	6/10/87	1,101	7.5	88	12	110	1.3	265	46	130
	10/21/87	1,088	7.4	94	14	120	1.2	284	43	130
OB2	6/10/87	881	7.7	65	16	90	2.5	226	49	76
	10/21/87	--	--	--	--	--	--	--	--	--
OB3	6/10/87	1,172	7.5	89	16	130	1.3	285	80	88
	10/21/87	1,283	7.3	129	21	130	1.2	347	52	170
OB4	6/10/87	999	7.4	88	15	100	1.7	321	63	58
	10/21/87	--	--	--	--	--	--	--	--	--
OB5	6/10/87	1,041	7.5	82	14	120	1.0	252	47	92
	10/21/87	1,026	7.4	82	13	140	.7	323	64	92
OB6	7/17/87	1,430	7.6	83	19	150	.6	313	49	47
	10/21/87	2,170	7.3	180	34	230	1.5	225	85	440
OB7	6/10/87	2,410	7.5	210	38	190	2.0	169	40	550
	10/21/87	--	--	--	--	--	--	--	--	--
OB8	6/10/87	1,123	7.5	99	17	100	1.3	285	44	130
	10/21/87	1,135	7.5	110	21	110	1.4	297	44	150
OB9	7/17/87	953	7.6	62	14	110	1.2	336	40	87
	10/21/87	969	7.6	79	16	110	1.0	324	40	100

Table 4. *Inorganic chemical analyses of water samples from a domestic well and observation wells, Harvey County Experiment Field, 1985-87*--Continued

Well number (fig. 5)	Date of sample (month/ day/ year)	Fluoride, dissolved as F (mg/L)	Silica, dissolved as SiO_2 (mg/L)	Nitrate, total as NO_3 (mg/L)	Nitrogen, ammonia, dissolved as NH_4 (mg/L)	Phosphate, total as PO_4 (mg/L)	Iron, dissolved as Fe (µg/L)	Manganese, dissolved as Mn (µg/L)
DW	11/5/85	--	--	--	--	--	--	--
	3/27/86	--	--	--	--	--	--	--
	3/17/87	--	--	--	--	--	--	--
	6/10/87	0.6	20	2.8	0.030	0.01	3	1
	7/17/87	.2	2.7	2.6	.039	.01	60	<10
	10/21/87	.6	22	4.3	.046	.01	6	2
	11/20/87	--	--	--	--	--	--	--
OB1	6/10/87	.5	20	2.1	.114	.03	3	3
	10/21/87	.5	24	1.4	.102	.01	33	94
OB2	6/10/87	.8	24	1.7	.086	.02	4	1
	10/21/87	--	--	--	--	--	--	--
OB3	6/10/87	.5	21	10.0	.057	.04	82	10
	10/21/87	.5	26	1.4	.072	.03	400	49
OB4	6/10/87	.5	21	3.0	.103	.05	6	9
	10/21/87	--	--	--	--	--	--	--
OB5	6/10/87	.4	22	2.9	.084	.01	13	3
	10/21/87	.4	26	2.5	.104	.01	17	100
OB6	7/17/87	.2	2.7	1.1	.077	.01	60	10
	10/21/87	.4	26	4.6	.101	.01	20	50
OB7	6/10/87	.4	24	8.5	.144	.02	20	10
	10/21/87	--	--	--	--	--	--	--
OB8	6/10/87	.4	21	2.4	.093	.02	5	1
	10/21/87	.5	25	3.7	.087	.01	540	54
OB9	7/17/87	.2	19	1.7	.038	.03	20	10
	10/21/87	.5	23	2.0	.080	.01	16	160

Table 5. *Herbicide concentrations in water samples obtained from observation wells, Harvey County Experimental Field, 1985-88*

[Concentrations are in micrograms per liter; NA, not analyzed for; ND, not detected]

