HYDROGEOLOGIC SETTIING AND SIMULATION OF PESTICIDE FATE AND TRANSPORT IN THE UNSATURATED ZONE OF A REGOLITH-MANTLED CARBONATE-ROCK TERRAIN NEAR NEWVILLE, PENNSYLVANIA by Daniel J. Hippe and David W. Hall

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> Lemoyne, Pennsylvania 1996

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATED WATER-QUALITY UNITS

Multiply	<u>By</u>	<u>To obtain</u>
	Length	
millimeter (mL)	0.03937	inch
centimeter (mL)	0.3937	inch
meter (m)	3.281	foot
kilometer (km)	0.6214	mile
meter per kilometer (m/km)	5.28	foot per mile
	Area	
hectare	2.4710	acre
square meters (m ²)	10.76	square foot
	Volume	
cubic meters (m ³)	0.0004087	cubic foot per second-day
	<u>Flow</u>	
cubic meter per second (m ³ /s)	35.31	cubic foot per second
liter per second (L/s)	15.85	gallon per minute
	Mass	
kilogram (kg)	2.205	pound
kilogram per hectare (kg/ha)	0.8924	pound per acre
	<u>Temperature</u>	-
degree Celsius (°C)	°F=1.8°C+32	degree Fahrenheit

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 the United States and Canada, called Sea Level of 1929.

Abbreviated water-quality units used in report: milliliters (mL) milligrams (mg) milligrams per liter (mg/L) micrograms per liter (µg/L) milliequivalents per liter (meq/L)

HYDROGEOLOGIC SETTING AND SIMULATION OF PESTICIDE FATE AND TRANSPORT IN THE UNSATURATED ZONE OF A REGOLITH-MANTLED, CARBONATE-ROCK TERRAIN NEAR NEWVILLE, PENNSYLVANIA

By Daniel J. Hippe and David W. Hall

ABSTRACT

Physical and chemical data were collected from May 1991 through April 1993 at a 4.5 hectare field site in Cumberland County, Pa., about 5 kilometers southeast of Newville. These data were used to define the hydrogeologic setting of a field site representative of the intensively farmed carbonate valleys of southeastern and south-central Pennsylvania. The environmental processing of commonly used pesticides (herbicides, fungicides, and insecticides) in the unsaturated zone was simulated with a process-oriented digital model to evaluate the environmental fate and transport of pesticides to ground water. Site data and modelling results provide a basis for a discussion of water-quality implications of agricultural bestmanagement practices.

The carbonate valleys of Pennsylvania comprise regolith-mantled carbonate-rock terrains that consist of broad undulating upland areas dissected by mostly dry valleys and widely spaced spring-fed creeks. The upland areas are farmed and exhibit possess a doline karst topography with many closed depressions, sinkholes, and bedrock outcrops.

Unsaturated materials at the field site consist of an almost continuous soil cover composed of finegrained residuum underlain by an intermediate vadose zone composed of karstified limestone. Soils are absent on scattered bedrock outcrops and are more than 12 meters thick in other areas of the site. The soil profile stores appreciable quantities of water with a volumetric average of about 36 percent water at field capacity. Organic carbon content of soil materials is about 1.7 percent in the Ap-horizon and from 0.1 to 0.3 percent throughout the full thickness of the B- and C-horizons.

Atrazine, metolachlor, simazine, and the atrazine soil metabolites deethylatrazine and deisopropylatrazine were detected at concentrations above $0.05 \ \mu g/L$ in just the upper 0.6 meters of soil materials. However, detectable concentrations of atrazine, simazine, and atrazine soil metabolites were measured in water samples from lysimeters installed in soil materials at depths of 1.2, 2.1, and 3.7 meters and from monitor wells completed in the saturated zone to depths of 122 meters.

Data collected from the field site were used to configure a pesticide screening model based on the pesticide version of the leaching estimation and chemistry model (LEACHP) developed by Wagenet and Hutson (1987). Model simulations show that most field-applied pesticides volatilize to the atmosphere, accumulate in soils, degrade in the subsurface environment, or leach to ground water. Model results were used to rank the leaching potentials of 66 pesticides. Eighteen of 32 herbicides, 4 of 9 fungicides, and 10 of 25 insecticides have moderate to large potential for leaching to ground water.

A review of available pesticide monitoring data suggests that many compounds given moderate or high leaching potentials have not been tested for in ground water and the presence of pesticides in Pennsylvania's ground water may be underreported. Monitoring data do not exist for more than twothirds of the pesticide compounds currently used in agricultural, carbonate areas of Pennsylvania.

Knowledge of processes that govern fate and transport of pesticides is needed to facilitate development of effective pesticide best-management practices. In addition to comprehensive monitoring for pesticides and pesticide degradation products in ground water downgradient of areas of pesticide use, improved (1) characterization of unsaturated flow and transport through regolith mantled carbonate rocks, (2) estimates of pesticide degradation rates, (3) understanding of soil-property controls on pesticide movement, and (4) management models developed from process-oriented research would aid in understanding the processes.

INTRODUCTION

Although synthetic organic pesticides have been used on cropland in the United States since the 1940's, few studies of pesticide contamination of ground water from nonpoint sources were conducted before the 1970's. Numerous monitoring studies have shown that some pesticides applied to agricultural areas have leached to ground water in many hydrogeologic settings, especially karst aquifers and surficial aquifers in coastal plain, fluvial, and glacial deposits (Garner and others, 1986). Karst areas in Pennsylvania underlie much of the row-crop production in the state and are susceptible to contamination from both point and nonpoint sources.

Triazine and chloroacetamide herbicides commonly used in corn and soybean production have been detected in ground water in the regolith-mantled carbonate-rock terrains of southeastern and southcentral Pennsylvania (Fishel and Lietman, 1986; Lietman and Hall, 1991; D.J. Wangsness, U.S. Geological Survey, written commun., 1990; Hippe and others, 1992, 1994) (fig. 1). The widespread detection and persistence of



Figure 1. Carbonate rock terrains of southeastern and south-central Pennsylvania.

trace concentrations of these herbicides and their degradation products in ground water in these areas indicate a nonpoint source of contamination, probably from leaching of materials applied to crop land. A better understanding of processes that control ground-water recharge and the fate and transport of pesticides (herbicides, fungicides, insecticides, and their toxic degradation products) in the unsaturated zone is needed to reduce possible ground-water contamination from use of these chemicals in agricultural areas underlain by carbonate rocks. In 1991, a 4.5 hectare field site in the Cumberland Valley about 5 km southeast of Newville, Pa. (fig. 2), was selected for investigation of these processes as part of a cooperative study between the U.S. Geological Survey (USGS) and the Pennsylvania Department of Environmental Protection, Bureau of Water Quality Management. Subsequently, a digital computer model, LEACH? (Hutsen and Wagenet, 1992), was configured by use of data from the field site and nearby areas in cultivated carbonate terrains to evaluate pesticide leaching potentials. Monitoring data and model result: provide a number of potential implications for development of agricultural best-management practices.



Figure 2. Area of investigation and selected physical and hydrologic features in Cumberland County, Pa.

Purpose and Scope

This report presents (1) a detailed description of the hydrogeologic setting of the field site relevant to the fate and transport of agricultural pesticides and some of their soil metabolites; and (2) an evaluation of the fate and transport of pesticides applicable to the unsaturated zone of regolith-mantled carbonate rock terrains of southeastern and south-central Pennsylvania by use of chemical and physical data from the field site and digital computer simulations; the evaluation includes a discussion of the results of model simulations that provide significant inforamtion for the development of agricultural best-management practices in carbonate-rock areas of southeastern and south-central Pennsylvania. The hydrogeologic setting of the field site is described on the basis of chemical, physical, and hydrologic data collected from May 1991 through April 1993. Physical and chemical properties of soils representative of regolith-mantled carbonate-rock aquifer systems in southeastern and southcentral Pennsylvania were used in a digital computer model, LEACHP, to simulate the fate and transport of 66 agricultural pesticides. The discussion of agricultural-management practices for pest control is based on model results and ground-water quality data collected in Pennsylvania, primarily from wells in the carbonate-rock terrains.

Previous Investigations

A number of water-resource investigations have been conducted to assess the effects of land use and agricultural practices on the ground- and surface-water quality of these environmentally sensitive areas. These investigations have documented (1) the presence of agricultural pesticides in stream base flow of carbonate-rock terrains, (2) the vulnerability to ground-water contamination in carbonate-rock terrains from agricultural chemicals compared with nearby noncarbonate areas, (3) the brief lag time between applications of agricultural chemicals and their transport to ground water, and (4) the widespread occurrence and persistence of trace levels of agricultural chemicals in ground water.

Water-resource investigations conducted in the Pequea Creek Basin, Lancaster County, $P\epsilon$., identified both nitrate and herbicide contamination of surface water from nonpoint sources (Lietman and others, 1983; Ward, 1987). Estimates of the annual load and yield under stormflow and base-flow conditions were made for selected herbicides and nutrients. Investigators determined that a substantial part of the loads of nitrate and herbicide in streams draining this carbonate-rock terrain was during base-flow conditions. However, these studies did not determine whether herbicides present in base flow were from discharges of ground water from the regional aquifer or from instream or nearstream sources.

Water-resource investigations conducted in the Conestoga River headwaters, Lancaster and Berl's Counties, Pa., showed that high concentrations of nitrate and detectable concentrations of triazine and chloroacetanilide herbicides were present in ground-water samples collected from a number of domestic wells (Fishel and Lietman, 1986). Herbicides were detected exclusively in water samples from wells in agricultural areas underlain by carbonate bedrock. Investigators indicated the source of herbicide contamination in the carbonate-rock terrain was from leaching of herbicides applied to agricultural land, which is a nonpoint source of contamination.

At an agricultural field site in the carbonate-rock terrain of Lancaster Valley, Lancaster County, Pz., the timing of herbicide applications was linked to herbicide detections in ground water beneath the site (Lietman and Hall, 1991). Herbicide concentrations were below detectable levels before herbicide applications at planting time but were detected for several months beginning with the first appreciable rainfall after the herbicide applications. Herbicide contamination of ground water was believed to originate in part from rapid downward movement of herbicides applied on the land surface to the aquifer, facilitated by transport through structured soils and karst features (sinkholes and shafts).

In the spring and summer of 1989, a reconnaissance study of water from wells, springs, and stream base flow in Cumberland County, Pa., indicated that triazine herbicides were present at low concentrations (generally less than $1 \mu g/L$) in ground water throughout much of the carbonate-rock terrain of the valley (D.J. Wangsness, U.S. Geological Survey, written commun., 1990). A resampling of sites in August and September indicated that triazine herbicides had persisted in ground water at most sites in the regolith-mantled carbonate-rock aquifer.

In the spring and fall of 1991 and 1992, reconnaissance studies of water from wells and springs in the Pequea, Mill, and Muddy Creek Basins of Lancaster County, Pa., indicated that high concentrations of nitrate and detectable triazine herbicides were present in ground water throughout much of the carbonate-rock aquifer (Durlin and Schaffstall, 1993, p. 279-337). A resampling of sites later in 1991 indicated that nitrate and herbicides persisted in ground water at most sampling locations.

A water-resource investigation of two karst springs in the carbonate-rock terrain of the Cumberland Valley, Cumberland County, Pa., during 1990 and 1991 indicated that the herbicide atrazine and deethylatrazine (a soil metabolite) were the only pesticides present in spring discharges throughout the study period, although a number of triazine and amid herbicides were applied to agricultural land in the recharge areas to the springs (Hippe and others, 1994). Daily mean concentrations of atrazine and deethylatrazine in the spring discharges were 0.2 and 0.4 μ g/L, respectively. A spring flush associated with rainfall after the application period during planting was not apparent. The high ratio of deethylatrazine to atrazine and the rarity of detectable deisopropylatrazine (an additional soil metabolite) in spring discharges suggest that much of the atrazine in the carbonate-rock aquifer was introduced by leaching through soils rather than by direct entry of surface runoff through sinkholes. About 0.6 percent of the annual atrazine applied to agricultural land in contributing areas to the springs was discharged from the springs.

The development of agricultural best-management practices related to chemical use and waterquality has been an active area of research during the past 20 years. Some recent contributions include Brown (1987), Pimentel (1987), Wolf (1987), Gates (1988), Logan (1990), Belluck and others (1991), Chambers (1993, p. 3-8), Hammond (1992), and Furtick (1993). However, few contributions address the range of water-quality concerns in environmentally sensitive carbonate-rock terrains.

Field studies and digital computer models have been used to facilitate the development of agricultural-management practices having water-quality goals. Digital computer models to evaluate pesticide fate and transport in agricultural soils have been developed by numerous researchers, including Jury and others (1983; 1984a; 1984b; 1984c; 1987; 1989), Rutledge and Helgesen (1989), Mackay (1991), and Mackay and Stiver (1991). Rao and others (1985) compared ranks of pesticide leaching potentials produced by six simple models. Two models of moderate complexity currently used to simulate pesticide fate and transport mechanisms in agricultural soils are LEACHM (Hutson and Wagenet, 1992, 1993) and PRZM2 (Mullins and others, 1993). Recent models designed to simulate water and solute flow in complex Pennsylvania terrains include work by Jabro and Fritton (1990), Grant and others (1991), and Jabro and others (1991).

A number of digital computer models to evaluate pesticide fate and transport have been designed for screening purposes by use of readily available soil, chemical, and climatic data. The U.S. Soil Conservation Service (SCS) Soil Pesticide Interaction Screening Procedure (SPISP) was designed to provide a preliminary assessment of pesticide leaching and runoff for all agricultural areas in the United States (Goss and Wauchope, 1991; Goss 1992; Kellogg and others, 1992). In the SPISP screening model, the SCS/Agricultural Research Service/Cooperative Extension Service Pesticide Properties Database (Wauchope and others, 1992) was combined with nationwide SCS soils data to provide input to the GLEAMS model of Leonard and others (1987). Although the current generation of screening models does not currently provide a reliable base of information from which to predict concentrations or to draft regulations (Wauchope, 1992), it is possible that models may be developed better to evaluate environmental risks associated with agricultural chemical use.

Land Use And Agricultural Practices

Land use in the carbonate valleys of southeastern and southcentral Pennsylvania is predominantly agricultural, but areas are undergoing additional urbanization around the Reading-Allentown, Lancaster, Lebanon, and Harrisburg metropolitan areas. The central part of the Cumberland Valley west of Carlisle (fig. 2.) is agricultural land. Smaller areas are forested and developed. Agricultural land includes fields cultivated for either animal feed or seed production, pasture for dairy or livestock grazing, and fallow fields. The field site and surrounding fields are used for production feed for dairy cattle. No-till and

minimum tillage crop-production systems are used at the field site. A broader spectrum of cropproduction systems is used elsewhere in the valley, depending on factors such as soil erosion hazards ard depth to bedrock.

Most of the agricultural-pesticide usage in southeastern and southcentral Pennsylvania is cricropland. Usually, the pesticides are used to control weeds, fungus, and insects so that they will not adversely affect the use and value of cropland, reduce the yield or the quality of crops, or increase the costs of production and harvest. The principal crops receiving pesticide applications in southeastern ard southcentral Pennsylvania are corn, alfalfa, tobacco, and soybeans (Gianessi and Puffer, 1991, 1992a, 1992b). Herbicides, fungicides, and insecticides commonly applied to these and other crops are listed in table 1 along with the quantity used in Pennsylvania, typical application rates, and water-quality standards for longterm exposure (U.S. Environmental Protection Agency, 1986, 1991).

Methods Of Data Collection and Analysis

Rainfall, physical and chemical properties of soil, ground-water levels, aquifer properties, ard subsurface water-quality data were collected at the field site (table 2). Locations of data-collection sites are shown in figure 3. The following sections describe the instrumentation and methods used to collect these data.

Rainfall

Rainfall data were collected by use of a tipping-bucket raingage with a data-collection platform ard satellite telemetry (table 2). Rainfall data were recorded in 0.25 mm increments at 15-minute intervals for the period June 1991 through November 1993. These data were primarily used to provide near-real time notification of rainfall for collection of water-quality data. Because calibrations and comparisons to rainfall data from nearby gages showed a variable, low bias in rainfall data collected at the site, these data were not used for quantitative hydrologic analysis.

