Hydrogeology, Herbicides and Nutrients in Ground Water and Springs, and Relation of Water Quality to Land Use and Agricultural Practices Near Carlisle, Pennsylvania

by Daniel J. Hippe, Emitt C. Witt, III, and Rhonda M. Giovannitti

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

Multiply	by	To obtain
	Length	
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
foot per mile (ft/mi)	0.1894	meter per kilometer
	Area	
acre	0.4047	hectare
square mile (mi^2)	2.590	square kilometer
	Volume	
cubic foot per second-day (ft^3/s-day)	2446.8	cubic meters
	Flow	
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
	Mass	
pound (lb)	0.4536	kilogram
pound per acre (lb/acre)	1.12	kilogram per hectare

Temperature

°C=5/9 (°F-32)

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD 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:

- milliliter (mL)
- milligrams (mg)
- milligrams per liter (mg/L)
- micrograms per liter (µg/L)
- milliequivalents per liter (meq/L)

HYDROGEOLOGY, HERBICIDES, AND NUTRIENTS IN GROUND WATER AND SPRINGS, AND RELATION OF WATER QUALITY TO LAND USE AND AGRICULTURAL PRACTICES NEAR CARLISLE, PENNSYLVANIA

By D.J. Hippe, E.C. Witt, III, and R.M. Giovannitti

ABSTRACT

Discharge and water-quality data collected in two adjacent karst-spring basins in Cumberland County, Pa., from May 1990 through April 1991 were used to (1) describe the hydrogeology of the study area; (2) determine concentrations of selected herbicides, herbicide-soil metabolites, and nutrients in water from wells and discharges from springs; (3) determine herbicide and nutrient discharges from springs; and (4) determine the relation of the presence of herbicides in ground water to land use and agricultural practices.

Ground-water resources in the study area consist of a regolith-mantled carbonate-rock aquifer system. Residual soils are well drained, primarily by deep percolation to the carbonate-rock aquifer; surface runoff is minimal.

Land use in the area is a combination of agricultural land, forest, and residential land. Agricultural land is used for dairy, livestock, and crop production. Herbicides are used primarily for corn production, with applications of cyanazine, atrazine, metolachlor, and alachlor accounting for about 90 percent of the total herbicide use on cropland in the area.

From May 1990 through April 1991 (the study period), mean daily discharges of Alexanders and Mount Rock Springs were 3.8 and 3.7 cubic feet per second and total discharge was 1,390 and 1,370 cubic foot per second-days. Recharge areas to each spring (determined from a water balance) are estimated to be about 2.8 square miles.

Trace quantities of selected triazine herbicides were detected in water from wells and springs throughout the study area. Atrazine was the only herbicide in common use that was detected in discharges from springs. Atrazine and the atrazine-soil metabolite deethylatrazine (DEA) were detected in spring discharges throughout the study period. Prometon and hexazinone were detected in discharges from springs after some periods of precipitation. Simazine and the atrazine-soil metabolite deisopropylatrazine (DIA) were only rarely detected in discharges from springs. The high ratio of DEA to atrazine in springs and the low percentage of samples containing DIA indicate that the primary flow path by which atrazine enters the carbonate-rock aquifer may be from leaching through soil materials rather than by direct entry of surface runoff through sinkholes.

Atrazine and DEA concentrations varied little during the study, and a spring flush of herbicides to ground water after application to cropland was not evident. Median daily concentrations of atrazine and DEA in discharge from Alexanders and Mount Rock Springs were 0.2 and 0.4 µg/L (micrograms per liter). Cumulative discharges of atrazine and DEA from Alexanders Spring were 1.2 and 3.0 lb (pounds) and from Mount Rock Spring were 1.5 and 3.2 lb. The atrazine and DEA discharges from Alexanders and Mount Rock Springs were about 0.5 and 0.6 percent of the estimated annual atrazine applications to cropland in their respective recharge areas.