Well number (fig. 5)	Date of sample (month/day/ year)	Atrazine[1]	Alachlor[2]	Cyanazine[3]	Metolachlor[4]	Metribuzin[5]
DW	11/5/85	29	NA	2.0	32	NA
	3/27/86	46	1.9	3.7	43	14
	3/17/87	29	1.3	4.4	18	7.2
	6/10/87	21	.75	3.8	15	4.9
	7/17/87	31	.81	2.7	20	5.7
	10/21/87	11	.96	NA	9.2	1.7
	11/20/87	8.5	.75	NA	5.5	1.5
	3/24/88	4.1	ND	ND	1.3	.41
	9/2/88	5.8	.73	NA	3.1	.84
	12/1/88	2.7	.45	NA	1.3	.58
	12/1/88[6]	3.0	.50	NA	2.0	.60
OB1	6/10/87	2	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB2	6/10/87	1.4	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB3	6/10/87	8.6	ND	NA	2.6	1.3
	10/21/87	4.3	ND	NA	1.4	.47
	3/24/88	2.7	ND	ND	.63	.25
	9/2/88	2.4	ND	NA	.65	.42
OB4	6/10/87	8.3	.33	NA	3.2	1.8
	10/21/87	4.3	.31	NA	1.4	1.2
	3/24/88	4.0	ND	ND	1.2	.89
	9/2/88	3.6	.32	NA	.87	.88
	12/1/88	3.6	.39	NA	.76	.76
	12/1/88[6]	3.1	.32	NA	.65	.68
OB5	6/10/87	ND	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB6	7/17/87	ND	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB7	6/10/87	ND	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB8	6/10/87	ND	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND
OB9	7/17/87	ND	ND	NA	ND	ND
	10/21/87	ND	ND	NA	ND	ND

[1] Detection limit is 1.2 micrograms per liter.

[2] Detection limit is 0.25 microgram per liter.

[3] Detection limit is 0.50 microgram per liter.

[4] Detection limit is 0.25 microgram per liter.

[5] Detection limit is 0.10 microgram per liter.

[6] Duplicate sample.

shown in figure 7. The water-table surface in figure 7 shows a cone of depression extending to about 200 feet from the pumped well. On October 21, 1987, herbicide concentrations also were symmetrical about the domestic well (DW), and all concentrations were less, except for alachlor in water from the domestic well. The concentration of alachlor in water from the domestic well increased slightly from 0.75 to 0.96 µg/L during the pumping interval. Alachlor concentrations in water from observation well 0B4 decreased slightly (0.33 to 0.31 µg/L). Of the three wells (0B3, 0B4, and DW) in which concentrations of atrazine, metolachlor, and metribuzin were detected in water samples both before and after pumping, the average percentage decrease in concentration was 50 percent. In water from two other wells where only atrazine was detected before pumping commenced (0B1 and 0B2), concentrations decreased to less than the detection limit of 1.2 µg/L.

SOURCE AND EXTENT OF CONTAMINATION

The five potential sources of contamination were examined in light of the hydrogeologic analysis. The first potential source, the sprayer-washout area, did not show a positive connection with contamination in the aquifer. Soil analyses within the grass-kill area revealed contaminated soil only in the top 18 inches of the soil layer. Cracks in the soil could have allowed limited lateral transport of herbicides during intense rainfall after a period of very little rainfall; however, the surface gradient is slightly uphill from the grass-kill area to the well. Also, the pattern of herbicide concentrations in water from the observation wells was not coincident with the grass-kill area. On the basis of observed grass recovery during the period of this investigation (August 1985 to December 1989), herbicide concentrations in the soil at this location have become insignificant.

The second potential source, the septic-tank lateral field, does not appear to be the source of herbicide contamination. The most obvious feature was the symmetrical distribution of herbicide concentrations around the domestic well. This distribution did not indicate any relation to the location of the septic-tank lateral field. A few inorganic constituents, such as sulfate, nitrate, and phosphate, did have slightly larger concentrations near the lateral field. The lack of a definite indication of sewage leachate could be a result of minimal usage of the septic system.