Physical Properties of the Soil

Physical properties of the soil were determined from analyses of continuous cores collected April 24, 1991, from two locations (MW1 and C1, fig. 3 and table 2). Physical properties measured or estimated include wet and dry bulk density, volumetric water and air content, and soil texture. Wet bulk density was determined on soil clods immediately after collection. Dry bulk density and volumetric water content of soil clods were determined gravimetrically after oven drying for 24 hours at 105°C. Volumetric air content was estimated by difference assuming an average grain density of 2.65 g/cm³. Soil texture was determined on dried, disaggregated soil samples. Sand content and sand fractions were measured by dry sieving using methods of Matthes and others (1992). The silt and clay content were determined by use of a modification of the single withdrawal pipette method of Matthes and others (1992) (R.A. Ludlow, U.S. Geological Survey, written commun., 1993).

Chemical Properties of the Soil

The soil cores collected on April 24, 1991, were analyzed for organic carbon and selected pesticides and pesticide soil metabolites (table 3). Determinations of organic carbon content in soil samples were performed at Merkel Soils Laboratory at The Pennsylvania State University by use of the Modified Mebius method (Nelson and Sommers, 1982, p. 571-573). Determinations of herbicide residue concentrations in soil samples were performed at the USGS Organics Research Laboratory in Lawrence, Kans. The method used is described in Adams and Thurman (1991).



Figure 3. Location of (A) field site and (B) rainfall, soil, and water-quality sampling sites near Newville, Pa.

Table 1. Selected herbicides, fungicides, and insecticides applied to agricultural land in Pennsylvania

[Kg, kilogram; Kg/ha, kilogram per hectare; μ g/L, microgram per liter; MCL, maximum contaminant level, the maximum permissible level of a contaminant in water which is delivered to any user of a public water system; HA, health adviscry level; Rfd, reference dose; --, no data]

Common name	Principal crops	Annual use in Pennsylvania (Kg/1000)	Typical annual application rate (Kg/ha)	Water-qualit, standards for longterm exposure (µg/L)
	Herbicides	······································		
Alachlor	Corn, soybeans, sorghum	230	1.7 - 4.5	2 (MCL)
Atrazine	Corn, sorghum	730	.2 - 3.4	3 (MCL)
Bensulide	Vegetables	3.4	6.2	
Bromoxynil	Corn, sorghum, small grains, alfalfa	.29	.26	
Butylate	Corn	54	4.5 - 6.7	350 (HA)
Chlorimuron	Soybeans, corn	.60	.009013	
Clomazone	Soybeans	.34	.8 - 1.1	
Cyanazine	Corn, sorghum	200	1.3 - 6.0	1 (MCL)
Dicamba	Pasture, corn, alfalfa, small grains	50	.16	200 (HA)
Diuron	Small grains, alfalfa	13	1.3 - 1.8	10 (HA)
EPTC	Corn, potatoes, alfalfa	91	3.4 - 6.7	25 (Rfd)
Fluazifop	Soybeans alfalfa	.32	.12	
Glyphosate	Corn, soybeans, small grains	240	.2 - 5.0	700 (HA)
Hexazinone	Alfalfa	11	.4 - 1.5	200 (HA)
Imazethapyr	Soybeans		.07	
Imazapyr amine salt	Soybeans		.07	
Linuron	Soybeans, corn	27	.3 - 1.1	2 (Rfd)
Maleic Hydrazide	Tobacco			4,000 (HA)
Metolachlor	Corn, soybeans, sorghum	640	1.3 - 3.4	100 (HA)
Metribuzin	Alfalfa, soybeans, potatoes	5.9	.2 - 1.1	200 (HA)
Metsulfuron	Small grains, pasture		.01	
Paraquat	Corn, soybeans, alfalfa	41	.3 - 3.4	30 (HA)
Pebulate	Tobacco, tomatoes	8.2	4.4	
Prometon	Noncropland only			100 (HA)
Pronamide	Alfalfa		.5 - 1.5	50 (HA)
Propachlor	Corn, sorghum	1.0	2.5 - 4.0	90 (HA)
Propazine	Sorghum	Discontinued ¹		10 (HA)
Quizalofap	Soybeans			
Sethoxydim	Soybeans, alfalfa	.22	.16	
Simazine	Corn, alfalfa	50	.6 - 1.7	4 (MCL)
Terbacil	Alfalfa	1.5	.34	90 (HA)
Trifluralin	Soybeans, alfalfa, small grains	1.2	.68	2(HA)
2,4-D	Pasture, corn, soybeans, small grains, orchard	64	.2 - 2.2	70 (MCL)
2,4-D dimethylamine	Corn, alfalfa		.16	

Table 1. Selected herbicides, fungicides, and insecticides applied to agricultural land in Pennsylvania-Continued

[Kg, kilogram; Kg/ha, kilogram per hectare; μ g/L, microgram per liter; MCL, maximum contaminant level, the maximum permissible level of a contaminant in water which is delivered to any user of a public water system; HA, health advisor/level; Rfd, reference dose; --, no data]

Common name	Principal crops	Annual use in Pennsylvania (Kg/1000)	Typical annual application rate (Kg/ha)	Water-quality standards for longterm exposure (µg/L)
	Fungicides	<u> </u>	····	
Benomyl	Orchards, Vegetables	6.6		50 (Rfd)
Captan	Orchards, grapes, strawberries, tomatoes	9.8	2.2 - 11	130 (Rfd)
Chlorothalonil	Orchards, vegetables, potatoes	42	2.8 - 17	15 (Rfd)
Dodine	Orchards	11	.8 - 1.0	
Ferbam	Orchards, grapes	13	3.0 - 5.7	
Maneb	Vegetables	19	2.7 - 7.9	5 (Rfd)
Metalaxyl	Tobacco, potatoes	1.2	.16	
Metiram	Orchards	47	20	
Thiophanate	Orchards, strawberries	13	.8 - 1.9	
Insecticides				
Acephate	Tobacco, green beans	.8	.8 - 1.1	
Azinphos-methyl	Orchards, vegetables, alfalfa	40	.4 - 2.2	
Carbaryl	Orchard, grapes, vegetables, potatoes	26	.8 - 2.9	700 (HA)
Carbofuran	Corn, alfalfa, orchards, potatoes, tobacco, vegetables	86	.3 - 2.6	40 (MCL)
Chlordane	Termite control	Discontinued 1974		2 (MCL)
Chlorpyrifos	Alfalfa, corn, tobacco	320	.6 - 2.2	20 (HA)
4,4'-DDT	Orchards, vegetables	Discontinued 1973		.1 (HA)
Diazinon	Corn, vegetables	8.7	.6 - 1.1	.6 (HA)
Dicofol	Apples, strawberries	1.6	1.7 - 2.2	
Dieldrin	Termite control	Discontinued 1974		.05 (Rfd)
Dimethoate	Alfalfa, orchards, vegetables	14	.20 - 1.1	.2 (Rfd)
Endosulfan	Orchards, vegetables	15	.8 - 1.5	
Esfenvalerate	Corn, orchards, vegetables	2.7	.0222	
Fenvalerate	Soy beans	.08	.1	
Lindane	Seed treatments, orchards			.2 (MCL)
Malathion	Corn, alfalfa, small grains, vegetables,	47	1.1 - 2.2	100 (HA)
Methamidophos	Vegetables, potatoes	4.2	1.1	
Methomyl	Orchards, corn, alfalfa	25	.6 - 1.7	200 (HA)
Methyl parathion	Orchards, grapes, sweet corn	10	.4 - 1.7	2 (HA)
Oxamyl	Apples, potatoes	7.4	.68	200 (MCL)
Parathion	Tobacco	43	.6 - 2.2	
Permethrin	Alfalfa, corn, vegetables	24	.1134	50 (Rfd)
Phorate	Corn, potatoes, soybeans	22	1.1 - 3.5	
Phosmet	Orchards, potatoes, alfalfa	30	.7 - 4.0	
Phosphamidon				

¹Registration revoked.

Table 2. Rainfall, ground-water level, water-quality, and soil sampling sites near Newville, Pa.

Site name	U.S. Geological Survey site identification number	Data-collection activities at site
Rain gage	400828077214701	Rainfall volume and intensity
Monitor Well 1 (MW1)	400829077214301	Soil physical and chemical properties; pesticides in water, ground-water level, hydraulic conductivity, gravity yield
Monitor Well 2 (MW2)	400827077214601	Water quality, including pesticides, field measurements of water quality, and major ions, and hydraulic conductivity
Monitor Well 3 (MW3)	400828077214801	Water quality, including pesticides, field measurements of water quality, and major ions, ground-water level, hydraulic con- ductivity and gravity yield
Culvert 1 (C1) with 3 trough and 5 disk lysimeters	400828077214501	Soil physical and chemical properties; pesticides in water from one trough lysimeter
Culvert 2 (C2) with 3 trough and 5 disk lysimeters	400827077214701	Pesticides in water from one trough lysimeter
Lysimeter Nest 1 (LN1) with 3 tube lysimeters	400829077214501	Water quality, including pesticides and field measurements of water quality from two tube lysimeters; pesticides in soil
Lysimeter Nest 2 (LN2) with 3 tube lysimeters	400827077214501	Water quality, including pesticides and field measurements of water quality from one tube lysimeter; pesticides in soil (no data were collected from this installation during the inten- sive monitoring period May through October 1991)
Lysimeter Nest 3 (LN3) with 3 tube lysimeters	400828077214701	Water quality, including pesticides and field measurements of water quality from three tube lysimeters; pesticides in spil

Table 3. Chemical data collected at water-quality and soil sampling sites near Newville, Pa.

[μS/cm at 25°C, microSiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; g/kg gram per kilogram; μg/L, microgram per liter; μg/kg, microgram per kilogram; --, not applicable; KS, USGS Organics Research Laboratory, Lawrence, Kans.; PA, USGS District Laboratory, Lemoyne, Pa.; PSU, The Merkel Soils Laboratory Pennsylvania State Univ., University Park, Pa.]

Physical property or chemical constituent	Sample Medium	Watstore/ Storet code	Analytical method	Minimum reporting level ¹	Where analyzed
Alkalinity, in mg/L as CaCO3	Water	95430	Fishman and Friedman (1970, p. 55-56)	1	PA
Specific conductance (μ S/cm at 25 ^o C)	Water	90095	Fishman and Friedman (1970, p. 461-463)	1	PA
pH, in standard units	Water	90400	Fishman and Friedman (1970, p. 363-364)	.1	PA
Organic Carbon (g/kg)	Soil	00687	Nelson and Sommers (1982, p. 571-573)	.01	PSU
Alachlor (μ g/L)	Water	46342	Thurman and others (1990)	.05	KS
Alachlor (µg/kg)	Soil	04006	Adams and Thurman (1991)	.05	KS
Ametryn (µg/L)	Water	38401	Thurman and others (1990)	.05	KS
Ametryn (µg/kg)	Soil	78505	Adams and Thurman (1991)	.05	KS
Atrazine (µg/L)	Water	39632	Thurman and others (1990)	.05	KS
Atrazine (µg/kg)	Soil	39631	Adams and Thurman (1991)	.05	KS
Cyanazine ($\mu g/L$)	Water	04004	Thurman and others (1990)	.0520	KS
Cyanazine (µg/kg)	Soil	04041	Adams and Thurman (1991)	.05	KS
Cyanazine amide (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS
Deethylatrazine ($\mu g/L$)	Water	75981	Thurman and others (1990)	.05	KS
Deethylatrazine (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS
Deethylcyanazine (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS
Deethylcyanazine Amide (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS
Deisopropylatrazine (µg/L)	Water	75980	Thurman and others (1990)	.05	KS
Deisopropylatrazine (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS
Metolachlor (µg/L)	Water	39415	Thurman and others (1990)	.05	KS
Metolachlor (µg/kg)	Soil	04005	Adams and Thurman (1991)	.05	KS
Metribuzin (µg/L)	Water	82630	Thurman and others (1990)	.05	KS
Metribuzin (µg/kg)	Soil	04000	Adams and Thurman (1991)	.05	KS
Prometon (µg/L)	Water	04037	Thurman and others (1990)	.05	KS
Prometon (µg/kg)	Soil	82402	Adams and Thurman (1991)	.05	KS
Prometryn (µg/L)	Water	04036	Thurman and others (1990)	.05	KS
Prometryn (µg/kg)	Soil	78688	Adams and Thurman (1991)	.05	KS
Propazine (µg/L)	Water	38535	Thurman and others (1990)	.05	KS
Propazine (µg/kg)	Soil	82534	Adams and Thurman (1991)	.05	KS
Simazine (µg/L)	Water	04035	Thurman and others (1990)	.05	KS
Simazine (µg/kg)	Soil	04008	Adams and Thurman (1991)	.05	KS
Terbutryn (μg/L)	Water	38888	Thurman and others (1990)	.05	KS
Terbutryn (μg/kg)	Soil	38890	Adams and Thurman (1991)	.05	KS
Triazines (by immunoassay as atrazine)	Water	34757	Thurman and others (1991)	.1	PA
2-Chloroacetanilide (μg/kg)	Soil		Adams and Thurman (1991)	.05	KS
2,6-Diethylaniline (µg/kg)	Soil		Adams and Thurman (1991)	.05	KS

¹Minimum reporting level is the smallest measured concentration of a constituent that may be reliably reported using a given analytical method.

Ground-Water Levels

Ground-water levels were measured in two wells, MW-1 and MW-3, both completed as open hcles in bedrock. Ground-water levels in well MW-1 were measured to the nearest 3 mm for the period July 1991 through November 1992 by use of a float system and graphical recorder. Ground-water levels in well MW-3 were recorded to the nearest 3 mm at 15-minute intervals for the period July 1991 through April 1993 by use of a pressure transducer and data logger. Ground-water levels were used to calculate changes in ground-water storage over time, evaluate timing of recharge relative to periods of rainfall and snowmelt, and estimate the gravity yield of the aquifer.

Aquifer Properties

Estimates of the transmissivity of aquifer materials adjacent to the open intervals of monitor wells MW-2 and MW-3 were made on the basis of slug tests. The water-level recovery in each well after the addition and removal of a cylindrical slug was monitored by use of a pressure transducer and data logger. Slug-test data were analyzed by use of methods of Bouwer and Rice (1976) that assume (1) the raising or lowering of the water level is small relative to the aquifer thickness, (2) there are no significant gains or losses of water within the zone of fluctuation of water level, (3) frictional well losses are negligible, and (4) the aquifer is homogeneous and isotropic. Errors arising as a result of departures from assumption^e 1 through 3 probably are minimal whereas, substantial departures from the assumption of homogeneous and isotropic aquifer materials may lead to substantial errors that may render the estimates inappropriate for many applications. Therefore, the transmissivity estimates presented in the report are given to indicate a range of possible values at the field site.

The gravity yield of the aquifer was determined by use of methods of Olmsted and Hely (1962) that relates the measured rise in ground-water levels (net recharge) to precipitation from a brief period of rainfall or snowmelt. The method assumes (1) evapotranspiration or change in soil moisture is negligible, (2) recharge is uniformly distributed, and (3) discharge from the aquifer relative to recharge is negligible. Discrete periods of rainfall or snowmelt between the months November and April were chosen for analysis because evapotranspiration rates are low and soils typically are at field capacity.

Subsurface-Water Quality

Subsurface water includes water sampled from depths between the unsaturated zone just beneath the soil surface and within the regional aquifer. A broad range of subsurface-water-sampling equipment—suction (porous tube and disk) lysimeters and gravity (trough) lysimeters completed in soil materials, piezometers completed at the soil-bedrock contact, and monitor wells completed as open holes below the water table in bedrock—was installed at the field site (table 2 and fig. 3). Diagrammatic cross-sections of equipment installation and sampling depths are shown in figure 4.

Specific conductance, pH, and alkalinity of water samples were measured according to USGS methods in Fishman and Friedman (1989). Triazine herbicides were analyzed by use of immunoassay methods (Thurman and others, 1990), and 13 herbicides were analyzed by use of gas chromatographymass spectrometry (GC/MS) methods (Thurman and others, 1990). The water-quality and chemical constituents determined on site, sample medium, citations of analytical methods, and the method reporting levels are summarized in table 3.