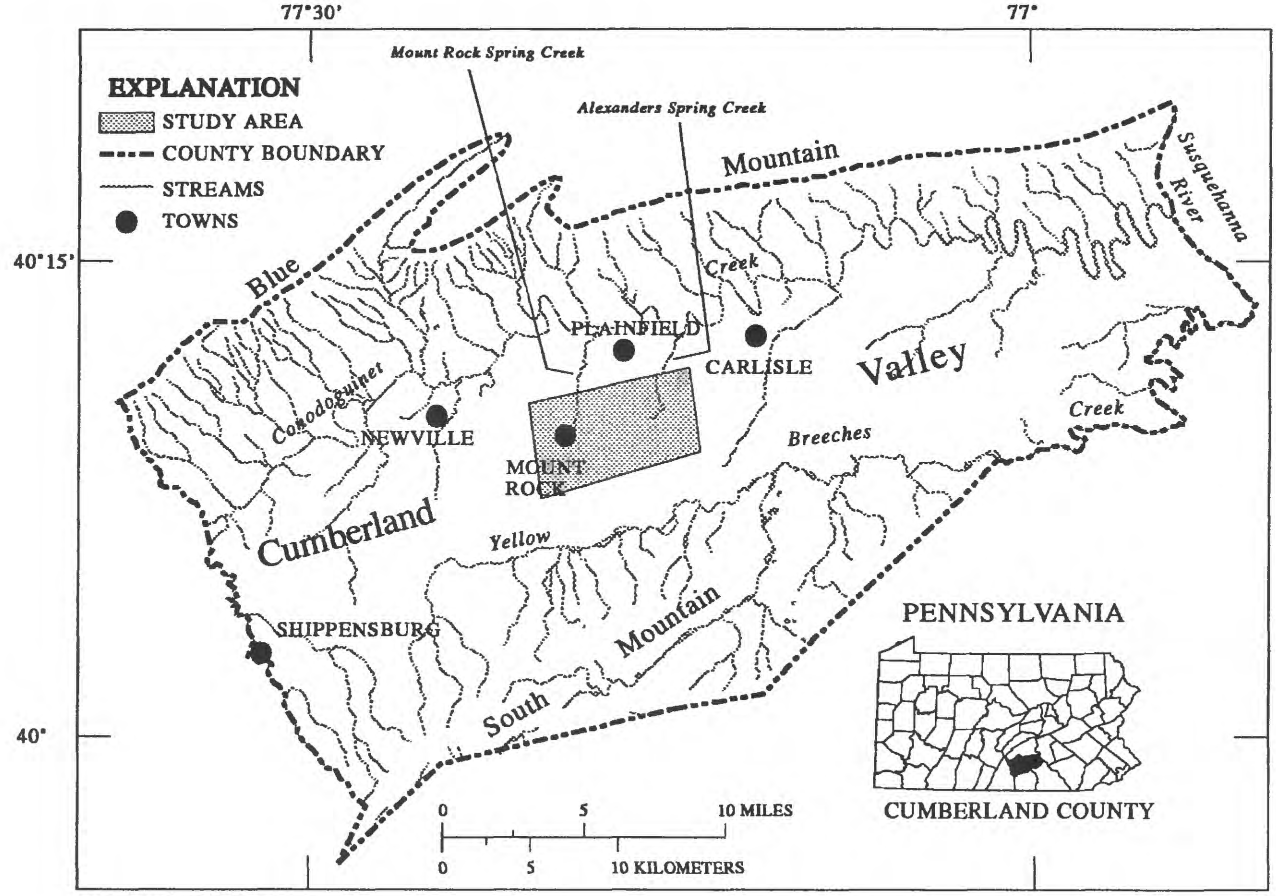
Nitrate was the principal form of nitrogen in water samples from wells and in discharges from springs. The median concentration of nitrate in water samples from wells was 6.6 mg/L (milligrams per liter) as N. Nitrate concentrations of greater than 10 mg/L were found in water from 16 percent of wells sampled. Temporal variation in nitrate concentrations in discharges from springs was minimal. Median daily concentrations of nitrate from Alexanders and Mount Rock Springs were 5.2 and 5.7 mg/L. Phosphorus was present near the minimum reporting level of 0.02 mg/L as P in most water samples from wells and discharges from springs. Cumulative discharges of nitrate from Alexanders and Mount Rock Springs were 39,000 and 44,000 lb as N, and cumulative discharges of phosphorus were 120 and 130 lb. Estimated yields of nitrate in the recharge areas to Alexanders and Mount Rock Springs were 22 and 24 pounds per acre, and estimated yields of phosphorus as P were 0.07 and 0.08 pounds per acre, respectively.