The third potential source of contamination was back-siphonage from a sprayer tank through the water-supply line, through the pump, down the inside of the well casing, and out the well foot valve into the aquifer. However, according to statements made by personnel working at the experimental field, there were no known pump failures during their employment. Therefore, this source of contamination is unlikely.

The fourth potential source was leaching of herbicides from the agricultural fields surrounding the experiment field buildings. Examination of observation-well herbicide data eliminated this source, as water from several of the observation wells located in the agricultural fields did not have detectable herbicide concentrations. The largest concentrations and the greatest variety of herbicides were found in water from the domestic well and the two closest observation wells (OB3 and OB4).

Examination of all the data from the hydrogeologic analysis indicated that the path of herbicide contamination was from the freeze-proof hydrant down the sand-filled trench of the water-supply line or along the foundation of the barn to the well, and down the annular space of the domestic well to the water table. A schematic diagram of the most probable route is shown in figure 8. Details of the weep hole and foot valve are shown in figure 4B. When the sprayer tank is full and the hydrant is closed, the fluid is immediately siphoned from the sprayer tank out through the weep hole in the bottom of the hydrant. The length of time that the hose remains in the tank determines the volume of the herbicide mixture that reaches the trench in which the water-supply line is laid.

The soil in which the trench was dug is silty clay, and it forms a trough down which the fluid mixture flows. The fill material in the trench consists of sand, gravel, and loosely packed soil, further enhancing the movement of the herbicides toward the well. Each time the hydrant is opened and closed, a small amount of