Because of dry, hot weather conditions that persisted through the intensive monitoring period from April through October 1991, water samples could not be collected from the disk-type suction lysimeters or piezometers and only a few samples could be obtained from gravity (trough) lysimeters and suction (tube) lysimeters installed at shallower depths. Also, sample volumes from suction lysimeters generally were insufficient for the desired field and laboratory measurements of water quality. Water samples of 120 mL or more in volume that were collected during the intensive monitoring period (from April through October 1991) were analyzed by use of the GC/MS method; few samples collected during this period were large enough to do additional analyses. Immunoassay analyses were performed on samples less than 120 mL in volume collected during the intensive monitoring period and all samples collected after the





Figure 4. Completion methods for (A) nested tube lysimeters and piezometers and (B) disk and trough lysimeters installed in culverts.

intensive monitoring period. During the intensive monitoring period, field measurements of water quality were performed on samples with either insufficient volume for GC/MS analysis and samples with volumes greater than necessary for GC/MS analysis. After the intensive monitoring period, field measurements of water quality were performed routinely on any water samples that were more than 40 mL.

Quality Assurance of Chemical Measurements

The principal sources of potential sample contamination were the lysimeter materials and samplecollection and processing equipment. A sample of the 200 mesh silica flour slurry used as a filter pack around suction lysimeters was analyzed and determined not to contain detectable quantities of pesticides. All suction lysimeters (and sample hoses) installed at the site were composed of polytetrafluoroethylene a chemically resistant material with little tendency to sorb or desorb organic compounds. Deionized water rinses of suction lysimeters that followed normal sampling were free of any detectable crosscontamination from pesticides, indicating no measurable desorption of herbicides from the lysimeters. Deionized water equipment blanks also did not contain detectable concentrations of pesticides, indicating that sample-collection and processing equipment and sample bottles were not a source of contamination.

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The USGS gratefully acknowledges the cooperation of Dan and Francis Mains and their families for providing the field site used for this water-resource investigation and for providing agricultural-practices information for the study area. The USGS is grateful to the Cumberland County Extension Agents for assistance in locating field sites. The USGS also is grateful for analytical work performed by student volunteers at the Organics Research Laboratory at the USGS district office in Lawrence, Kans., under the direction of E. Michael Thurman.

HYDROGEOLOGIC SETTING OF THE FIELD SITE

The field site is on an undulating upland surface that occupies the central axis of the Cumberland Valley. The hydrogeologic setting of the part of the Cumberland Valley that includes the field site has been described as a regolith-mantled carbonate-rock aquifer system (Chichester, 1991). Much of this upland area is in the Conodoguinet Creek watershed--part of the Susquehanna River Basin. The upland area is partially dissected by mostly dry valleys and widely spaced spring-fed creeks. The maximum topographic relief is about 90 m. Dissolution of the carbonate bedrock that underlies much of the upland area has produced a karst landscape dotted with numerous closed depressions and sinkholes (Kochanov, 1989). This type of landscape has been called "doline karst" (White, 1988). The landscape is well drained, primarily by subsurface drainage. The nearest streams, Mount Rock Spring and Big Spring Creeks, are about 4.8 km from the field site (fig. 2).

Recharge to this aquifer system is distributed over much of the upland surface and dry valleys. Discharge from the aquifer system is to spring-fed creeks and to Conodoguinet Creek. Ground water is stored in regolith having intergranular porosity and consolidated carbonate rock having mostly secondary porosity including partings parallel to bedding and foliation, fractures, and dissolution openings. Ground-water levels in wells near the field site ranged from 3.4 to 43 m below the land surface with a potentiometric surface slope of 7 to 11 m/km in a northeasterly direction (Hippe and others, 1994).

Average annual precipitation for 62 years of record (beginning in 1929) is 986 mm at Shippensburg, Pa. (U.S. Department of Commerce, 1992), which is about 8 km southwest of the field site. On average, precipitation is evenly distributed throughout the year (fig 5). Precipitation typically is greater than potential evapotranspiration from October through April and less than potential evapotranspiration from May through September. This relation between precipitation and potential evapotranspiration results in large seasonal variation in soil moisture content, recharge rates, ground-water levels, and stream base flow. This relation may influence the types and quantities of pesticides that leach to ground water.



Figure 5. Relation between precipitation, potential evapotranspiration, and pesticide application periods in southeast and south-central Pennsylvania.

The unsaturated and saturated zones at the field site are comprised of layers of soil and bedrock having different physical and chemical properties. These properties influence the environmental processing of agricultural pesticides applied at the site. For this report, the term "unsaturated zone" refers to the interval of subsurface materials that extends from the land surface to the top of the regional aquifer; it may include one or more intervals of limited areal extent having intermittent perched water-table conditions. The unsaturated zone comprises an interval of soil and an additional interval of carbonate bedrock situated above the normal zone of fluctuation of the regional aquifer. The part of the unsaturated zone within carbonate bedrock commonly is called an intermediate vadose zone or epikarst. Because most methods for investigation in unsaturated media are not well suited to the intermediate vadose zone, only the soil and regional aquifer were instrumented for this field study. Therefore, hypotheses regarding hydrologic processes or contaminant behavior in the intermediate vadose zone are based on indirect observations made as part of this field study and concepts presented in recent karst literature (Williams, 1983, 1985; White, 1988; Field, 1989).

Soil

Soils in the central part of the Cumberland Valley are formed from fine-grained residuum weathered from the underlying carbonate bedrock. These soils are classified as fine-loamy, mixed, mesic Ultic Hapludalfs and mapped as the Duffield-Hagerstown Association (Zarichansky, 1985). The soils are characterized as deep (generally greater than 1.5 m) moderate to well-drained silt loam on gentle to moderate slopes (Zarichansky, 1985, p. 7). The Duffield-Hagerstown Association underlies a large part of the prime agricultural land in southeastern and southcentral Pennsylvania. Soil cores and excavations of Duffield-Hagerstown Association soils at the field site indicate that the soil profile consists of a partial covering of plant litter underlain by a mineral soil with three prominent master horizons, designated Ap, B, and C.

The Ap horizon consists of 0 to 40 cm of grayish brown sandy loam with granular structure and numerous roots and burrows. Coarse fragments of quartzite and shaley limestone comprise less than 10 percent of bulk volume (table 4). The Ap horizon is nearly absent on tops of limestone pinnacles where it has been removed by erosion and mechanical cultivation. Typical thickness of this horizon is about 30 cm.

The B horizon is 0 to 150 cm thick and consists of medium to light brown sandy and silty loam with a slightly sticky and slightly plastic texture. Soil structure is well developed and blocky, changing to weakly developed and platy at depth. Argillic material coats ped faces and large pores; many coatings are black. Abundant black (presumably hematite or goethite) concretions are distributed throughout soil peds. Roots are less abundant in the B-horizon than in the Ap-horizon; most large roots are between peds in the upper, blocky part of horizon. Coarse fragments of quartzite or shaley limestone may exceed 20 percent of the bulk volume. Typical thickness of the B horizon is 75 cm. The B horizon has a sharp or slightly gradational contact with overlying A horizon and gradational contact with underlying C horizon.

The C horizon consists of 0 to over 1,000 cm of light brown, moderate yellowish-brown, and dark yellowish orange sandy and silt loam that is slightly sticky and slightly to moderately plastic. The C horizon is massive or sparsely layered with darkly stained clay films along widely spaced, mostly vertical subplanar fractures. This horizon generally lacks roots and burrows. Coarse fragments of quartzite and shaley limestone comprise less than 10 percent of the bulk volume. Typical thickness of the C horizon is 300 cm.

Table 4. Textural data for soil samples from monitor well MW1 and culvert C1 near Newville, Pa.

[mm, millimeter; >, greater than; <, less than]

				Perce	nt of bulk	weight				Weig <2	ght perco mm frac	ent of ction
Donth			San	d-sized fra	ction							
interval (meters)	Gravel (total) >2.0 mm	Very coarse 2.0-1.0 mm	Coarse 1.0-0.5 mm	Medium 0.50-0.25 mm	Fine 0.25-0.125 mm	Very fine 0.125-0.062 mm	Sand (total)	Silt (total) 0.062-0.004 mm	Clay (total) <0.004 mm	Sand	Silt	Clay
					Monito	or well MW	/1					
030	9.1	7.2	21.2	10.6	12.9	9.5	61.4	20.4	6.4	70.4	22.4	7.1
.3061	1.3	2.8	2.2	3.3	23.2	14.0	45.6	39.8	12.7	46.9	40.3	12.9
.61 - 1.2	16.3	27.5	7.3	9.9	4.4	5.2	54.2	15.2	9.5	70.5	18.2	11.3
1.2 1.8	.5	.5	5.9	11.6	6.1	28.8	52.9	29.4	17.0	53.4	29.5	17.1
1.8 - 2.4	18.8	12.2	11.9	6.6	7.6	13.5	51.7	12.3	11.7	70.5	15.1	14.4
2.4 - 3.0	9.8	16.6	14.9	15.5	12.5	14.6	74.1	6.9	7.8	83.9	7.6	8.6
3.0 - 3.7	16.8	14.0	24.8	12.7	7.2	12.5	71.3	4.2	5.8	88.0	5.0	7.0
3.7 - 4.3	3.2	12.0	16.0	15.8	14.0	16.4	74.2	10.6	11.2	77.4	10.9	11.6
4.3 - 4.9	9.1	22.6	25.2	13.9	11.9	8.6	82.3	3.8	4.1	91.3	4.2	4.5
4.9 - 5.5	2.5	30.2	14.8	14.9	9.7	18.8	88.4	5.1	3.8	90.9	5.2	3.9
5.5 - 6.1	3.7	6.6	28.6	18.5	13.7	14.0	81.4	7.0	7.3	85.1	7.3	7.6
6.1 - 6.7	7.6	16.3	20.7	18.6	12.1	11.6	79.3	3.2	8.9	86.9	3.5	9.6
6.7 - 7.3	2.1	8.8	5.8	6.3	4.9	26.2	52.0	25.2	19.4	54.5	25.7	19.8
					Cu	Ivert C1						
030	7.2	12.7	16.6	13.1	11.0	9.9	63.3	20.1	7.3	70.4	21.7	7.9
.3061	30.1	16.4	11.3	3.5	7.8	12.5	51.5	7.1	5.7	81.6	10.2	8.2
.61 - 1.2	17.9	10.2	15.8	17.8	10.7	12.2	66.7	6.4	6.2	84.6	7.8	7.6
1.2 1.8	15.6	18.0	9.0	9.5	8.3	14.5	59.3	12.2	9.1	74.8	14.4	10.8
1.8 - 2.4	1.5	19.7	26.1	17.4	12.5	9.9	85.6	4.9	7.8	87.1	5.0	7.9
2.4 - 3.0	8.6	8.1	5.3	9.5	16.5	24.5	63.9	10.9	14.3	72.5	11.9	15.7
3.0 - 3.7	5.9	25.8	11.8	11.1	11.7	15.1	75.5	7.2	10.4	81.3	7. 7	11.1
3.7 - 4.3	1.2	3.9	11.9	6.7	19.0	26.4	67.9	14.6	16.1	69.0	14.8	16.3
4.3 - 4.9	.4	2.4	3.8	6.2	9.8	11.8	34.0	35.4	29.9	34.4	35.5	30.0
4.9 - 5.5	.9	2.8	18.0	2.0	12.7	22.9	58.4	21.0	19.5	59.2	21.2	19.7
5.5 - 5.9	1.9	16.5	22.1	12.9	9.1	15.4	76.0	10.5	11.3	77.9	10.7	11.5

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The water content of soil samples collected in April 1991 (with soil-moisture conditions approaching, field capacity) was about 32 percent in samples collected from near the soil surface and as high as 50 percent in samples from deeper, clay-rich intervals (table 5). The moisture content of soil materials at the field site is substantial because of the soil thickness and the high soil-moisture retention. About 310 cm of total soil moisture was present in the 730-cm thick profile at the location of monitor well MW1 at near field capacity. Much of the soil moisture above the C horizon of Duffield Series soils is plant-available; from 20 to 30 cm of water may be available from the change in volumetric soil-moisture content at matric potentials between 33 and 150 Kp (1/3 bar and 15 bars) (E.J. Ciolkosz, The Pennsylvania State University, written commun., 1991).

Organic material is present throughout the full thickness of soil materials at the site. The Ap horizor has the greatest percentage of organic carbon at 1.7 weight percent (table 5). Samples from the B and C horizons typically contained from 0.1 to 0.3-weight percent organic carbon with no apparent trend ir content of organic carbon with depth.

Table 5. Selected physical and chemical data for soil samples at the monitor well

		Physical or c	hemical measu	rement	
Depth interval (meters)	Blow count (blows per 0.15 meters penetration)	Recovery (volume percent)	Dry bulk density (g/cm ³)	Moisture content (weight percent)	Organic carbon (weight percent)
····		Monitor well	MW1		
030	2, 3	92	1.53	35	1.7
.3061	4,6	92	1.74	32	.76
.61 - 1.2	2, 3, 6, 8	73	1.71	33	.20
1.2 - 1.8	3, 3, 4, 5	73	1.65	35	.11
1.8 - 2.4	3, 5, 7, 10	96	1.73	37	.14
2.4 - 3.0	3, 5, 7, 7	¹ 48	1.53	35	.15
3.0 - 3.7	4, 7, 7, 9	100	1.61	37	.092
3.7 - 4.3	3, 6, 7, 10	88	1.65	37	.11
4.3 - 4.9	3, 5, 5, 6	73	1.37	40	.14
4.9 - 5.5	3, 3, 5, 7	69	1.61	46	.14
5.5 - 6.1	3, 3, 5, 5	100	1.60	44	.12
6.1 - 6.7	2, 2, 3, 4	81	1.47	47	.14
6.7 - 7.3	3, 4, 6, 5		1.27	46	.14
		Culvert C	1		
030	2, 2	58	1.44	33	1.7
.3061	3, 8	58	1.63	31	.32
.61 - 1.2	3, 5, 5, 8	81	1.59	33	.19
1.2 - 1.8	3, 5, 6, 10	81	1.58	27	.10
1.8 - 2.4	5, 8, 12, 16	92	1.59	40	.10
2.4 - 3.0	6, 7, 9, 12	100	1.60	39	.12
3.0 - 3.7	4, 6, 8, 10	100	1.57	43	.13
3.7 - 4.3	3, 3, 5, 6		1.38	42	.18
4.3 - 4.9	3, 3, 3, 2	71	1.04	51	.33
4.9 - 5.5	2, 4, 4, 6	54	1.67	50	.20
5.5 - 5.9	3, 4, 50,	84	1.45	49	.17

[g/cm³ gram per cubic centimeter; --, not determined]

MW1 and culvert C1 near Newville, Pa.

¹Recovery decreased by obstruction of soil sampler by rock fragment.

Carbonate Bedrock

Bedrock beneath the site is part of the Shady Grove Formation of Upper Cambrian age. It is composed of gravish black, thinly bedded, micritic limestone with an estimated thickness of 244 to 305 m (Becher and Root, 1981). Bedding in outcrops of the Shady Grove and Stoufferstown Formations nearby the field site strike east-northeast and is nearly vertical. Foliation is parallel to bedding and quartz-filled fractures are common both parallel to and crosscutting bedding. Drilling logs and cuttings from three monitor wells completed at the site reveal extreme spatial differences in karstification of carbonate bedrock. Monitor well MW1 (total depth of 122 m below the land surface) yielded less than 0.03 L/s on completion and had no evidence of appreciable fractures or voids in the unsaturated interval or discernible water-bearing zones. Monitor well MW2 (total depth of 61 m) yielded about 0.1 L/s and had numerous fractures and small voids in the unsaturated zone and numerous, low yielding water-bearing zones from the regional water table to a depth of 46 m. Monitor well MW3 (total depth of 38.1 m) yielded about 1.3 L/s and had numerous fractures and small voids in the unsaturated zone and additional mudfilled voids and water-bearing zones; a 4 m thick cavernous void was encountered starting at 24 m below the land surface. In well MW3, some water was encountered in bedrock at 12 m below the land surface. This was above the static water level of the regional aquifer, showing that a perched water-table aquifer was present in the shallow bedrock.