Water from springs and wells had similar median concentrations of triazine herbicide residues, as determined by use of enzyme-linked immunosorbent assay methods. Median triazine residue concentrations in samples collected from Alexanders and Mount Rock Spring were 0.4 and 0.5 µg/L. Triazine residues were detected at concentrations equal to or greater than 0.1 µg/L in ground water from 86 percent of wells sampled; the median concentration was 0.5 µg/L.

No significant difference was determined between areas of residential and agricultural land use with respect to (1) detection or concentration of triazine herbicide residues in ground water, and (2) nitrate concentrations or presence of nitrate in excess of 10 mg/L as N in ground water.

INTRODUCTION

Much of the prime agricultural land in southeastern and south-central Pennsylvania is in areas underlain by carbonate bedrock composed of limestone and dolomite. Chemical weathering of these areas has resulted in karst topography and substantial subsurface drainage. The water resources of these karst areas are susceptible to contamination. The U.S. Geological Survey (USGS), in cooperation with the Pennsylvania Department of Environmental Resources (PaDER), Bureau of Water Quality Management, began a study in 1990 to evaluate nonpoint-source contamination of ground water by herbicides and nutrients in a part of the Cumberland Valley near Carlisle (fig. 1).



Base from U. S. Geological Survey
Cumberland County, Pa. 1-50,000, 1974

Figure 1.—Study area and selected physical and hydrologic features in Cumberland County, Pa.

The USGS has investigated the carbonate-rock systems of the Cumberland Valley and the Lancaster Valley in cooperation with the Susquehanna River Basin Commission, PaDER, and U.S. Department of Agriculture. These investigations provided information on nutrients and herbicides in the water resources of the two valleys.

In the Pequea Creek Basin, Lancaster Valley, nutrients and herbicides were detected in several streams draining agricultural areas underlain by carbonate bedrock (Lietman and others, 1983; Ward, 1987). Although substantial quantities of nitrate and herbicides discharged in streams during base flow, investigators did not determine whether the flow path by which these contaminants entered the stream included the carbonate-rock aquifer or simply the streambed or nearstream areas.

In the headwaters of the Conestoga River Basin, an intensely farmed area in the Lancaster Valley, concentrations of nitrate greater than 10 mg/L and detectable concentrations of triazine and chloroacetanilide herbicides in water from wells were related to areas of the basin underlain by carbonate bedrock (Fishel and Lietman, 1986). Study results indicate that leaching of nitrate and herbicides to ground water is more likely in areas underlain by carbonate bedrock than in areas underlain by other rock types.

Additional investigations at an agricultural field site in the headwaters of the Conestoga River Basin revealed rapid changes in ground-water levels and quality after precipitation (Gerhart, 1986; Lietman and Hall, 1991). These rapid changes were attributed to the flow of recharge water along rather direct pathways that include fractures and sinkholes.

In areas of agricultural land use in the Cumberland and Lancaster Valleys, analyses of synoptic samples from wells, springs, and stream base flow after springtime application of fertilizer and herbicides have confirmed that the water resources of those areas underlain by carbonate bedrock commonly contain detectable quantities of triazine herbicide residues and nitrate concentrations greater than the Maximum Contaminant Level (MCL) (D.J. Wangsness, U.S. Geological Survey, written commun., 1990; Hippe and others, 1992; G.E. Baumbach, U.S. Geological Survey, oral commun., 1991; M.J. Langland, U.S. Geological Survey, oral commun., 1992). Resampling of these synoptic sites during the late summer or fall typically yielded nitrate and triazine herbicide residue concentrations similar to those in spring. The similarity indicates that these constituents may persist in ground water in these areas.