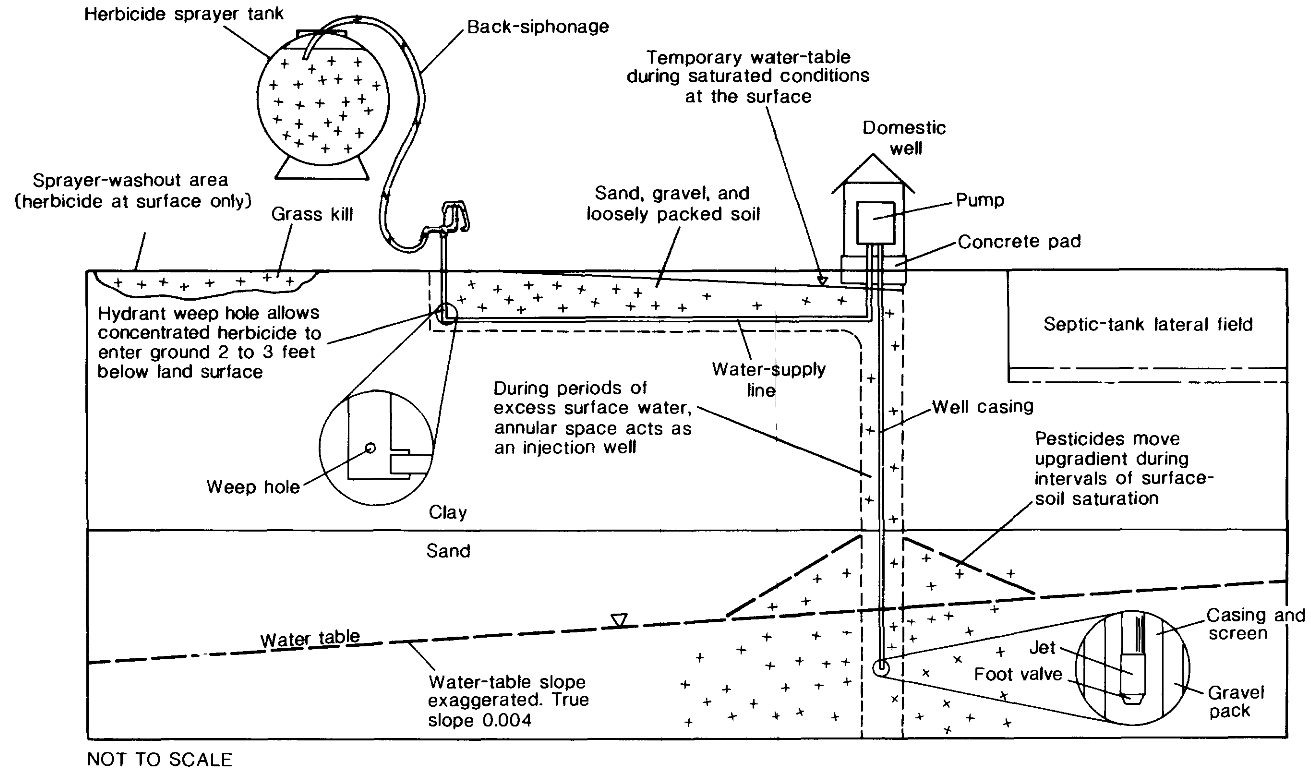


Figure 8. Most probable route of herbicide movement from land surface to saturated zone.

water flows from the weep hole, which may aid in the transport of the herbicide back toward the well. Once the contamination reaches the wellhead it then can seep down the annular space between the well casing and the borehole. The only seal for the well is a concrete pad on which the pump house is built. Visual examination under the pad revealed pea-sized gravel, used to pack the well screen, extending at least 6 feet below the land surface. Water in the water-supply line trench from back-siphonage or from excess surface water during intense rainfall helped transport the herbicides down the annular space of the well. Under a hydraulic head of 15 feet, the herbicides were able to move into the aquifer in all directions.

This process explains the reason why herbicide concentrations were in a nearly circular pattern around the domestic well and why the herbicides were able to move to areas that were upgradient from the domestic well. Major back-siphonage through the hydrant or significant precipitation would fill the water-supply line trench completely. The hydraulic head in the trench would be at or just below the surface. The hydraulic head in the aquifer would be at least 15 feet lower. Therefore, the 15-foot head difference would force the water and herbicide mixture from the annular space of the borehole into the aquifer equally in all directions. Slight differences in lateral transmissivity caused by interbedding of the sand and clay layers limited the movement of the herbicides to the east to observation well OB9 (fig. 7). This partially explains the fact that the lines of equal herbicide concentrations are nearly concentric with the position of the domestic well. The small transmissivity of the aquifer and the small regional ground-water gradient combine to inhibit movement of the contamination away from the immediate area of its source.

FATE OF HERBICIDES IN SOIL AND GROUND WATER

When herbicides were initially detected at the Harvey County Experiment Field in 1985, concentrations in the ground water were large enough to cause concern. By the spring of 1988, herbicide concentrations in the ground water had decreased by more than one order of magnitude (table 5). Herbicide concentrations in the soil at the grass-kill area and in the waterline trenches had become smaller than average agricultural-field surface concentrations (table 2). Maximum concentrations of atrazine in water from the domestic well and the closest observation wells for March 24, 1988, ranged from 2.7 to 4.1 µg/L. The decrease in herbicide concentrations in the ground water is thought to be a result of extensive pumping of the domestic well and degradation of parent compounds.

The remaining herbicide contamination at the surface should degrade to levels that are less than detection limits by 1990 as long as no additional spillage occurs. Therefore, removal of soil material probably is not needed. The remaining traces of the herbicides in the ground water could be reduced further by pumping the domestic well. Because the concentration in the water of any herbicide is less than 5 µg/L, the water could be disposed of by simple surface application to agricultural fields.

DEGRADATION OF HERBICIDES IN SATURATED ZONE

The herbicides detected in the ground water below the Harvey County Experiment Field were determined to have entered the aquifer by means of the domestic well, a point source. Over a period of 2 years, the herbicide concentrations decreased as a decay-type function. A case study of the decrease in concentrations of the five herbicide detected--atrazine, alachlor, cyanazine, metolachlor, and metribuzin--was conducted to determine if herbicides were degrading and to determine their degradation half-lives.