Estimates of gravity yield and hydraulic conductivity of the carbonate-rock aquifer at the site span one and two orders of magnitude, respectively. These estimates provide a very limited assessment of the actual spatial distribution of porosity and permeability in carbonate bedrock beneath the site. Estimates of the gravity yield for five storms from precipitation data from the National Oceanic and Atmospheric Administration (NOAA) weather station at Shippensburg, Pa., and ground-water levels from monitor well MW1 were analyzed by use of the methods of Olmsted and Healy (1962, p. 16). The average gravity yield for the five storms was 3.4 percent and ranged from 0.5 to 7 percent (table 6). On average, soils at the site have about 12 times the average water content of an equal thickness of the regional aquifer. The average hydraulic conductivity of the open interval was estimated from slug tests (fig. 6) by use of the methods of Bouwer and Rice (1976). A smaller diameter slug was used in monitor well MW2 to fit the reduced annular space from the presence of a dedicated submersible pump and discharge line in the well bore—this is shown by the lesser initial water-level displacement of well MW2 relative to wells MW1 and MW3 in figure 6. The average hydraulic conductivities of the open intervals of monitor wells MW2 and MW3 were 0.14 and 1.4 m/day, respectively. The water-level decline at well MW1 was small over the test pericd, showing a very low permeability. The response from this well was not suitable for determining hydraulic conductivity by use of the Bouwer and Rice method.

Recharge period	Precipitation quantity (millimeters)	Ground- water level rise (millimeters)	Gravity yield (volume percent)
November 21-22, 1991	39.6	576	6.9
March 6-7, 1992	44.7	2,280	2.0
April 21-22, 1992	55.4	1,030	5.4
March 4-5, 1993	64.3	12,560	.51
March 13-24, 1993	124	6,190	2.0

Table 6. Gravity yield of the regional aquifer for selected periods of recharge from precipitation near Newville, Pa.



Figure 6. Water-level response of slug introduction for monitor wells MW1, MW2, and MW3 near Newville, Pa.

Recharge Mechanisms

In this regolith-mantled karst terrain, recharge may follow multiple pathways from the land surface to the regional aquifer. The three recharge mechanisms that are of most interest to the transport of agricultural chemicals are areally-distributed recharge, topographically-enhanced recharge, and sinkhole recharge (fig. 7). Recharge and contaminant transport through soil and the intermediate vadose zone (epikarst) are described as they apply to leaching of agricultural pesticides by the three recharge mechanisms.

Areally-distributed recharge results from infiltration of rainfall and snow melt through soil materials on parts of the regolith-mantled karst landscape that neither generate nor receive appreciable overland flow. Areally-distributed recharge is the predominant form of recharge on soil-covered, flat or gently sloping upland areas. Because most of the soil types farmed in the carbonate terrains in southeastern and southcentral Pennsylvania are relatively free of subsurface zones that are limiting with respect to deeper percolation of water, the recharge rate is controlled by the permeability and moisture content of soil materials.



Figure 7. Ground-water levels at monitor wells near Newville, Pa., and precipitation at Shippensburg, Pa., May 1991 through April 1993.

Soil and climatic conditions are most conducive to areally-distributed recharge from December through April of most years (fig. 5). During this part of the year, the soil-moisture losses incurred over the growing season have been made up by additional rainfall, and soil hydraulic conductivities approach their maximum. In winter and early spring, areally-distributed recharge can be expected from rainfall or snowmelt for any period when soils are not frozen.

Soil concentrations of most pesticides applied during the growing season are relatively low during the winter and spring when conditions are favorable for areally-distributed recharge. Appreciable quantities of most herbicides, insecticides, and fungicides degrade or volatilize between the time of application and the winter months. The pesticides and their degradation products that are most likely to leach from areally-distributed recharge are those that are mobile in the soil environment and either (1) have long half lives, so that pesticides persist in the soil beyond the growing season, or (2) are applied after harvest or just prior to the growing season. Residual quantities of the more persistent pesticides and their degradation products may be retained in the soil at environmentally significant concentrations well after the application period, so that these compounds may leach to the regional aquifer by areally distributed recharge. Fall or early spring application of herbicides to control winter annual weeds is the most notable agricultural practice that may lead to high soil concentrations during the period when there is substantial areally-distributed recharge.

The undulating topography of most regolith-mantled karst landscapes contains numerous swales and closed depressions that receive appreciable quantities of local runoff from adjacent areas that are subject to topographically-enhanced recharge. The added water from local runoff causes soils in these areas to remain moist for a greater part of the year than soils on adjacent slopes. Therefore, recharge to the regional aquifer is likely to occur from rainfall or snowmelt in greater quantity and over a greater part of the year in these areas than on uplands and adjacent slopes.

Climatic conditions conducive to recharge in these topographically low areas may extend into the growing season. Pesticides and their degradation products having the greatest probability of leaching to ground water from topographically-enhanced recharge include those compounds that are mobile in the soil environment and (1) are applied in the fall; (2) are applied in the spring as burnoff, preplant, or preemergent treatments; or (3) have long soil half lives so that pesticides persist in the soil beyond the growing season. Fall applications of herbicides to control winter annual weeds and springtime applications of burnoff, preplant, and preemergent herbicides are agricultural practices that may lead tc high soil concentrations during the period when there is potential topographically-enhanced recharge.

Sinkholes and shafts are ubiquitous features throughout the carbonate valleys of southeastern and southcentral Pennsylvania. Because these features allow rapid recharge to the aquifer and bypass the soil matrix and intermediate vadose zone, they are potentially important pathways for recharge and contaminant transport. Recharge through sinkholes may occur any time local runoff is generated. Recharge through sinkholes may reach the regional aquifer within hours of rainfall or snowmelt and may include pesticides and their degradation products that are otherwise readily volatilized or degraded in the soil environment or, because of their low solubility, exhibit little mobility in soil materials. Recharge through sinkholes also may occur when soils are frozen. Sinkholes or shafts in the instrumented part of the field site are not evident. However, many are visible along strike of bedding within 500 m to the east and west of the instrumented area.

Because the carbonate bedrock that comprises the intermediate vadose zone is not uniformly permeable, a perched aquifer may develop in soils and the uppermost part of the intermediate vadose zone. Williams (1983, 1985) and Field (1989) indicate that much of the recharge to mantled carbonate-rock aquifers is focused through sporadically distributed dissolutional openings (called shafts or subcutaneous drains) that breach the intermediate vadose zone. Perched ground water may move in a radial patterr toward shafts for considerable horizontal distances in the soil and epikarst prior to recharging the regional aquifer.

Most closed surface depressions coincide with dissolutional features that breach the intermediate vadose zone. Precipitation and runoff that collect in closed depressions may saturate soils and recharge the regional aquifer at various times of the year, including periods with high potential for evapotranspiration.

Recharge through closed depressions must first pass through the soil that covers these dissolutional features but may then be transported rapidly through the intermediate vadose zone (fig. 8). Sinkholes provide an even more direct connection between the land surface and the regional aquifer so that runcff into sinkholes is transported to the aquifer after minimal contact with the soil and intermediate vadose zone.

Because soils at the site are thick and have a large specific retention of soil moisture, the quantity of water contained in the soil is large relative to the average annual recharge through soils to the regional aquifer. Therefore, most diffuse recharge is stored for a time in the soil before transport to the regional aquifer. Soil moisture and water-soluble contaminants could reside there for several years, assuming conditions of diffuse recharge and uniform flow through the unsaturated zone. Depending on degradation rates and sorption to soil particles, concentrations of the more labile contaminants in soil water may be greatly reduced prior to their transport to the regional aquifer. However, preferential flow paths in the scil (root casts, animal burrows, and interpedal surfaces) and in the intermediate vadose zone allow part of the recharge to bypass the unsaturated materials and create a broad range of residence times.

Ground-water-level data provide some insights into recharge periods and recharge mechanisms. Over the study period, ground-water levels in the regional aquifer at the site ranged from 7.6 to 32 m below the land surface (fig. 8) or about 183 to 158 m above sea level. The rate of decline in ground-water levels during extended periods of dry weather was between 0.02 and 0.04 m/d. The initial rise in ground-water levels commonly lagged behind the onset of rainfall or snowmelt by a few hours; the highest ground-water levels were from 2 to 5 days later. Ground-water levels had a pronounced annual cycle—the highest levels were during March or April and the lowest levels were from November to as late as February. This cycle was the result of recharge to the regional aquifer from rainfall and snowmelt during November through April. However, recharge also was observed from rainfall during the summer and fall when there was a combination of high potential for evapotranspiration and dry soil conditions. The short lag time between the onset of precipitation and recharge to the regional aquifer and the occurrence of recharge during periods of high potential for evapotranspiration and dry soil conditions suggest that recharge occurs in part along preferential pathways in the unsaturated zone.

Chemical Measurements of Soils and Subsurface Water

Chemical measurements of soils and subsurface water at the field site near Newville, Pa., were evaluated to describe processes responsible for changes after pesticide applications made during the 1991 growing season. In 1991, above average temperatures began in May about 7°C above normal and remained about 3° above normal from June through August. Precipitation recorded at Shippensburg, Pa., for the period May through August (U.S. Department of Commerce, 1992) was 89 mm below average rainfall for 62 years of record. The above average temperature and below average precipitation during the 1991 growing season lead to a crop failure and negligible ground-water recharge during the intensive monitoring period. The chemical data collected during this period document (1) changes in pesticide concentrations in shallow soil samples caused by their application with subsequent drought conditions, and (2) little change in subsurface water quality because of a negligible ground-water recharge.

Pesticide Concentrations In Soils

Pesticide concentrations in soils were evaluated on the basis of their distribution with depth in the soil profile and their change in concentration from April to August 1991. Measurable concentrations of three herbicide and two pesticide degradation products were present only in the top 0.6 m of the two continuous soil cores collected April 1991 prior to the planting season (table 7). Atrazine, simazine, metolachlor, and deisopropylatrazine were present in the top 0.1 m of each soil core; concentrations of these compounds ranged from 3.3 to 15.9 μ g/kg. Atrazine, deethylatrazine, and deisopropylatrazine also were present at a depth of 0.3 to 0.6 m in the soil core at monitor well MW1. The pesticides were the residual carryover from simazine, atrazine, and metolachlor applied alfalfa grown in 1989 and corn grown in 1990 for weed control. Deethylatrazine is a soil metabolite of atrazine whereas deisopropylatrazine is a soil metabolite of both atrazine and simazine.





Table 7. Pesticides detected in soil samples from monitor well MW1 and culvert C1 near Newville, Pa., April 1991

Sampla	Pesticide						
depth interval (meters)	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine		
		Monitor	well MW1				
010	5.2	15.8	15.7	1.3	9.3		
.3061	1.0	<.05	<.05	2.0	10.6		
.61 - 1.2	<.05	<.05	<.05	<.05	<.05		
1.2 - 1.8	<.05	<.05	<.05	<.05	<.05		
1.8 - 2.4	<.05	<.05	<.05	<.05	<.05		
2.4 - 3.0	<.05	<.05	<.05	<.05	<.05		
3.0 - 3.7	<.05	<.05	<.05	<.05	<.05		
3.7 - 4.3	<.05	<.05	<.05	<.05	<.05		
4.3 - 4.9	<.05	<.05	<.05	<.05	<.05		
4.9 - 5.5	<.05	<.05	<.05	<.05	<.05		
5.5 - 6.1	<.05	<.05	<.05	<.05	<.05		
6.1 - 6.7							
6.7 - 7.3	<.05	<.05	<.05	<.05	<.05		
		Culv	ert C1				
010	5.5	6.8	15.9	<.05	3.3		
.3061	<.05	<.05	<.05	<.05	<.05		
.61 - 1.2	<.05	<.05	<.05	<.05	<.05		
1.2 - 1.8	<.05	<.05	<.05	<.05	<.05		
1.8 - 2.4	<.05	<.05	<.05	<.05	<.05		
2.4 - 3.0	<.05	<.05	<.05	<.05	<.05		
3.0 - 3.7	<.05	<.05	<.05	<.05	<.05		
3.7 - 4.3	<.05	<.05	<.05	<.05	<.05		
4.3 - 4.9	<.05	<.05	<.05	<.05	<.05		
4.9 - 5.5	<.05	<.05	<.05	<.05	<.05		
5.5 - 5.8	<.05	<.05	<.05	<.05	<.05		

[All concentrations in micrograms per kilogram; <, less than the indicated minimum reporting level; --, not determined]

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On May 29, 1991, corn was planted at the field site and atrazine and metolachlor were applied w⁻th a boom sprayer at rates of 1.7 and 2.2 kg/ha, respectively. The application resulted in an initial, average soil concentration of about 1,100 μ g/kg of atrazine and 1,500 μ g/kg of metolachlor in the top 100 mm of soil (assuming the pesticide was uniformly distributed on the soil surface and the soil had an average dry bulk density of 1.5 g/cm³). Concentrations of atrazine and metolachlor in soil samples collected 6 days after application were lower than the average initial concentration (table 8). At this time, the concentration of deethylatrazine was higher than it was before application. However, the concentrations of simazine or deisopropylatrazine changed very little. Average concentrations of atrazine, deethylatrazine, and deisopropylatrazine decreased substantially from 6 to 84 days after application; concentrations of metolachlor and simazine decreased only slightly over the same time.

 Table 8. Concentrations of pesticides detected in top 0.30 m of soil near Newville, Pa.

[All concentrations in micrograms per kilogram; <, less than the indicated minimum reporting level]

Sample location	Sample date	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine
		<u>35 d</u>	ays prior to applic	ation		
MW1	04/24/91	5.2	15.8	15.7	1.3	9.3
C1	04/24/91	5.5	6.8	15.9	<.05	3.3
Near LN1	05/28/91	4.2	8.9	12.9	1.4	<.05
Near LN1	05/28/91	4.7	6.7	15.0	1.6	5.5
Near LN2	05/28/91	5.1	16.7	13.8	1.1	4.4
Near LN2	05/28/91	5.8	24.2	26.5	1.7	13.0
Near LN3	05/28/91	5.0	38.1	13.1	2.0	8.5
Near LN3	05/28/91	5.9	8.2	13.2	2.9	6.6
Near LN3	05/28/91	3.1	8.6	8.3	<.05	<.05
Near LN3	05/28/91	2.3	8.6	9.6	<.05	<.05
Average:		4.5	15	14	1.4	4.8
6 days after application						
Near LN1	06/04/91	5.5	8.1	<.05	1.2	5.8
Near LN2	06/04/91	214	280	11	4.1	<.05
Near LN3	06/04/91	275	320	19.7	14.4	9.1
Near LN3	06/04/91	270	448	11.7	10.4	<.05
Near LN3	06/04/91	496	427	23	39	17.6
Near LN3	06/04/91	253	355	16.3	16.8	9.9
Average:		252	306	14	14	7.1
		<u>84</u>	days after applica	ation		
Near LN1	08/21/91	41	227	7.6	3.2	5.2
Near LN1	08/21/91	64	289	19	4.9	9.2
Near LN3	08/21/91	39.3	303	13.7	2.6	3.6
Near LN3	08/21/91	14.2	201	4.9	1.4	1.7
Near LN3	08/21/91	18.4	361	4.8	2.3	<.05
Near LN3	08/21/91	13	207	13.6	2.0	2.9
Average:		32	265	10.6	2.7	3.8

Subsurface-Water Quality

Field measurements of water quality indicate spatial and temporal variation in the mineral content and alkalinity of soil-water samples. Water samples from depths of 1.2 and 3.7 m below the land surface from lysimeter LN1, in a gently sloping area of the field site (fig. 3), had lower average specific conductance, pH, and alkalinity than samples collected at similar depths from lysimeters LN2 and LN3, both in an adjacent swale (table 9). Water samples collected at various depths from lysimeters LN1 and LN3 indicate that average specific conductance and alkalinity decrease substantially and average pH decreases slightly with increasing depth below the land surface. However, on the basis of available dz^+a , the apparent changes in mineral content and alkalinity with increasing depth in the soil profile and with topographic position cannot be explained.

The concentrations of major ions and dissolved organic carbon in ground water for monitor wells MW2 and MW3 changed little during the intensive monitoring period. The dissolved-solids concentration determined by sum of constituents of ground water from wells at the site ranged from 653 to 724 mg/L (table 10). Calcium and bicarbonate are the dominant dissolved ions in ground water, with lesser concentrations of dissolved chloride, nitrate, and magnesium. The saturation of water with respect to common rock-forming minerals calculated from the geochemical model WATEQ4F (Ball and others, 1927) indicates that ground water is oversaturated with respect to quartz, undersaturated with respect to dolomite, and saturated to oversaturated with respect to calcite.

Water samples collected from the field site were analyzed for 11 herbicides and 6 herbicide soil metabolites listed in table 3. Only atrazine, metolachlor, prometon, simazine, deethylatrazine, and deisopropylatrazine were detected.