Additional study of the distribution of herbicides and nutrients in the ground-water resources of carbonate-rock areas is necessary to (1) determine the overall water quality of the water resource; (2) assess health risks associated with exposure of the rural population to agricultural chemicals in drinking-water supplies; and (3) assess potential adverse effects on stream ecology from agricultural chemicals in ground-water discharges.

Purpose and Scope

This report describes the distribution of herbicide residues and nutrients in ground water and spring discharges in an agricultural area underlain by carbonate bedrock located near Carlisle, Pa. Specific objectives are to

1. Describe the hydrogeology of the study area so the data and interpretations may be compared to similar investigations in other areas;
2. Determine the concentrations of triazine herbicide residues, chloroacetanilide herbicides, and nutrients in ground water and in discharges from springs;
3. Provide estimates of daily mean and cumulative discharges of selected herbicide residues and nutrients in discharges from springs; and
4. Relate quality of water from domestic wells and discharges from springs to land use and agricultural practices in the area of investigation.

Data were collected from springs and selected domestic water wells. Continuous stream-stage data were collected at streamflow-gaging stations near spring outlets from May 1990 through September 1991. Stream discharge, selected physical properties, and concentrations of herbicides and nutrients were measured periodically from May 1990 through April 1991. Ground-water levels, selected physical properties, and concentrations of triazine herbicide residues and nutrients in ground water were measured at domestic water wells during March 1991.

Most data collected during this investigation are included in this report. Streamflow records from gaging stations near the spring outlets were previously published in a U.S. Geological Survey Water-Data Report (Durlin and Schaffstall, 1992). Nutrient concentration data and an evaluation of these data were published in a report by Witt and others (1992).

Methods Of Data Collection and Analysis

Water-quality data were collected from springs and domestic water wells. Stream-stage and streamflow data were collected at three streamflow-gaging stations. Water-quality data were collected at four spring outlets. Ground-water-level and water-quality data were collected at 50 wells. The following sections describe the methods for measurement and analysis of discharge, ground-water levels, and water quality.

Discharge

Daily mean discharges and cumulative discharge data were analyzed to determine the flow characteristics and discharges of dissolved constituents from the springs. Discharge data were also analyzed to estimate the size of areas contributing water to the springs.

Discharge data were collected at three streamflow-gaging stations from May 1990 through September 1991. Continuous stream-stage recording gages were installed on Alexanders and Mount Rock Spring Creeks in reaches immediately downstream from spring outlets (table 1). An additional gage was installed on an unnamed tributary to Mount Rock Spring Creek that is fed by the combined flow of springs Sp-33 and Sp-34 (fig. 2). The streamflow-gaging stations consisted of a reference staff gage and a stilling well that was instrumented with an electric-tape gage and a float system with a digital recorder. Stream stage was recorded to the nearest hundredth of a foot at 15-minute intervals. The stream-stage control on Alexanders Spring Creek (site 01569775) was a natural stream riffle whose bed was stable during the course of the study. The stream-stage control on Mount Rock Spring Creek (site 01569730) was a flat-crested, nearly rectangular weir composed of field stones. The stream-stage control on the unnamed tributary to Mount Rock Spring Creek (site 01569740) was a concrete weir with two shallow U-shaped notches.

Table 1.—Streamflow-gaging stations and ground-water sampling sites

Site identification number (spring number)	Location		Streamflow or water-quality station name and description	Data-collection activities at sites
	Latitude	Longitude		
01569775	40°10'08"N	77°15'45"W	Alexanders Spring Creek near Plainfield, Pa., about 500 feet downstream from Sp-16	Stage and discharge
01569730	40°09'44"N	77°18'58"W	Mount Rock Spring Creek at Mount Rock, Pa., about 150 feet downstream from Sp-17	Stage and discharge
01569740	40°10'10"N	77°18'41"W	Unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa., fed by multiple spring outlets, including Sp-33 and Sp-34	Stage, discharge, and selected physical properties
401003077155301 (Sp-16)	40°10'03"N	77°15'53"W	Alexanders Spring, principal outlet	Selected physical properties, nutrients, and herbicides
400941077185901 (Sp-17)	40°09'41"N	77°18'59"W	Mount Rock Spring, principal outlet	Selected physical properties, nutrients, and herbicides
40100977184002 (Sp-33)	40°10'09"N	77°18'40"W	Unnamed spring that discharges to the unnamed tributary to Mount Rock Spring Creek	Selected physical properties, nutrients, and herbicides
40100977184003 (Sp-34)	40°10'09"N	77°18'40"W	Unnamed spring that discharges to the unnamed tributary to Mount Rock Spring Creek	Selected physical properties, nutrients, and herbicides