After the first indication that the shallow aquifer had been contaminated, all activity involving herbicide usage was closely monitored. After August 1985, no additional herbicides entered the contamination pathway. Hydrogeologic analysis of the site indicated that the aquifer was shallow (21 feet) and thin (2 feet) at the domestic well and was interbedded with clay lenses. The local ground-water gradient was slight (0.004), and transmissivity through the saturated material was small (average 1.14 feet squared per day). The combination of these factors result in slow movement of water through the aquifer. In fact, the initial volume of herbicide contamination did not move laterally. Pumpage from the domestic well was negligible prior to the aquifer test conducted between July and October 1987. Therefore, it was assumed that decreases in herbicide concentrations in water from the domestic well and observation wells 0B3 and 0B4 before July 1987 were caused primarily by degradation of parent compounds.

A plot of the decrease in concentrations of the five herbicides from August 1985 to April 1988 is shown in figure 9 for the domestic well and in figure 10 for observation well OB4. Concentrations decreased as a decay function until the aquifer test, which started July 17 and ended October 20, 1987. Intermittent pumping after October 20, 1987, resulted in modified rates of decreasing concentrations. The recovery of the cone of depression from October 20, 1987, to March 24, 1988, created an asymmetrical herbicide distribution for the March 24, 1988, sampling (table 5).

Estimation of the degradation half-life for each of the five herbicides in the saturated zone was made from the plots in figure 9, and these values are listed in table 6. The degradation half-life for each herbicide in the soil-root zone (Perry and others, 1988) is listed also. Apparently, half-lives in the saturated zone may be more than 10 times longer than those in the soil. These degradation half-lives are compared graphically with the concentrations of herbicides detected after October 21, 1987, in water from the domestic well (fig. 9) and observation well OB4 (fig. 10). Extensive pumping of the domestic well decreased the concentration of cyanazine to less than detection levels. Pumping substantially decreased the concentrations of atrazine, alachlor, and metribuzin and made the rate of decrease change. The apparent increase in the concentrations of alachlor after the aquifer test in water from both the domestic well and observation well OB4 does not have a plausible explanation.

The estimated degradation half-life for atrazine of 1,000 days is supported also by the concentrations of two degradation products of atrazine--deisopropylatrazine (DIA) and deethylatrazine (DEA). The concentrations of these two degradation products are small in comparison to the parent compounds (table 7).