During the intensive monitoring period, water samples were collected and analyzed from lysimeter LN3 at 2.1 m below the land surface and from lysimeters LN1 and LN3 at 3.7 m below the land surface. Atrazine, simazine, deethylatrazine, and deisopropylatrazine were detected and metolachlor was not detected in all samples (table 11). However, metolachlor was detected in one water sample collected from a trough lysimeter (from Culvert C1 at 1.2 m below the land surface). Triazine pesticides that were measured by immunoassay methods in each water sample not analyzed by GC/MS methods, were present at concentrations ranging from the minimum reporting level of 0.1 to 4.0 μ g/L.

Similar concentrations of triazine residue were measured in soil-water samples collected from 1.2 m below the land surface at the location of each of the lysimeter nests. Concentrations in soil-water samples at this depth typically were lower than concentrations in samples collected at greater depths. Concentrations of triazine herbicide residue decreased through the sampling period from lysimeter LN1 at 3.7 m and lysimeter LN3 at 2.1 m; concentrations in water samples collected from the other lysimeters showed no observable systematic variation. The cause of these spatial and temporal changes in triazine residue concentrations is not known.

Traces of atrazine, simazine, deethylatrazine, and deisopropylatrazine were measured in water samples from each of the monitor wells (table 12). Metolachlor was measured in water from wells MW1 and MW3, and prometon was measured in monitor wells MW2 and MW3. Concentrations of deethylatrazine were higher than the other pesticides measured; concentrations ranged from 0.38 to $1.12 \mu g/L$. Concentrations of all detected pesticides except prometon decreased slightly in ground water during the intensive monitoring period. Because prometon is not applied to crop land, the presence of prometon in water from monitor wells at the field site suggests an outside source of contaminants. The source of prometon is not known. However, the other pesticides may be related to agricultural activities at or near the field site prior to 1991.

Climatic and ground-water-level data indicate a lack of substantial recharge during the intensive monitoring period. Therefore, the observed subsurface-water quality can be assumed to be the result of environmental factors and agricultural activities prior to the monitoring period. Slight changes in concentrations over the intensive monitoring period were related to physical and chemical processes taking place within the unsaturated zone and aquifer system and not from changes related to recharge during the 1991 growing season.

Table 9. Field measurements of water quality for samples from lysimeters near Newville, Pa.

[μ S/cm, microsiemen per centimeter at 25 degrees Celsius; mg/L as CaCO₃, milligram per liter as calcium carbonate; m, meters below land surface; --, not determined]

Sample location and depth below land surface	Sample date	Specific conductance (µS/cm)	рН	Alkalinity (mg/L as CaCO ₃)
LN1 at 1.2 m	04/02/92	299	7.2	26
	04/10/92	343	7.2	33
	04/22/92	397	6.8	25
	05/11/92	431	6.0	18
	06/09/92	433	6.1	19
	06/19/92	427	7.0	15
	07/07/92	428	6.0	13
	08/18/92	452	5.7	11
	09/05/92	461	6.3	16
	10/06/92	456	6.2	13
	11/10/92	460	6.2	17
Average:		417	6.4	19
LN1 at 37 m	08/09/91	370	7.1	
	08/12/91		7.0	
	$\frac{02}{26}$	281	6.5	2
	04/02/92	257	5.4	7
	04/10/92	223	62	4
	04/22/92	223	6.2	4
	05/11/92	233	49	3
	06/09/92	233	53	2
	06/16/92	231	5.0	2
	07/07/92	2231	47	1
	08/05/92	228	47	
	08/18/92	220	51	2
	09/04/92	231	60	7
	10/06/92	232	49	2
	11/10/92	220	5.2	3
	11/18/92	225	65	10
Average	11/10/92	232	57	4
I N2 at 1.2 m	05/11/92	691	72	121
LINZ at 1.2 III	05/11/02	660	7.2	118
	06/16/92	578	79	89
	07/07/92	655	78	93
	08/05/92	640	7.5	98
	08/18/92	550	76	78
Average [.]	00,10,2	629	7.6	100
LN3 at 12 m	04/10/92	440	68	79
	04/22/92	525	7.7	84
	05/11/92	626	74	107
	06/09/92	620	80	93
	06/16/92	644	79	93
	07/07/92	660	69	95
	08/05/92	682	67	104
	08/18/92	685	72	95
	09/04/92	709	74	104
	10/06/02	709	60	111
	11/10/92	760	69	120
	11/10/92	700	60	125
Auora 201	11/10/74	654	70	101
Average		0.00	1.2	101

Table 9. Field measurements of water quality for samples from lysimeters near

 Newville, Pa.—Continued

[μ S/cm, microsiemen per centimeter at 25 degrees Celsius; mg/L as CaCO₃, milligram per liter as calcium carbonate; m, meters below land surface; --, not determined]

Sample location and depth below land surface	Sample date	Specific conductance (µS/cm)	рН	Alkalinity (mg/L as CaCO ₃)
LN3 at 2.1 m	08/09/91	540	7.0	
	08/12/91	510	7.2	
	09/10/91	550		
	02/26/92	386	7.3	84
	04/02/92	374	7.5	105
	04/10/92	385	7.5	98
	04/22/92	381	7.4	112
	05/11/92		7.5	81
	06/09/92	347	7.4	79
	06/16/92	339	7.9	77
	07/07/92	337	7.8	74
	08/05/92	332	7.0	68
	08/18/92	317	7.1	55
	09/04/92	318	6.9	50
	10/06/92	317	6.9	47
	11/10/92	305	6.8	46
	11/18/92	312	6.6	47
Average:		378	7.2	73
LN3 at 3.7 m	08/09/91	870	7.4	
	02/26/92	490	8.1	81
	04/02/92	364	6.9	69
	04/10/92	313	6.6	48
	04/22/92	321	7.0	50
	05/11/92	292	6.6	37
	06/09/92	286	7.0	36
	06/16/92	278	7.1	33
	07/07/92	272	6.4	31
	08/05/92	266	6.4	26
	08/18/92	267	6.4	23
	09/04/92	270	7.0	33
	10/06/92	261	6.4	21
	11/10/92	273	6.7	25
	11/18/92	274	6.3	23
Average:		340	6.8	38

Table 10. Concentrations of major ions and dissolved organic carbon in ground water from monitor wells nearNewville, Pa.

		Monitor	well MW2			Monitor well MW3			
Constituent	07/*	19/91	10/3	31/91	07/1	0/91	11/()1/91	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	
Calcium	150	7.5	150	7.5	160	8.0	160	8.0	
Magnesium	8.3	.68	10	.82	7.1	.58	6.9	.57	
Sodium	11	.48	15	.65	19	.83	18	.78	
Potassium	3.1	.08	5.4	.14	3.0	.08	2.9	.07	
Sum of cations		8.74		9.11		9.49		9.42	
Bicarbonate	346	5.7	394	6.5	359	5.9	386	6.3	
Sulfate	27	.56	25	.52	27	.56	20	.42	
Nitrate ¹	48.7	.79	38.5	.62	53.2	.86	57.6	.93	
Chloride	50	1.4	53	1.5	82	2.3	63	1.8	
Sum of anions		8.45		9.14		9.62		9.61	
Silica	9.0		9.4		8.6		9.1		
Dissolved organic carbon	.6		.9		.8		.9		
Sum of constituents	653		700		719		724		

[mg/L, milligram per liter; meq/L, milliequivalents per liter; -- not applicable]

¹Reported as nitrate (NO $\frac{3}{3}$).

Table 11. Concentrations of pesticides detected in water from lysimeters near Newville, Pa.

[All concentrations in micrograms per liter; m, meters below land surface; <, concentration less than the indicated minimum reporting level; --, not determined]

Sample		Pesticide residue						
location and depth below land surface	Sample date	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine	Triazines by immunoassay	
LN1 at 1.2 m	04/02/92						0.2	
	04/10/92						.2	
	04/22/92						.1	
	05/11/92						.1	
	06/09/92						.4	
	06/16/92						.3	
	07/07/92						.1	
	08/18/92						.2	
	09/05/92						.2	
LN1 at 2.1 m	08/18/92						.9	
LN1 at 3.7 m	08/09/91	0.40	< 0.05	0.18	0.90	0.47		
	08/12/91	.56	<.05	.20	1.06	.49		
	08/15/91	.62	<.05	.16	1.02	.55		
	08/19/91	.52	<.05	.14	1.30	.60		
	08/20/91	.54	<.05	.14	.95	.38		
	08/21/91	.56	<.05	.14	1.00	.53		
	08/21/91	.60	<.05	.14	1.09	.53		
	09/04/91						1.2	
	09/10/91						1.0	
	09/14/91						.8	
	09/16/91						.9	
	09/25/91	.30	<.05	.08	.75	.25		
	10/07/91						.7	
	10/11/91						.7	

Table 11. Concentrations of pesticides detected in water from lysimeters near Newville, Pa.-Continued

[All concentrations in micrograms per liter; m, meters below land surface; <, concentration less than the indicated minimum reporting level; --, not determined]

location and depth below land surface Sample data surface Deletyl- attazine Deletyl- attazine Deletyl- attazine Triazines by immunoassay LN1 at 37 m 10/18/91 - - - - - 6 10/31/91 - - - - - 6 11/14/91 - - - - - 6 12/00/91 - - - - - 3 12/00/91 - - - - - 3 12/00/91 - - - - - 3 12/00/91 - - - - - 3 12/00/92 - - - - - 3 10/18/92 - - - - - 3 10/10/92 - - - - - 7 04/10/92 - - - - - 7	Sample				Pesti	cide residue		
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	location and depth below land surface	Sample date	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine	Triazines by immunoassay
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	LN1 at 3.7 m	10/18/91						.6
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		10/31/91						.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		11/14/91						.5
12/02/91 - - - - - 3 12/03/91 - - - - - 3 12/07/91 - - - - - 3 12/07/92 - - - - - 3 01/09/92 - - - - - 3 02/26/92 - - - - - 3 02/26/92 - - - - - 4 04/02/92 - - - - - 4 04/02/92 - - - - - 7 06/07/92 - - - - 7 7 06/07/92 - - - - 7 7 06/07/92 - - - - 7 7 06/07/92 - - - - 1		11/22/91						.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		12/02/91						.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		12/03/91						.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		12/09/91						.3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		12/17/91						.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		01/09/92						.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		02/06/92						3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		02/00/92						3
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		02/20/92						.0
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		04/02/92						.+
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		04/10/92						.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		04/22/92						.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		05/11/92						.4
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		06/09/92						./
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		06/19/92						./
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		07/07/92						.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		08/18/92						.7
LN2 at 1.2 m 04/02/92		09/05/92						.7
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	LN2 at 1.2 m	04/02/92						.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		04/10/92						.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		04/22/92						.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		05/11/92	-					.2
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$		06/09/92						.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		06/16/92						.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		07/07/92						.1
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		08/05/92						.2
LN2 at 3.7 m $04/02/92$ 0.2 04/10/92 6 LN3 at 1.2 m $04/02/92$ 5 04/22/92 5 04/22/92		08/18/92						.4
LN3 at 1.2 m $04/10/92$ 2 04/10/922 04/10/925 04/02/924 04/10/924 04/10/924 06/16/924 06/16/924 06/16/924 06/16/925 08/05/924 07/07/924 08/08/18/923 08/18/923 09/04/923 08/04/923 08/09/91 .13 08/08/15/91 .5.2 .0.5 .334 .0.84 .0.94 .1.4 08/12/91 .4.3 .0.5 .322 .80 .888 .1.3 08/15/91 .5.2 .0.5 .337 .977 .1.31 08/19/91 .5.1 .0.5 .36 .90 .96 08/20/91 .5.8 .0.5 .333 .101 .977 08/20/91 .5.8 .0.5 .333 .101 .977 08/21/91 .5.6 .0.5 .32 .977 .91 09/14/9110 09/16/9110 09/14/9110 09/14/9110 09/14/9110 09/14/91 .3.1 .0.5 .23 .61 .5.8 10/07/91 .3.1 .0.5 .22 .63 .5.8	LN2 at 3.7 m	04/02/92						0.2
LN3 at 1.2 m $04/02/92$ 2 04/10/92		04/10/92						.6
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	LN3 at 12 m	04/02/92						.2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		04/10/92						.5
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		04/22/92						.4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		05/11/02						3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		05/11/72		_				4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		06/09/92						4
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		07/07/02						.+ 2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		0//0//92						.2
LN3 at 2.1 m $09/04/92$ 3 09/04/92 3 LN3 at 2.1 m $07/29/91$ 1.7 08/09/91 0.47 <0.05 0.34 0.84 0.94 1.4 08/12/91 .43 <0.05 .32 .80 .88 1.3 08/15/91 .52 <0.05 .37 .97 1.31 08/19/91 .51 <0.05 .36 .90 .96 08/20/91 .58 <0.05 .33 1.01 .97 08/21/91 .56 <0.05 .32 .97 .91 08/21/91 .56 <0.05 .32 .97 .91 09/14/91 1.0 09/16/91 1.0 09/25/91 .30 <0.05 .23 .61 .58 10/07/91 .31 <0.05 .25 .62 .58 10/07/91 .28 <0.05 .22 .63 .58		08/05/92						.5
LN3 at 2.1 m $07/29/91$ 1.7 08/09/91 0.47 <0.05 0.34 0.84 0.94 1.4 08/12/91 4.3 <0.05 3.2 80 88 1.3 08/15/91 5.2 <0.05 3.7 97 1.31 08/19/91 5.1 <0.05 3.6 90 $9608/20/91$ 5.8 <0.5 3.3 1.01 $9708/21/91$ 5.6 <0.5 3.32 97 $9108/21/91$ 5.6 <0.5 3.32 97 $9108/21/91$ 5.6 <0.5 3.22 97 $9109/14/91$ 1.0 09/16/91 1.0 09/25/91 3.0 <0.5 2.3 61 $5810/07/91$ 3.1 <0.5 2.5 62 $5810/1/91$ 2.8 <0.5 22 63 58		08/18/92						.5
LN3 at 2.1 m $07/29/91$ 1.7 08/09/91 0.47 <0.05 0.34 0.84 0.94 1.4 08/12/91 .43 <0.05 .32 .80 .88 1.3 08/15/91 .52 <0.05 .37 .97 1.31 08/19/91 .51 <0.05 .36 .90 .96 08/20/91 .58 <0.05 .33 1.01 .97 08/21/91 .56 <0.05 .32 .97 .91 09/14/91 1.0 09/16/91 1.0 09/25/91 .30 <0.05 .23 .61 .58 10/07/91 .31 <0.05 .25 .62 .58 10/11/91 .28 <0.05 .22 .63 .58		09/04/92						.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	LN3 at 2.1 m	07/29/91						1./
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		08/09/91	0.47	<0.05	0.34	0.84	0.94	1.4
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		08/12/91	.43	<.05	.32	.80	.88	1.3
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		08/15/91	.52	<.05	.37	.97	1.31	
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		08/19/91	.51	<.05	.36	.90	.96	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		08/20/91	.58	<.05	.33	1.01	.97	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		08/21/91	.56	<.05	.32	.97	.91	
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		09/14/91						1.0
09/25/91 .30 <.05		09/16/91						1.0
10/07/91 .31 <.05 .25 .62 .58 10/11/91 .28 <.05 .22 .63 .58		09/25/91	.30	<.05	.23	.61	.58	
10/11/91 .28 <.05 .22 .63 .58		10/07/91	.31	<.05	.25	.62	.58	
		10/11/91	.28	<.05	.22	.63	.58	

Table 11. Concentrations of pesticides detected in water from lysimeters near Newville, Pa.-Continued

[All concentrations in micrograms per liter; m, meters below land surface; <, concentration less than the indicated minimum reporting level; --, not determined]

Sample		Pesticide residue					
location and depth below land surface	Sample date	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine	Triazines by immunoassay
LN3 at 2.1 m	10/18/91	0.29	<0.05	0.23	0.62	0.57	
	11/14/91						.6
	11/22/91						.7
	12/02/91						.6
	12/03/91						.8
	12/09/91						.6
	12/17/91						.7
	01/09/92						.6
	02/06/92		-				.5
	02/26/92						.4
	04/02/92						.5
	04/10/92						.5
	04/22/92						.4
	05/11/92			-			.3
	06/09/92						.6
	06/16/92						.4
	07/07/92						.3
	08/05/92						.4
	08/18/92						.5
	09/04/92						.4
LN3 at 3.7 m	08/09/91	0.77	< 0.05	0.19	0.96	0.74	
	09/14/91						1.0
	04/02/92						1.3
	04/10/92						1.3
	04/22/92						1.4
	05/11/92					, 	1.3
	06/09/92						1.8
	06/16/92						1.6
	07/07/92						1.3
	08/05/92						1.6
	08/18/92						1.6
	09/04/92						1.5
C1 at 1.2 m	10/07/91	<.05	.49	<.05	<.05	<.05	
	04/02/92						.1
C1 at 2.1 m	04/02/92						1.0
C2 at 2.1 m	06/09/92						4.0

Table 12. Pesticide concentrations in water from monitor wells near Newville, Pa.