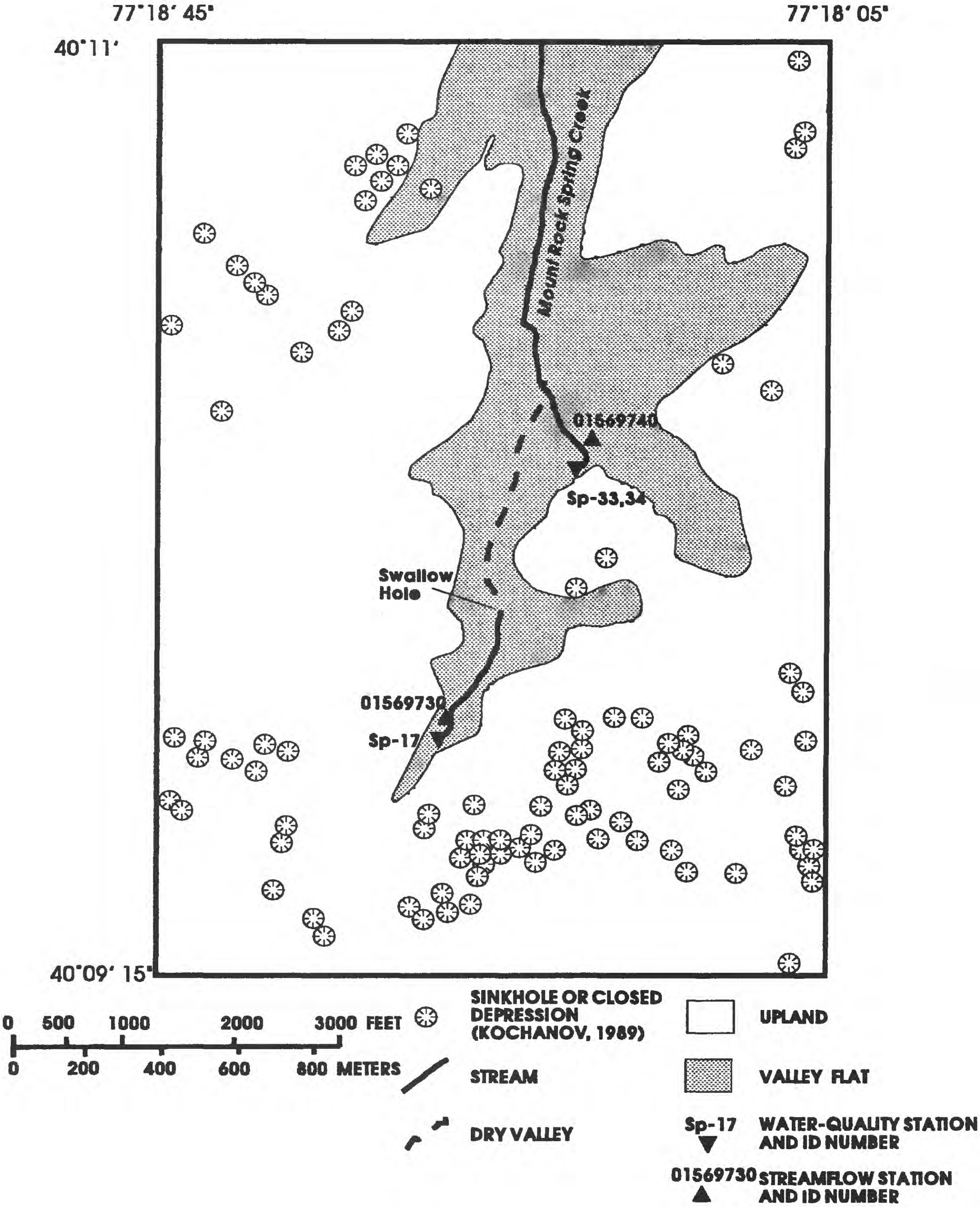