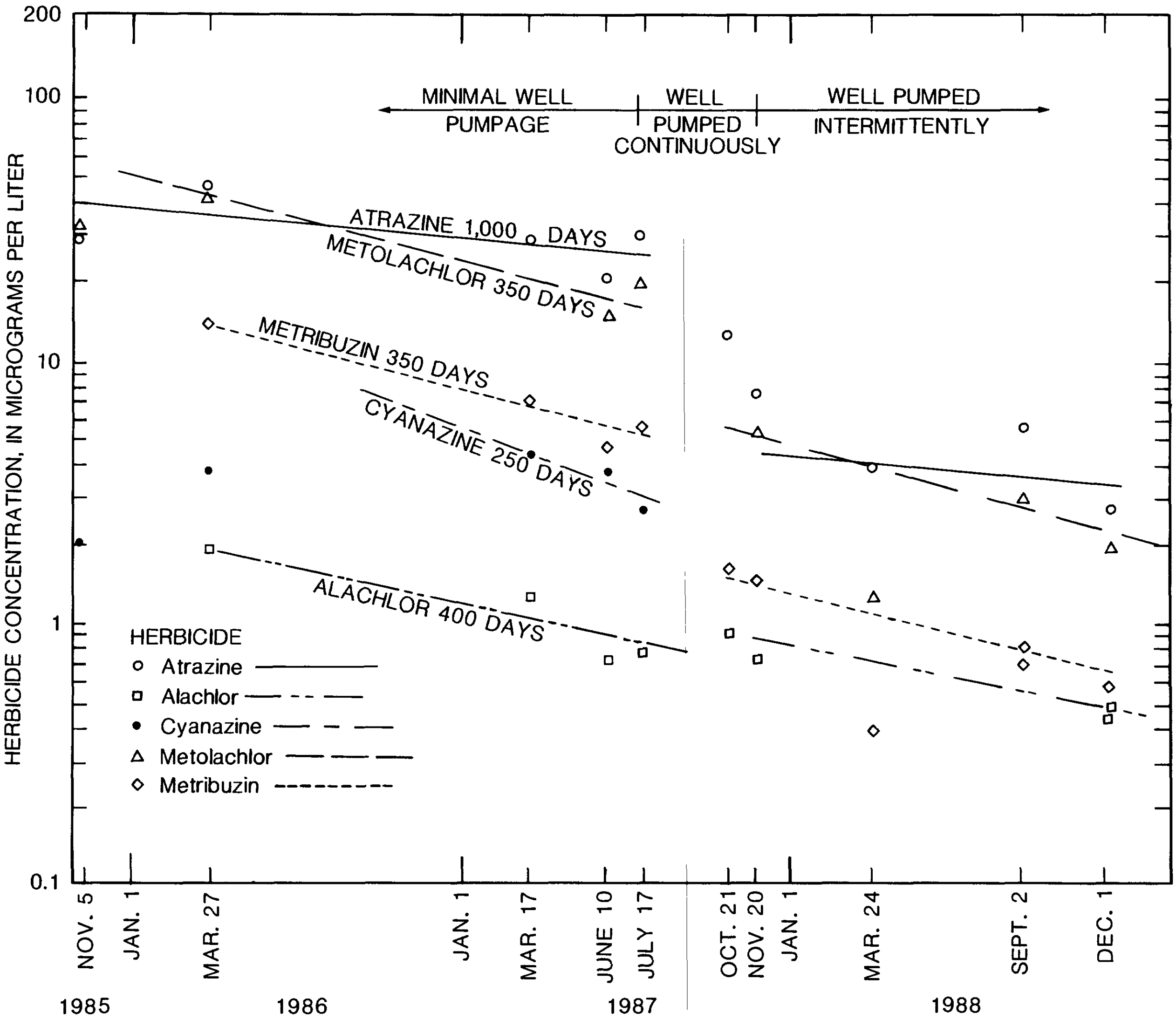


Figure 9. Degradation half-life determinations for herbicides in saturated zone, Harvey County Experiment Field domestic well, August 1985 to July 1987, and comparison of those half-lives with concentrations observed October 1987 to December 1988.

Table 6. *Degradation half-lives for atrazine, alachlor, cyanazine, metolachlor, and metribuzin in soil and saturated zone*

Herbicide	Degradation half-life in soil (days) (from Perry and others, 1988)	Estimated degradation half-life in saturated zone (days)
Atrazine	67-365	1,000
Alachlor	26-70	400
Cyanazine	14-20	250
Metolachlor	15-50	350
Metribuzin	7-28	350