[All concentrations are in micrograms per liter; <, less than; --, not determined]

					Pesticide			
Sample location	Sample date	Atrazine	Metolachlor	Simazine	Deethyl- atrazine	Deisopropyl- atrazine	Prometon	Triazines by immunoassay
MW1	06/04/91	0.32	0.06	0.07	0.38	0.12	<0.05	0.6
MW2	06/04/91	.64	<.05	.39	1. 12	.79	.09	1.5
	07/10/91	.64	<.05	.44	1.11	.77	.10	1.4
	08/12/91	.56	<.05	.29	.87	.53	.12	1.5
	10/31/91	.30	<.05	.14	.55	.29	.14	
MW3	07/10/91	.56	.07	.26	.84	.44	.13	1.2
	11/01/91	.50	.05	.20	.58	.30	.17	

SIMULATION OF PESTICIDE FATE AND TRANSPORT

The digital-computer model selected to evaluate pesticide leaching potentials in agricultural carbonate terrains of Pennsylvania was the pesticide component (LEACHP) of the Leaching Estimation and Chemistry Model (LEACHM) by Hutson and Wagenet (1992). LEACHP is process-based model of water and solute movement and chemical reactions in soils. Fates of pesticides were compared at the end of a simulated 2-year period by use of the model. Model estimates included the percentages of pesticides remaining undissolved on the soil surface, residuals in the soil profile, losses by a combination of evaporation and volatilization, losses by degradation, and losses by leaching. The modeling approach is based on the assumption that pesticides will reach ground water in the same relative proportions that they leach from the top 2 m of soil, thereby enabling ranking of potentials for pesticide leaching to ground water. Modeling results are discussed in terms of their possible implications for the development of agricultural best-management practices.

A brief discussion of the configuration of the screening model, modeled soil hydrology, model processes used to calculate pesticide transport, and simplifications used in the modeling approach follows.

Configuration of the Screening Model

Hutson and Wagenet (1992) documented the LEACHP digital computer model. A simplified flowchart of the LEACHP model, as configured for this study, is shown in figure 9. Soils data from the field site, temperature and precipitation data from the Shippensburg, Pa., NOAA station (U.S. Department of Commerce, 1993), and pan evaporation data from the Landisville, Pa., NOAA station (U.S. Department of Commerce, 1992) were used to simulate transport of 66 pesticides through the top 2 m of a typical agricultural carbonate soil during a typical 2-year period. Agricultural carbonate areas of Pennsylvaria currently use 62 of the 66 pesticides. The discontinued insecticides chlordane, DDT, and dieldrin and the discontinued fungicide benomyl were used in Pennsylvania agriculture and were included in the simulations for comparative purposes. Each year of the 2-year simulation used climatic data from the 1932 calendar year, a year of near-normal annual precipitation. Precipitation measured at the Shippensburg, Pa., gage during 1992 was 103.1 cm, or 4.6 cm greater than the 30-year average precipitation measured during the period 1951-80 (U.S. Department of Commerce, 1993). The model simulated a pesticide application made on May 16 for each of 2 years at a rate of 1.12 kg/ha.

Assumptions and Simplifications

The modeling approach in this report employed several assumptions and simplifications regarding climatic conditions, soil properties, pesticide properties, and reaction types and kinetics. Some of the most significant assumptions and simplifications used in the LEACHP model, as configured for this report, include:

- 1. Physical and chemical properties of pesticides are in some instances estimated (as discussed in Wauchope and others, 1992). Significant errors in estimated organic carbon partition coefficients and pesticide degradation rates (on the basis of estimated half lives) affect pesticide leachability rankings.
- 2. The simulations used near annual-average climatic conditions. Excessively dry or wet years may produce different model results.
- 3. Algorithms describing water and solute movement in the screening model assume homogeneous conditions within model layers, an assumption that is not representative of most soil environments in mantled karst terrains. Specifically, focused recharge and preferential flow of water and solutes were not simulated.
- 4. Only the top 2 m of soil were simulated, the model assumes that pesticides will reach ground water in the same relative proportions that they leach through the top 2 m of soil.
- 5. Complex pesticide transformation and degradation processes, including biotransformation, chemical hydrolysis, photolysis, and oxidation-reduction reactions are combined into the pesticide degradation rate value for each model layer.

LEACHP initializes all arrays and variables, then transfers control to MAINP, the effective main program, from which the following subroutines are called:





- 6. A uniform application rate of 1.12 kg/ha (approximately 1 pound/acre) was used, although there is a broad range of pesticide application rates based on desired selectivity of the product, formulation, application method, crop, soil conditions, and climatic conditions.
- An application date of May 16 was used, although actual application dates for the many pesticides tested vary depending on their use, crop, soil conditions, and climatic conditions.

Soil Hydrology

The screening model used physical and chemical data from the uppermost 2 m of soil at monitor well MW-1 (tables 4 and 5). Each of 20 vertical layers, 100-mm thick were initialized with a volumetric water content of 0.3, an arbitrary value that lies between soil field capacity and saturation. Model algorithms used methods of Rawls and Brakensiek (1985) to describe soil-moisture retention and Campbell's (1974) equation to calculate hydraulic conductivities for each model layer as a function of volumetric water content. Then the transient flux of water through the unsaturated zone and the rate of water evaporation from the soil surface are then estimated by a finite-difference approximation of Richard's equation:

$$\frac{\delta\theta}{\delta t} = \frac{\delta}{\delta z} \left[K(\theta) \frac{\delta H}{\delta z} \right] - U(z, t) , \qquad (1)$$

where θ is volumetric water fraction of the soil (unitless)

- *H* is hydraulic head (length),
- K is hydraulic conductivity (length per time),
- t is time,
- *z* is depth (length—positive upwards), and
- U is sink term representing water lost per unit time by transpiration (1/time).

The subroutines POTET and ETRANS (fig. 9) estimated evapotranspiration from user-input evaporation potentials and estimated flux of water across the soil water and atmosphere interface. The screening model was configured without crop simulations and approximated from pan evaporation data in the subroutine POTET. The fraction of evaporation lost during a day varies sinusoidally as a function of daily temperature. The subroutine ETRANS approcimates the evapotranspiration lost by the following formula:

$$f = \frac{\left[\cos 2\pi \left(t_1 - 0.3\right) - \cos 2\pi \left(t_2 - 0.3\right)\right]}{2} , \qquad (2)$$

where *f* is evapotranspiration lost during a daily 12 hour period,

- t_1 is 0.3 day (0712 hours), and
- t_2 is 0.8 day (1912 hours).

The model estimated drainage to below 2-m of soil depth was 57 cm of water per year, or about 55 percent of the annual precipitation inputs using climatic data from the 1992 calendar year. Evaporative losses were about 45 percent of precipitation inputs. The simulated recharge rate was appreciably higher than the 41 percent of annual precipitation estimated for the carbonate-rock terrain of the Conodoguinet Creek Basin for a 5-year period (Becher and Root, 1981). However, the simulated recharge rate was nearly identical to the 53 percent of annual precipitation estimated at an agricultural field site in a carbonate terrain of Lancaster County for a 6-year period (Hall and Risser, 1993).

Pesticide Transport

The pesticide properties database of Wauchope and others (1992) was the chief source of pesticide input used for the simulations. The pesticide properties are summarized in tables 13-15. The subroutine SOLP (fig. 9) models solute transport by use of the following general convection/dispersion equation:

$$\frac{\delta c_{L}}{\delta t} \left(\theta + pK_{d} + \varepsilon K_{H}^{*} \right) = \frac{\delta}{\delta z} \left[\theta D(\theta, q) \frac{\delta c_{L}}{\delta z} - qc_{L} \right] = \phi \quad , \qquad (3)$$

where z is soil depth (length),

- θ is saturated soil volumetric water content (unitless),
- *p* is soil bulk density (mass per volume)
- *q* is macroscopic water flux (volume per time),
- $D(\theta, q)$ is an apparent diffusion coefficient (length squared per time),
 - c_L is concentration in the liquid phase (mass per volume), and
 - ϕ is a term to account for sources and sinks.

Volatilization in SOLP is calculated according to the following equation:

$$J = -K_{soil} c_{L} , \qquad (4)$$

- where *J* is total diffusive flux of chemical from the soil-liquid to the atmosphere [mass/(time × length squared)],
 - K_{soil} is overall mass transfer coefficient for diffusion across the soil-water/atmosphere interface (length per time), and
 - c_L is concentration of chemical in soil water (mass per length cubed).

The following equation assumes pesticide sorption is linear:

$$c_{s} = K dc_{L} , \qquad (5)$$

where C_{s} is concentration of the chemical in the sorbed phase (mass chemical/mass soil),

- *Kd* is partition coefficient (volume per mass) calculated from the organic carbon partition coefficient Koc times the fraction of organic carbon in the soil, and
- c_l is concentration in solution (mass per volume).

Pesticide degradation coefficients [kdeg, mass/(time in days)] for layers 1 through 10 in the uppermost 1 m of the model were calculated from estimated field half lives, assuming first-order decay, according to the following formula:

$$kdeg = \frac{0.693}{half life in days}$$
 (6)

Pesticide degradation rates are commonly assumed to decrease with decreasing soil carbon content at depth (Buyanovsky and others, 1993, p. 65). By use of this assumption, degradation coefficients for the 1 to 2 m depth of the model were reduced in proportion to the average carbon content of the soil. The average organic carbon content of layers 11 through 20 was 0.12—approximately 16 percent of the average organic carbon content of 0.76 in layers 1 through 10. Therefore, pesticide degradation coefficients for layers 11 through 20 were calculated by multiplication of the coefficients for layer 1 through 10 by 0.16.

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Table 13. Physical and chemical properties of herbicides

[data are from Wauchope and others (1992); g/m³, gram per cubic meter; mg/dm³, milligram per cubic decimeter; L/kg, liter per kilogram]

Common name	Gram molecular weight	Solubility in water (g/m ³)	Vapor density (mg/dm ³)	Organic carbon partition coefficient (L/kg)	Degradation rate constant (days ⁻¹)
Alachlor	269.77	240	2.04 E-4	170	4.62 E-2
Atrazine	215.69	33	3.35 E-6	100	1.15 E-2
Bensulide	397.54	5.6	1.72 E-5	1,000	5.77 E-3
Bromoxynil octanate	403.0	0.08	1.04 E-4	10,000	9.90 E-2
Butylate	217.4	44	1.52 E-1	400	5.33 E-2
Chlorimuron-Ethyl	414.8	1,200	8.92 E-11	110	1.73 E-2
Clomazone	239.7	1,100	1.74 E-4	300	2.88 E-2
Cyanazine	240.7	170	2.08 E-8	19 0	1.95 E-2
Dicamba salt	221.04	400,000	8.92 E-11	2	4.95 E-2
Diuron	233.1	42	8.66 E-7	480	7.70 E-3
EPTC	189.32	344	3.46 E+1	200	1.15 E-1
Fluazifop-p-butyl	383.4	2	5.15 E-6	5,700	4.62 E-2
Glyphosate	169.1	900,000	6.83 E-11	24,000	1.47 E-2
Hexazinone	252.3	33,000	2.72 E-6	54	7.70 E-3
lmazapyr	261.3	11,000	1.13 E-6	100	7.70 E-3
Linuron	249.11	75	2.28 E-4	400	1.15 E-2
Maleic hydrazide	150.2	400,000	6.06 E-11	20	2.31 E-2
Metolachlor	283.80	530	4.78 E-4	200	7.70 E-3
Metribuzin	214.3	1,220	1.15 E-4	60	1.73 E-2
Metsulfuron-methyl	381.4	9,500	5.13 E-11	35	2.31 E-2
Paraquat	257.2	620,000	1.04 E-10	1,000,000	6.93 E-4
Pebulate	203.36	100	9.77 E-2	430	4.95 E-2
Prometon	225.3	720	9.37 E-5	150	1.38 E-3
Pronamide	256.13	15	1.17 E-3	800	1.15 E-2
Propachlor	211.69	613	2.61 E-4	80	1.15 E-1
Propazine	229.7	8.6	1.62 E-6	154	5.13 E-3
Quizalofop-ethyl	372.8	0.31	6.02 E-6	510	1.15 E-2
Sethoxydim	327.5	4,390	2.82 E-6	100	1.38 E-1
Simazine	201.66	6.2	2.39 E-7	130	1.15 E-2
Terbacil	216.7	710	3.61 E-6	55	5.77 E-3
Trifluralin	335.28	0.3	1.99 E-4	8,000	1.15 E-2
2,4 D acid	221.04	890	9.46 E-5	20	6.93 E-2

Sensitivity Analysis of the Model

A sensitivity analysis determined which variables most influence pesticide leaching within a broad range of pesticide and soil-properties data values (table 16). The analysis used the top three layers of the model. The chemical properties of atrazine were used in the sensitivity analysis of soil properties, and ϵ pesticide application rate of 1.12 kg/ha or about 112 mg/m².

Increases in the organic-carbon fraction of the soil caused moderate decreases in simulated pesticide concentrations in leachate (fig. 10). However, concentrations of pesticide leachate were relatively insensitive to a broad range of soil textures.



Figure 10. Model sensitivity to variation in soil properties.

Table 14. Physical and chemical properties of fungicides

[data are from Wauchope and others (1992); g/m³, gram per cubic meter; mg/dm³, milligram per cubic decimeter; L/kg, liter per kilogram; >, greater than]

Common name	Gram molecular weight	Solubility in water (g/m ³)	Vapor density (mg/dm ³)	Organic carbon partition coefficient (L/kg)	Degradation rate constant (days ⁻¹)
Benomyl	290.3	2.0	1.56 E-9	1,900	1.03 E-2
Captan	300.61	5.1	1.33 E-6	200	2.77 E-1
Chlorothalonil	265.92	.6	1.43 E-2	1,380	2.31 E-2
Dodine Acetate Salt	287.44	700	1.51 E-6	100,000	3.46 E-2
Ferbam	416.50	120	2.18 E-4	300	4.07 E-2
Maneb	265.29	6	1.07 E-11	>2,000	9.90 E-3
Metalaxyl	279.3	8,400	8.44 E-5	50	9.90 E-3
Metiram	1,088.7	.1	4.39 E-10	500,000	3.46 E-2
Thiophanate-Methyl	342.40	3.5	1.84 E-6	1,830	6.93 E-2

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Figure 11. Model sensitivity to variation in pesticide properties.

Changes in pesticide solubility, vapor density, organic carbon partition coefficient, and degradatior rate each affected the modeled pesticide concentration in leachate. The organic carbon partition coefficient (Koc) and the pesticide degradation rate constant were the pesticide properties having the largest effect or leachate concentrations. Leachate concentrations decreased sharply as Koc's increase from 1 to 1,000 (fig. 11), at which point the pesticide concentrations in leachate approached zero. Concentrations of pesticide present in leachate also decreased sharply as degradation rates increased from 0.0001 (half life of greater than 4,000 days) to 0.1 per day (half life of less than 1 day; fig. 11). Pesticide solubility affected pesticide concentrations occurred for water solubilities from 0 to 1 gm/m³. The test range of vapor densities also produced a nonlinear response in leachate concentrations. Leachate concentrations were insensitive to vapor densities of less than 1.0E-5 mg/dm³ but decreased sharply with vapor densities greater than from $1.0E^{-5}$ to $1.0E^{-2}$ mg/dm³ (fig. 11).