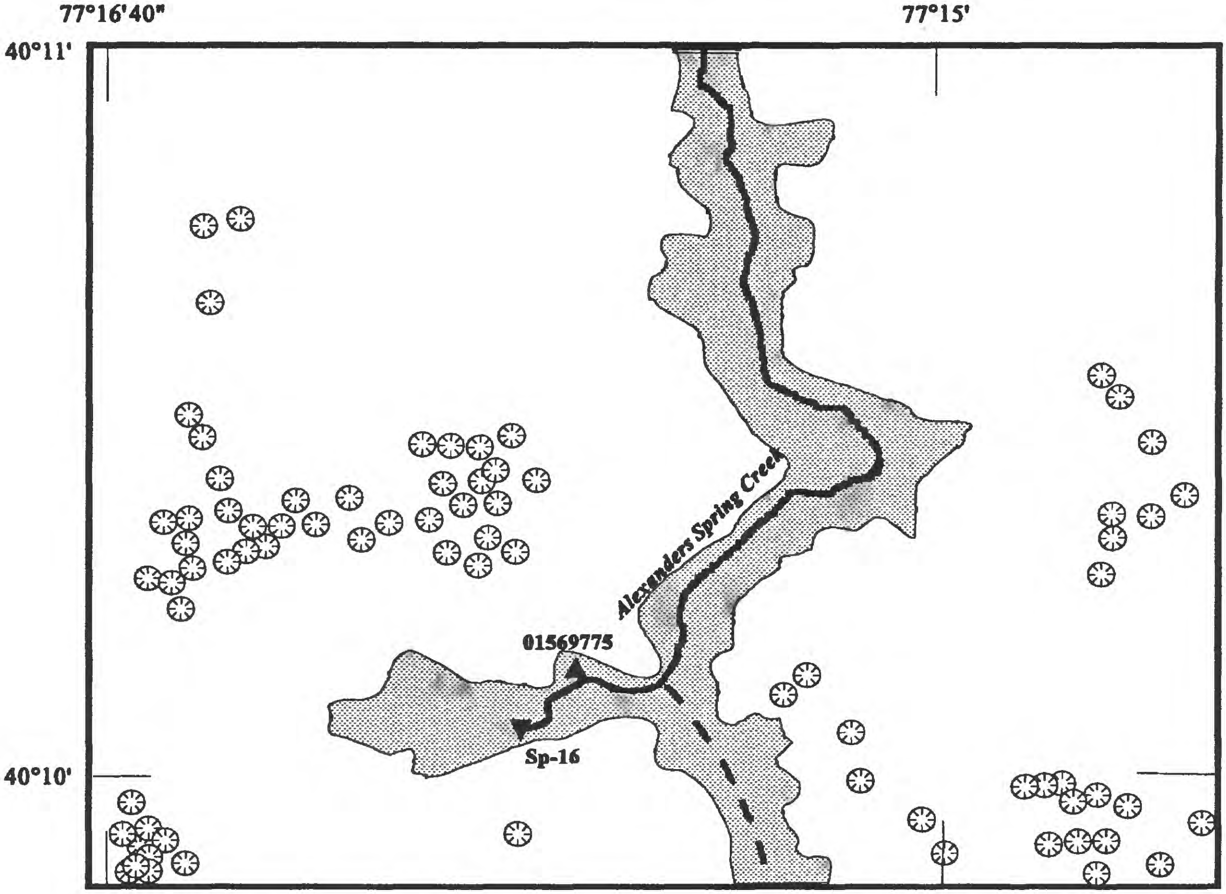