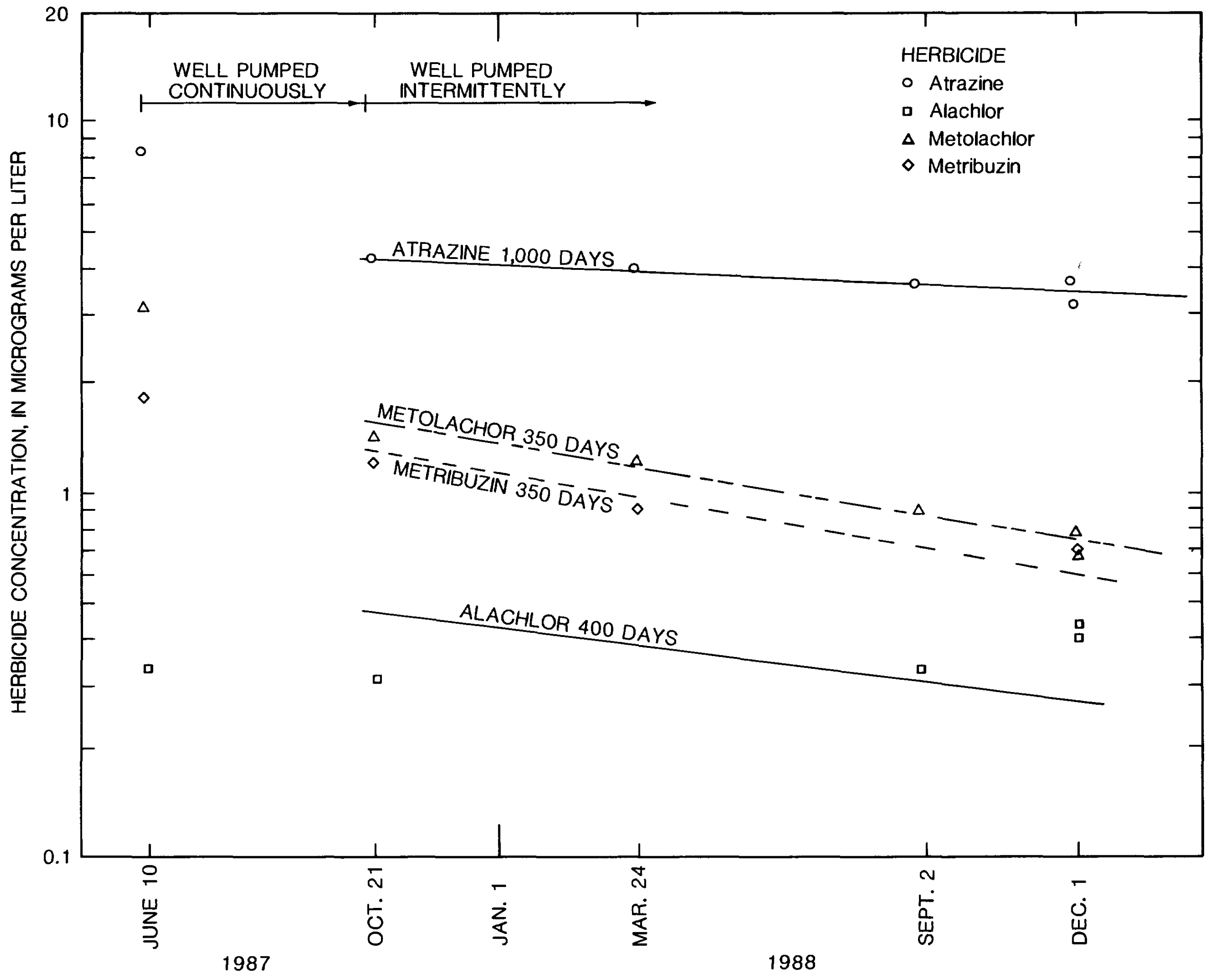


Figure 10. Estimates of degradation half-lives for herbicides in domestic well, Harvey County Experiment Field, compared with concentrations in water from observation well OB4, June 1987 to December 1988.

Ratios of DIA to atrazine range from 0.001 to 0.008, and the ratios of DEA to atrazine range from 0.017 to 0.04. If the atrazine had been degrading in a manner that was typical of the soil zone, these ratios would have been two to three orders of magnitude larger. The concentrations of an important degradation product of atrazine, hydroxyatrazine, were not determined because of the lack of a reliable analytical procedure. It is possible that hydroxyatrazine may be the major degradation product in a saturated environment. There are at least four other major degradation products of atrazine for which concentrations were not possible to obtain. Because the environment of a saturated aquifer at depth is much different than that of surface soil, the degradation products of atrazine should differ. The absence or small concentrations of any one degradation product does not necessarily imply that degradation is not occurring. Therefore, the degradation rates for atrazine and the other herbicides listed in table 6 could be considered conservative.