Simulated Pesticide Fate and Transport

Digital simulations were used to classify and rank the leaching potential for the 66 pesticides (herbicides, fungicides, and insecticides). Pesticides were classified as a small leaching potential if less than 0.1 mg/m² (about 0.1 percent of the initial application) of pesticide leached from the top 2 m of soil during the 2-year simulation period, and less than 0.1 mg/m² of pesticide residual remained in the soil profile. Pesticides were classified as having a medium leaching potential if less than 0.1 mg/m² of

Table 15. Physical and chemical properties of insecticides

[data are from Wauchope and others (1992); g/m³, gram per cubic meter; mg/dm³, milligram per cubic decimeter; L/kg, liter per kilogram]

Common name	Gram molecular weight	Solubility in water (g/m ³)	Vapor density (mg/dm ³)	Organic carbon partition coefficient (L/kg)	Degradation rate constant (days ⁻¹)
Acephate	183.16	818,000	1.68 E-5	2	2.31 E-1
Azinphos-methyl	317.33	29	3.42 E-6	1,000	6.93 E-2
Carbaryl	201.23	120	1.30 E-5	300	6.93 E-2
Carbofuran	221.25	351	7.14 E-6	22	1.38 E-2
Chlordane	409.80	¹ .056	2.20 E-4	² 38,000	² 1.98 E-4
Chlorpyrifos	350.62	.4	3.21 E-4	6,070	2.31 E-2
4,4'-DDT	354.49	1.056	¹ 1.90 E-4	² 240,000	² 1.80 E-4
Diazinon	304.3	60	9.82 E-4	1,000	1.73 E-2
Dicofol	370.51	.8	7.97 E-5	5,000	1.54 E-2
Dieldron	380.91	¹ .186	¹ 3.67 E-6	³ 12,000	³ 7.98 E-4
Dimethoate	229.28	39,800	3.08 E-4	20	9.90 E-2
Endosulfan	406.91	.32	3.73 E-6	12,400	1.38 E-2
Esfenvalerate	419.9	.002	2.49 E-7	5,300	1.98 E-2
Fenvalerate	419.9	.002	2.49 E-7	5,300	1.98 E-2
Lindane	290.85	7	5.16 E-4	1,100	1.73 E-3
Malathion	330.3	130	1.43 E-4	1,800	6.93 E-1
Methamidophos	141.13	1,000,000	6.10 E-3	5	1.15 E-1
Methomyl	162.2	58,000	4.36 E-4	72	2.31 E-2
Methyl parathion	263.21	60	2.12 E-5	5,100	1.38 E-1
Oxamyl	219.3	282,000	2.72 E-4	25	1.73 E-1
Parathion	291.27	24	7.83 E-5	5,000	4.95 E-2
Permethrin	391.30	.006	2.73 E-7	100,000	2.31 E-2
Phorate	260.38	22	8.96 E-4	1,000	1.15 E-2
Phosmet	317.33	20	8.36 E-6	820	3.64 E-2
Phosphamidon	299.7	1,000,000	2.66 E-4	7	4.07 E-2

¹Brown and Myers, 1992.

²Jury and others, 1987.

³Jury and Ghodrati, 1989.

Table 16. Properties of soils and pesticides used in model sensitivity analysis and relative effect on simulated pesticide leaching

[gm/m³, grams per cubic meter; mg/dm³, milligrams per cubic decimeter]

Value	Range	Effect on simulated pesticide leaching
Soil clay fraction (percent)	0 to 75	Small
Soil silt fraction (percent)	0 to 75	Small
Soil organic carbon fraction (percent)	0 to 10	Medium
Pesticide solubility (gm/m ³)	0 to 1.0 E+06	Medium
Pesticide vapor density (mg/dm³)	1.0 E-11 to 1.0 E+01	Medium
Pesticide organic-carbon partition coefficient	1.0 E+00 to 1.0 E+06	Very large
Pesticide degradation rate constant, in days	6.93 E-01 to 1.73 E-04	Very large

pesticide leached from the top 2 m of soil during the 2-year simulation period, and 0.1 mg/m² or more cf pesticide residual remained in the soil profile. Pesticides were classified as having a large potential for leaching to ground water if pesticide concentrations of 0.1 mg/m² or more were present in leachate.

Relative potentials for pesticide leaching to ground water were ranked within each group. Pesticides within each small and medium group were ranked by use of the maximum depth of penetration of the pesticide in soil, as indicated by the relative depths of the 99th percentile of cumulative pesticide breakthrough. Pesticides in the large leaching-potential group were ranked according to the leachate concentrations; larger masses indicate of greater leaching potentials. Among pesticides in the large leaching-potential groups, when ties occurred, the pesticide with the larger residual mass in the soil profile was assigned the larger leaching potential. If ties also occurred in the soil profile residual values, the pesticide with the greater penetration depth in soils was assigned the larger leaching potential

Herbicides

Degradation or a combination of volatilization and evaporation are the primary environmental fates of 29 of the 32 herbicides for the simulated 2-year period. Three herbicides—bensulide, paraquat, and prometon—were primarily retained in the soil profile as a result of rather low vapor densities and low degradation rates, however, of these three compounds, only prometon leached under the modeled conditions (table 17). A percentage of 18 herbicides was retained in the soil profile at the end of the simulated 2-year period. From 0.1 to 4.1 percent of seven of these compounds leached beyond the maximum depth of 2,000 mm and were assigned a large leaching potential. On the basis of the screening model, 11 herbicides were assigned a medium leaching potential, and 14 a small leaching potential.

On the basis of the screening model, seven of the eight agricultural herbicides (alachlor, atrazine, cyanazine, dicamba, glyphosate, metolachlor, and 2,4-D) most used in Pennsylvania (applications greater than 50,000 kg/yr from Gianessi and Puffer, 1991) are primarily lost from soils by degradation. Butylate, the other high-use herbicide, is primarily lost by volatilization and evaporation. Of the high-use herbicides, only atrazine was given a large leaching potential. Glyphosate and metolachlor were given a moderate leaching potential; the other five most-used herbicides were given a small leaching potential.

Prometon is the only herbicide with a class I human toxicity rating and a large leaching potential based on the screening model. Prometon is used for long-acting, nonselective control of vegetation on noncropland. Usage data for prometon in Pennsylvania is not available. The other herbicides given a class I human toxicity rating are lost from soils by degradation (2,4-D) or a combination of volatilization and evaporation (trifluralin).

Fungicides

Degradation or volatilization and evaporation are the primary environmental fates of the nin^o fungicides for the simulated 2-year period. Chlorothalonil was lost primarily from volatilization and evaporation, and the other fungicides were lost primarily from degradation (table 18). A percentage cf four fungicides was retained in the soil profile at the end of the simulated 2-year period. Of these, only tho fungicide metalaxyl was present in leachate beyond the maximum depth of 2,000 mm. Metalaxyl was given a large leaching potential, three other fungicides were given a medium leaching potential, and five fungicides were give a small leaching potential based on the screening model.

Metiram and chlorothalonil are the most used fungicides on agricultural land in Pennsylvania; they are lost from soils by degradation and a combination of volatilization and evaporation, respectively, based on the screening model. Metiram was given a moderate leaching potential and chlorothalonil was given a small leaching potential. Metalaxyl, the only fungicide given a large leaching potential, has an estimated annual use in Pennsylvania of 1,200 Kg on potato and tobacco crops (Gianessi and Puffer, 1992a).

Chlorothalonil and dodine are the only fungicides with class I human toxicity ratings--evaluated with the model. Model calculations indicate that these fungicides have a relatively low leaching potential.

Pesticide	Remaining undissolved on soil surface (percent of applied))	Remaining in soil profile (in percent of applied)	Lost by volatilization and evaporation (percent of applied)	Lost by degradation (percent of applied)	Lost by leaching (percent of applied)/ (mg/m ²)	Maximum depth of leaching (mm)	Group by leaching potential	Rank by leaching potential	Human toxicity class ¹
Alachlor	0	0	5	95	0	670	S	21	II
Atrazine	0	3	<1	96	<1/.1	>2,000	L	5	ш
Bensulide	0	80	18	2	0	360	Μ	7	III
Bromoxynil octanate	0	0	99	<1	0	0	S	28.5	п
Butylate	0	0	87	13	0	750	S	20	Ш
Chlorimuron ethyl	0	1	0	99	0	1,300	Μ	15	ш
Clomazone	0	<1	42	58	0	450	Μ	17	ш
Cyanazine	0	0	0	100	0	600	S	22	II, III
Dicamba salt	0	0	0	100	0	2,000	S	18	III
Diuron	0	9	<1	91	0	380	Μ	10	ш
EPTC	0	0	87	13	0	0	S	28.5	III
Fluazifop-P-butyl	0	0	7	93	0	180	S	25	IV
Glyphosate	0	2	0	98	0	130	Μ	14	ш
Hexazinone	0	0	35	65	0	0	S	28.5	IV
lmazapyr	0	0	<1	99	0	0	S	28.5	IV
Linuron	0	4	5	91	0	390	Μ	12	III
Maleic hydrazide	0	<1	0	99	<1/.2	>2,000	L	4	IV
Metolachlor	0	8	11	81	0	860	Μ	11	III
Metribuzin	0	1	2	96	<1/.1	>2,000	L	5	ш
Metsulfuron methyl	0	<1	0	99	<1/.1	>2,000	L	6	IV
Paraquat	0	76	0	24	0	99	Μ	8	п
Pebulate	0	0	87	13	0	440	S	23	III
Prometon	0	57	2	40	<1/.6	>2,000	L	2	I
Pronamide	0	36	49	15	0	400	Μ	9	IV
Propachlor	0	0	6	94	0	0	S	28.5	III
Propazine	0	18	2	79	<1/.2	>2,000	L	3	IV
Quizalofop ethyl	0	4	32	64	0	330	Μ	13	111
Sethoxydim	0	0	0	100	0	0	S	28.5	111
Simazine	0	<1	78	21	0	1,300	Μ	16	IV
Terbacil	0	15	3	80	2/4.1	>2,000	L	1	IV
Trifluralin	0	0	99	1	0	200	S	24	I, II, III
2,4D acid	0	0	2	98	0	1,900	S	19	I, III

Table 17. Fate of herbicides after simulated 2-year period, evaluation of leaching potentials, and human toxicity class [mg/m², milligrams per square meter; mm, millimeter; S, small; M, medium; L, large; <, less than; >, greater than]

¹From Sine (1993). See appendixes 1 and 2.

Insecticides

Degradation or volatilization and evaporation are the primary environmental fates of 21 of the 25 insecticides for the simulated 2-year period. Four insecticides—dieldrin, esfenvalerate, fenvalerate, and permethrin—were primarily retained in the soil profile as a result of rather low vapor densities and low degradation rates (table 19). None of the four insecticides retained in the soil profile leached to greater than 180 mm during the simulated 2-year period. A percentage of nine insecticides were retained in the soil profile at the end of the simulation period. However, only one insecticide, carbofuran, leached beyond the maximum depth of 2,000 mm; it was the only insecticide assigned a large leaching potential. Ten insecticides were assigned a medium leaching potential, and 14 a small leaching potential based on the screening model.

Table 18. Fate of fungicides after simulated 2-year period, evaluation of leaching potentials, and human toxicity class

[mg/m², milligrams per square meter; mm, millimeter; S, small; M, medium; L, large; I, most toxic, IV, least toxic; <, les⁺ than; >, greater than]

Fungicide	Remaining undissolved on soil surface (percent of applied))	Remaining in soil profile (in percent of applied)	Lost by volatilization and evaporation (percent of applied)	Lost by degradation (percent of applied)	Lost by leaching (percent of applied)/ (mg/m ²)	Maximum depth of leaching (mm)	Group by leaching potential	Rank by leaching potential	Human toxicity class ¹
Benomyl	0	5	0	95	0	220	М	4	ĪV
Captan	0	0	1	99	0	0	S	9	IV
Chlorothalonil	0	0	98	2	0	970	S	5	1, II
Dodine acetate salt	0	0	<1	99	0	99	S	8	I
Ferbam	0	0	5	95	0	450	S	6	IV
Maneb	0	6	0	94	0	210	М	2	IV
Metalaxyl	0	5	2	92	<1	>2,000	L	1	III
Metiram	23	5	0	72	0	99	Μ	3	IV
Thiophanate methyl	0	0	2	98	0	220	S	7	IV

¹From Sine (1993). See appendixes 1 and 2.

Five of the six agricultural insecticides (carbaryl, carbofuran, malathion, methomyl, and parathior) most used in Pennsylvania (applications greater than 25,000 kg/yr from Gianessi and Puffer, 1992b) are primarily lost from soils by degradation based on the screening model. Chlorpyrifos, the other high-use insecticide, is primarily lost by volatilization and evaporation. Of the high-use insecticides, only carbofuran was assigned a large leaching potential. Methomyl was assigned a medium leaching potential, and the four other high-use insecticides were assigned a small leaching potential.

Twelve insecticides had formulations with a class I human toxicity rating. Four of these insecticides were high-use compounds. Carbofuran was applied to about 8 percent of the corn and 13 percent of the potatoes planted in Pennsylvania during 1991 and ranked second only to chlorpyrifos in total annual insecticide use on agronomic crops in the state (Gianessi and Puffer, 1992b). Carbaryl, methomyl, and parathion also are high-use insecticides with a class I human toxicity rating; however, they have small and medium leaching potentials based on the screening model.

Relation of Pesticide Use and Model-Derived Leaching Potentials to Pesticides Detected in Ground Water

Ground-water quality data collected in southeastern and south-central Pennsylvania by the USGS between 1983 and 1993 were primarily analyzed for triazine and amid herbicides and selected soil metabolites. Ground-water-quality data for most of the fungicides and insecticides and several of the herbicides used in Pennsylvania (Jacoby, 1992) does not exist. Pesticide leaching potentials from the model simulations are compared to those pesticides detected in samples collected and analyzed by the USGS in table 20. These comparisons are qualitative, and any relations in the data must be interpreted with caution, because it is not known what pesticides have or have not been applied on land in the recharge areas to the wells.

The compounds detected with greater frequency in ground-water samples collected and analyzed by the USGS are high-use herbicides (alachlor, atrazine, and metolachlor), soil metabolites of high-use herbicides (deethylatrazine, deisopropylatrazine, and diethylaniline), and triazine herbicides of lessor crunknown use (simazine and prometon). The detected compounds span the range of leaching potential groups and are ranked from the second highest leaching potential (prometon) to a tie for the lowest leaching potential (EPTC) of the herbicides evaluated using the model simulations. The principal environmental fates of the compounds detected based on model simulations include losses from the soil by volatilization and evaporation (EPTC, pebulate, and simazine), by degradation (alachlor, atrazine,
 Table 19. Fate of insecticides after simulated 2-year period, evaluation of leaching potentials, and human toxicity class

[mg/m², milligrams per square meter; S, small; M, medium; L, large; I, most toxic, IV, least toxic; <, less than; >, greater than]

Insecticide	Remaining undissolved on soil surface (percent of applied))	Remaining in soil profile (in percent of applied)	Lost by volatilization and evaporation (percent of applied)	Lost by degradation (percent of applied)	Lost by leaching (percent of applied)/ (mg/m ²)	Maximum depth of leaching (mm)	Group by leaching potential	Rank by leaching potential	Human toxicit <i>i</i> class ¹
Acephate	0	0	0	100	0	0	S	22.5	<u>III</u>
Azinphos-methyl	0	0	0	100	0	280	S	17	I
Carbaryl	0	0	0	100	0	450	S	14	I, II, III
Carbofuran	0	2	<1	97	<1/1.6	>2,000	L	1	I, II
Chlordane	0	<1	0	99	0	180	М	8	II
Chlorpyrifos	0	0	99	1	0	190	S	18	II, III
4,4'-DDT	0	<1	99	0	0	99	S	11.5	II
Diazinon	0	0	23	77	0	280	S	16	II, III
Dicofol	0	2	27	71	0	190	М	6	II, III
Dieldrin	0	50	35	15	0	180	М	2	I
Dimethoate	0	0	7	93	0	0	S	22.5	II
Endosulfan	0	3	23	74	0	150	М	5	I
Esfenvalerate	93	1	5	1	0	150	Μ	9.5	II
Fenvalerate	93	1	5	1	0	150	Μ	9.5	II
Lindane	0	12	76	12	0	320	Μ	3	II
Malathion	0	0	3	97	0	0	S	22.5	III
Methamidophos	0	0	48	52	0	0	S	22.5	I
Methomyl	0	<1	10	89	0	1,500	Μ	7	I, IV
Methyl parathion	0	0	1	99	0	0	S	22.5	I
Oxamyl	0	0	6	94	0	0	S	22.5	I
Parathion	0	0	17	83	0	190	S	19	I
Permethrin	90	<1	5	4	0	99	М	11.5	II, III
Phorate	0	3	25	72	0	280	Μ	4	I
Phosmet	0	0	5	95	0	290	S	15	II
Phosphamidon	0	0	6	94	0	1,900	S	13	I

¹From Sine (1993). See appendixes 1 and 2.

cyanazine, linuron, metolachlor, and propazine), and retention in the soil (prometon). According to the simulation, three of the compounds detected (atrazine, prometon, and propazine) were expected to lea^h to ground water. However, five of the compounds detected in ground water (alachlor, cyanazine, EPTC, pebulate, and simazine) were not expected to leach to ground water.