SUMMARY

Herbicides were detected in the ground water at the Harvey County Experiment Field in August 1985 as part of a program to sample water from shallow aquifers in agricultural regions. A comprehensive assessment of herbicides in the ground water was conducted in March 1986, and indicated concentrations of 46 µg/L for atrazine, 1.9 µg/L for alachlor, 3.7 µg/L for cyanazine, 43 µg/L for metolachlor, and 14 µg/L for metribuzin. The Kansas State University Agronomy Department, the Kansas Department of Health and Environment, and

Table 7. *Concentrations of atrazine and two of its degradation products in water samples from observation wells, Harvey County Experiment Field, 1988*

[ND, not detected]

Well number (fig. 5)	Date of sample (month/day/year)	Concentrations, in micrograms per liter		
		Atrazine[1]	Deethyl-atrazine[1]	Deisopropyl-atrazine[1]
DW	9/2/88	5.8	0.23	0.05
	12/1/88	2.7	.05	.006
	12/1/88[2]	3.0	.05	.004
OB3	9/2/88	2.4	.06	.01
OB4	9/2/88	3.6	.06	.01
	12/1/88	3.6	.13	.007
	12/1/88[2]	3.1	.05	ND

[1] Detection limit 0.005 microgram per liter.

[2] Duplicate sample.

the U.S. Geological Survey cooperated in an investigation to determine the origin, extent, future movement, and degradation of herbicides in contaminated soil and ground water.

The major source of the contamination of the shallow aquifer most likely was back-siphonage from a sprayer tank or spillage of herbicide mixtures into the waterline trench from the domestic well, or spillage and movement of herbicide mixtures along the foundation of the nearby buildings. The herbicides could move downgradient to the well through sand used to backfill the waterline trench or the building foundations.

The construction of the domestic well was perhaps the most important factor in allowing the surface herbicide spillage to reach the aquifer. The annular space between the well casing and the undisturbed soil and unsaturated-zone formations had been filled with very permeable pea-sized gravel. This gravel, which was used to pack the well screen, provided a conduit from the surface to the aquifer. Whenever excess water accumulated at the surface, during rainfall or sprayer-tank spillage, this conduit was filled with water containing herbicides. As much as 15 feet of hydraulic head could be produced between the aquifer water level and the water level within the annular space. This configuration resulted in the injection of the surface water containing the herbicides into the shallow aquifer. The nearly circular pattern of herbicide concentrations around the domestic well supports this scenerio.

Nine observation wells installed around the contaminated domestic well revealed minimal movement of the herbicides laterally. Concentrations of three of the five herbicides were concentric around the domestic well. Gamma logs of the observation wells indicated a series of thin interbedded sand lenses. Results of an aquifer test further indicated that the sand lenses are virtually discontinuous. Transmissivity at six selected observation wells, as determined from the 3-month aquifer test, ranged from 0.30 to 2.23 feet squared per day, with an average of 1.14 feet squared per day. The average storage coefficient was 8.6 x 10^{-5}.

Chemical analyses of soil and ground

water from several locations onsite supports the conclusion that the contamination originated at the domestic well following a pathway down the annular space around the well casing to the aquifer.

The herbicides remaining in the soil have degraded to levels that are comparable to concentrations normally found in agricultural soils. In the absence of additional contamination, herbicide concentrations in the soil should be less than the limits of detection by the end of 1990 as a result of normal degradation processes. Herbicides and their degradation products remaining in the aquifer can be removed by pumping the domestic well. Because the herbicide concentrations are less than 5 µg/L, the pumped water can be disposed by normal application to agricultural fields.

A hydrogeologic analysis of herbicide contamination at the Harvey County Experiment Field yielded additional information on the degradation half-lives of herbicides in the saturated zone. Because the contaminants did not move laterally to any significant degree, and domestic pumpage had been minimal between 1985 and 1987, the decrease in parent herbicide concentrations were assumed to be caused by degradation. Estimated herbicide half-life in the saturated environment of the shallow aquifer was approximately 1,000 days for atrazine, 400 days for alachlor, 250 days for cyanazine, 350 days for metolachlor, and 350 days for metribuzin.

The concentrations of two of the three major degradation products of atrazine, deisopropylatrazine and deethylatrazine, indicate that some degradation of the parent compound has taken place. Without concentrations of the other degradation products, including hydroxyatrazine, it is not possible to determine the degradation rates precisely. The degradation half-life estimates given, therefore, should be considered conservative. Actual half-lives could be longer.

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