The necessary chemical and physical properties of the soil metabolites of atrazine (deisopropylatrazine and deethylatrazine), simazine (deisopropylatrazine), and alachlor (diethylanaline) detected in ground water were not known such that their environmental fate could be simulated with the LEACHP model. The toxicity of these soil metabolites also was not known.

The model simulations would not have predicted the leaching of several compounds that have been detected with some frequency in ground water from agricultural carbonate rock terrains of southeastern and south-central Pennsylvania. The poor predictive capability of the model could be an indication that either (1) the processes by which some or all of the detected pesticides leach to ground water in these karst areas were not accurately represented by the LEACHP model as it was configured for these simulations, or (2) one or more of the pesticide or soil variables used as input to the model are substantially different from actual field conditions.

 Table 20.
 Pesticides detected in ground water from selected wells, lysimeters, and springs in southeastern and south-central Pennsylvania, 1983 through 1993

[; S, small leaching potential; M, medium leaching potential; L, large leaching potential; NR, not rated; --, not analyzed]

Pesticide	Estimated leaching potential from the model simulation	Percentage of 28 sites sampled in 1983 with detects ¹	Percentage of 11 sites sampled in 1989 with detects ²	Percentage of 7 sites sampled as part of this study with detects	Percentage of 37 sites sampled in 1991 with detects ³	Percentage of 30 sites sampled in 1993 with detects ⁴
Alachlor	S	12	9	0	3	27
Atrazine	L	41	82	86	43	93
Bromacil	NR					3
Cyanazine	S	0	0	0	0	3
Deethylatrazine	NR		82	86	81	77
Deisopropylatrazine	NR		64	86	22	
Diethylanaline	NR			0		3
EPTC	S		0			7
Linuron	М					3
Metolachlor	М	7	45	43	11	77
Pebulate	S					7
Pendimethalin	NR					3
Prometon	L			29	24	77
Propazine	L	0	0	0	3	0
Simazine	М	0	0	86	22	37
Tebuthiuron	NR					3

¹From Fishel and Lietman (1986).

²From D.JK. Wangsness (U.S. Geological Survey, written commun., 1990).

³From Durlin and Schaffstall (1993).

⁴From B.D. Lindsey (U.S. Geological Survey, written commun., 1994).

For this report, the LEACHP model was configured to represent pesticide fate and transport in a uniform flow field through the subsurface with both vertical downward infiltration and deep percolatior. Although the model simulations provide quantitative estimates of pesticide fate, it may be most useful for a qualitative understanding of how the combined soil and pesticide properties may influence pesticide leaching through agricultural soils in the carbonate rock terrains of southeastern and south-central Pennsylvania. As configured, quantitative estimates from the model could systematically underpredict the depth of movement and net pesticide losses from nonuniform subsurface flow and leaching from highly structured soils. The model may not be appropriate for prediction of even the presence or absence of pesticides in ground water in areas where focused recharge through karst features is an important process or where lateral flow associated with the development of locally perched aquifers is appreciable.

The LEACHP model, as configured for this report, simulated pesticide sorption and degradation by use of a single organic carbon partition coefficient and degradation rate constant for each pesticide to represent a multitude of soil processes. The model assumes that (1) sorption processes can be described by a linear relation, and (2) degradation processes can be described by a first order equation and a decreased degradation rate at depth in the soil. The sensitivity analysis presented earlier in the report demonstrated that of the variables evaluated, the organic-carbon partition coefficient and pesticide degradation rate had the largest relative effect on pesticide leaching (table 16). However, it is unknown if the degradation-rate constants used in the model simulations are close to actual degradation rates or that the actual sorption and degradation processes are represented properly by the relations used in the model. Degradation-rate constants probably are the least certain of the model input variables used in these model simulations (Wauchope and others, 1992).

Predictive capability of a screening model could be improved (1) by use of locally derived pesticidor properties data, (2) an improved representation of processes that control ground-water recharge and pesticide transport in areas with regolith-mantled karst landscapes, and (3) additional ground-water monitoring data for leachable pesticides in areas of known use.

Implications for the Development of Aaricultural Best-Management Practices

Ground-water quality data collected from USGS studies and results of the model simulations provide information that could be significant for the development of agricultural best-management practices in carbonate-rock areas of southeastern and south-central Pennsylvania Three general findings follow.

1. The pesticides detected in ground water from the agricultural, carbonate-rock terrains of southeastern and south-central Pennsylvania, include compounds with a broad range of ground-water leaching potentials and environmental fates. Related findings include:

Although the pesticides detected included those compounds assigned large, medium, and small ground-water leaching potentials, the pesticides detected with the greatest frequency generally had medium or large leaching potentials and high use on agricultural land relative to most other compounds evaluated.

The pesticides detected include compounds that are lost from the soil primarily by each of the environmental processes simulated by the model, so that the occurrence of these compounds in ground water can not be attributed to the action of just one pesticide property or environmental process.

Current water-quality data probably best represent pesticide occurrence of only those chemicals that are ubiquitous in use on major crops. A more thorough evaluation of the use and limitations of pesticide screening models needs additional water-quality data. Available data do not include analyses for several high-use compounds and compounds with large or moderate leaching potentials.

Addition of pesticide-use data in recharge areas to wells and springs sampled could provide useful comparisons of pesticide use and the presence or absence of pesticides in ground water. This approach is essential for evaluating the leaching potentials of lessor used pesticides and pesticides with much of their total use limited to either small geographic areas or minor crops.

2. Use of area specific estimates of variables describing pesticide-soil interactions, specifically sorption and degradation, and additional characterization of pesticide transport pathways through regolithmantled karst areas may improve the predictive capability of pesticide screening models in the carbonaterock terrains of southeastern and south-central Pennsylvania. Related findings include:

The pesticide properties used to describe pesticide-soil interactions and degradation rates in the screening model were compiled from field studies conducted at many locations throughout the United States, or in many cases they were estimated from properties of similar compounds (Wauchope and others, 1992). The existing pesticideproperties data may not be representative of the climate, soils, and pesticide- application practices in southeastern and south-central Pennsylvania.

The screening model assumes uniform one dimensional flow and transport through the unsaturated zone. Significant departures from this assumption in areas underlain by regolith-mantled carbonate rocks is evident, including focused recharge, preferential flow paths in structured soils, radial flow to shafts, and runoff into sinkholes. 3. Model simulations indicate that many pesticides used in Pennsylvania are degraded in the soil environment. The compounds formed from the partial degradation of pesticides could be a substantial part of all pesticide residues present in ground water. Related findings include:

Pesticide degradation products are among the most frequently detected pesticide residues in ground water in southeastern and south-central Pennsylvania (Durlin and Schaffstall, 1993; Hippe and others, 1994; B.D. Lindsey, U.S. Geological Survey, written commun., 1994) and in the United States (Jacoby, 1992).

For many pesticides, the principal sequences of degradation reactions have not been elucidated, and the various degradation products have not been fully characterized with respect to their physical and chemical properties, their stability in soil and ground water, and their effects on human-health and the environment (Somasundaram and Coats, 1991).

Degradation products of some pesticides have larger solubilities and higher vapor pressures than the parent compounds, giving them greater mobility in water and in the atmosphere (Somasundaram and Coates, 1991). Large changes in mobility or toxicity to plants, animals, and humans can cause some pesticide degradation products to impose an environmental or human health hazard greater than the parent compounds.

SUMMARY AND CONCLUSIONS

Because karst areas have a demonstrated susceptibility to ground-water contamination, ar improved understanding of the processes that control ground-water recharge and leaching of pesticides through soils may aid in developing agricultural practices that minimize adverse effects on ground-water quality.

The study area, a 4.5-hectare field site, is situated in a regolith-mantled carbonate-rock terrain typical of the carbonate-rock terrains in southeastern and south-central Pennsylvania. Unsaturated materials at the field site consist of an upper vadose zone composed of soils formed from weathering of limestone bedrock and an intermediate vadose zone composed of karstified limestone. Soils are absent or scattered bedrock pinnacles and are more than 12 m thick in other areas of the site. Organic carbon content of soil materials is about 1.7 percent in the Ap-horizon and from 0.1 to 0.3 percent throughout the full thickness of the B- and C-horizons.

Because soils at the site are thick with a large specific retention of soil moisture, the quantity of water contained in the soil is large relative to the average annual recharge through soils to the regional aquifer. From assumptions of diffuse recharge and uniform flow through the unsaturated zone, it was determined that soil moisture and water-soluble contaminants would generally have a residence time of several years. However, preferential flow paths in the soil (root casts, animal burrows, and interpedal surfaces) and ir the intermediate vadose zone allow part of the recharge to bypass most of the unsaturated materials creating a broad range of residence times.

Ground-water levels in the field site had a pronounced annual cycle; the highest levels occurred during March or April and the lowest levels between November and February. The initial rise in ground-water levels commonly lagged behind the onset of rainfall or snowmelt by a few hours. The highest ground-water levels occur from 2 to 5 days later. Recharge from rainfall occurred during the summer and fall even when there was a combination of high potential for evapotranspiration and dry soil conditions. The short lag between the onset of precipitation and recharge to the regional aquifer and the occurrence of recharge during periods of high potential for evapotranspiration and dry soil conditions suggest that recharge occurs in part along preferential pathways in the unsaturated zone.

Recharge through sinkholes and other preferential flow paths to the regional aquifer within hours of rainfall or snowmelt may include contaminants that are otherwise readily degraded in the soil environment and contaminants that, because of their low solubility, exhibit little mobility in soil materials. For example, at the field site, atrazine, metolachlor, simazine, and the atrazine soil metabolitee deethylatrazine and deisopropylatrazine were at concentrations above the minimum reporting level of 0.05 μ g/L in just the upper 0.6 m of bulk soil samples collected from land surface to a depth of 7.3 m.

However, concentrations of atrazine, simazine, and atrazine soil metabolites were detected in water samples from lysimeters installed in soil material at depths of 1.2, 2.1, and 3.7 m and from monitor we'ls completed in the regional aquifer.

Data collected to characterize the field site were used to configure a pesticide screening model. Model simulations indicate that most field-applied pesticides have a tendency to volatilize to the atmosphere, accumulate in soils, degrade in the subsurface environment, or leach to ground water. Model results were used to rank the leaching potentials of a total of 66 herbicides, fungicides, and insecticides. Model results suggested that 18 of the 32 herbicides, 4 of the 9 fungicides, and 11 of the 25 insecticides have a moderate to large potential for leaching to ground water. Pesticides given a large or moderate potential to leach to ground water span a broad range of total use on agricultural land in Pennsylvania and have a wide range of toxicities to humans.

A comparison with available pesticide monitoring data suggests that the presence of pesticides in Pennsylvania's ground water may be under-reported. Monitoring data do not exist for more than two-thirds of the pesticide compounds currently used in Pennsylvania. Many of these compounds have a large or moderate potential for leaching to ground water.

Comprehensive monitoring for pesticides and pesticide-degradation products in ground water downgradient of areas of pesticide use improved characterization of the physical properties of agricultural, carbonate soils, and improved management models developed from process-oriented research would facilitate development of effective pesticide best-management practices.

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APPENDIXES

Appendix 1. Pesticide human toxicity categories (from Sine, 1993)

Toxicity (Human)

The AAPCO¹ has adopted these regulatory principles relating to the determination of highly toxic materials:

"Highly Toxic: An economic poison which, when it falls within any of the following categories when tested on laboratory animals (mice, rats, and rabbits), is highly toxic to man within the meaning of these principles: "(a) Oral toxicity: Those which produce death in half or more than half the animals of any species at a dosage of 50 milligrams at a single dose, or less, per kilogram of body weight when administered orally to 10 or more such animals of each species.

"(b) Toxicity on inhalation: Those which produce death in half or more than half of the animals of any species at a dosage of 200 parts or less by volume of the gas or vapor per million parts by volume of air when administered by continuous inhalation for one hour or less to ten or more animals of each species, provided such concentrations is likely to be encountered by man when the economic poison is used in any reasonable foreseeable manner.

"(c) Toxicity by skin absorption: Those which produce death in half or more than half of the animals (rabbits only) test at a dosage of 200 milligrams or less per kilogram of body weight when administered by continuous contact with the bare skin for 24 hours or less to 10 or more animals. Provided, however, that an enforcement official may exempt any economic poison which meets the above standard but which is not in fact highly toxic to man, from these principles with respect to economic poisons highly toxic to man, and may after hearing designate as highly toxic to man any economic poison which experience has shown to be so in fact."

Hazard indicators	I	11		IV
Oral LDs	up to and including 0.2 mg/liter	from 50 thru 500 mg/kg	from 500 thru 5,000 mg/kg	greater than 5,000 mg/kg
Inhalation LDs	up to and including 0.2 mg/liter	from 0.2 thru 2 mg/liter	from 2.0 thru 20 mg/liter	greater than 20 mg/liter
Dermal LDs	up to and including 200 mg/kg	from 200 thru 2,000	from 2000 thru 20,000	greater than 20,000
Eye Effects	Corrosive; corneal opacity not revers- ible within 7 days	Corneal opacity reversible within 7 days; irritation per- sisting for 7 days	No corneal opacity; irritation reversible within 7 days	No irritation
Skin Effects	Corrosive	Severe irritation at 72 hours	Moderate irritation at 72 hours	Mild or slight irrita- tion at 72 hours

¹ Association of American Pesticide Control Officials, Inc.

Toxicity Categories

The USEPA has published regulations for use of human hazard signal words on pesticide labels:

Signal words assigned by levels of toxicity

(A) Toxicity Category I

All pesticide products meeting the criteria of Toxicity Category I shall bear on the front panel the signal word "Danger." In addition, if the product was assigned to Toxicity Category I on the basis of its oral, inhalation, or dermal toxicity (as distinct from skin and eye local effects), the work "Poison" shall appear in red on a background of distinctly contrasting color and the skull and crossbones shall appear in immediate proximity to the word "Poison."

(B) Toxicity Category II

All pesticide product meeting the criteria of Toxicity Category II shall bear on the front panel the signal word "Warning."

(C) Toxicity Category III

All pesticide products meeting the criteria of Toxicity Category III shall bear on the front panel the signal word "Caution."

(D) Toxicity Category IV

All pesticide products meeting the criteria of Toxicity Category IV shall bear on the front panel the single word "Caution."

(E) Use of signal words

Use of signal word(s) associated with a higher Toxicity Category is not permitted except when the Agency determines that such labeling is necessary to prevent unreasonable adverse effects.

Appendix 2. Risk assessment

Risk assessments are beyond the scope of this report, however, human- toxicity data from Sine (1993; appendix 1) have been included on tables 18-20 to provide a preliminary indication of relative hazards to human health. Effective pesticide management strategies will address the presence of pesticide residues in water, soil, air, biota, and vegetation, and will consider the effects of pesticide use on humans, animals (Sine, 1993, p. E14- E17), birds, fish, and bees (Sine, 1993, p. E18-E20), and other non-target animals, insectrand plants. Toxicity of herbicides to rats and rabbits is discussed in Penn State Cooperative Extension Agrichemical Fact Sheet 2a, toxicity of fungicides is discussed in Fact Sheet 2b, and toxicity of pesticides is discussed in Fact Sheet 2c, all by Dr. Winand K. Hock, Professor of Plant Pathology at Penn State. A "may affect" pesticide list for endangered species is in Sine (1993, p. D13), and includes several pesticides currently used in agricultural, carbonate terrains of Pennsylvania, including acephate, azinphos-methyl, carbofuran, chlorpyrifos, endosulfan, fenvalerate, parathion, permethrin, phorate, and trifluralin. An example of a risk assessment for pesticides in ground water was published by Kastenburg and Yeh (1995).