Figure 2.—Locations of streamflow and water-quality sampling stations and selected karst features, near Carlisle, Pa.



Base from U. S. Geological Survey
Plainfield, Pa. 1-24,000, 1969

Figure 2.--Locations of streamflow and water-quality sampling stations and selected karst features, near Carlisle, Pa.--Continued.

Stage and discharge were measured and computed according to methods described in Rantz and others (1982a; 1982b). The stage-discharge relation was developed from 14 discharge measurements at Alexanders Spring Creek, 13 at Mount Rock Spring Creek, and 15 at the unnamed tributary to Mount Rock Spring Creek. Streamflow records were rated good for the streamflow-gaging station on Alexanders Spring Creek and fair for the streamflow-gaging stations on Mount Rock Spring Creek and the unnamed tributary to Mount Rock Spring Creek (Durlin and Schaffstall, 1992).

Ground-Water Levels

Ground-water levels were measured in 47 of the 50 domestic water wells inventoried. Depths to ground water below land surface were measured to the nearest tenth of a foot by use of an electric tape. Land-surface altitudes of the wells were estimated from USGS 7-1/2 minute topographic maps having contour intervals of 10 ft. Ground-water-level altitudes were computed to the nearest 5 ft by subtracting the measured depths from the estimated land-surface altitudes.

Water Quality

The springs were sampled monthly from May 1990 through May 1991; additional samples were collected after selected rainstorms. Water samples were unfiltered grab samples from the center of flow.

Ground-water samples were collected once from each of 50 domestic water wells during March 1991 (Appendix 1). The wells sampled were distributed throughout the study area and were in areas of either residential or agricultural land use. A discharge hose was connected to water systems (ahead of inline water-treatment devices) at the spigot nearest the well. Wells were purged for a minimum of 20 minutes. Some purge water was directed to a flowthrough chamber for measurement of its temperature, pH, and specific conductance. In all of the wells, specific conductance, pH, and temperature stabilized in the 20-minute period. Unfiltered water samples were collected after purging.

Water samples for determination of nutrient concentrations were collected in 250-mL amber high-density polyethylene containers. Samples were chilled immediately after collection and were kept unfrozen at less than 4°C before analysis. Water samples held for longer than 24 hours before delivery to the laboratory were preserved by addition of a 1-mL solution containing 13 mg of mercuric ion (Hg_{2+}). Determinations of nutrient concentrations were made by the PaDER, Bureau of Laboratories. Analytical methods and minimum reporting level (MRL[1]) for each chemical constituent are summarized in table 2.

Concentrations of nutrients in 304 water samples were determined; 154 of the samples were quality-assurance samples. The quality-assurance samples included 7 deionized or preservation blanks, 4 pairs of sequential replicates analyzed by separate laboratories, 2 U.S. Environmental Protection Agency (USEPA) Quality Control Samples, 24 USGS Standard Reference Water Samples, and 56 sets of churn-split or sequential replicate samples. Nutrient data and related quality-assurance information are discussed in greater detail in Witt and others (1992). They concluded that sampling procedures and analytical methods used during the study provided results that were representative of nitrate and total phosphorus concentrations in ground water and discharges from springs in the study area.

All water samples for determination of herbicide concentrations were collected in 1-L, amber borosilicate-glass bottles and were chilled immediately. Two methods of analysis were used in this determination: gas chromatography and enzyme-linked immunosorbent assay (ELISA). Gas chromatography analyses were done by the USGS National Water Quality Laboratory (NWQL) in Arvada, Colo., on 120 samples, according to the methods of Wershaw and others (1987) (Appendix 1). ELISA analyses were done at the USGS Pennsylvania District Laboratory on 131 samples, according to methods described in Thurman and others (1990, p. 2,044) (Appendix 2). The analytical methods used and the MRL for each chemical constituent are listed in table 2.

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[1] The smallest measured concentration of a constituent that may be reliably reported using a given analytical method.

Table 2.—Analytical data collected at water-quality sampling sites, near Carlisle, Pa.

[μS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; μg/L, microgram per liter; USGS, U.S. Geological Survey; USEPA, U.S. Environmental Protection Agency; --, not applicable]

Property or constituent	Watstore/ Storet code	Analytical method	Minimum reporting level[1]	Where analyzed[2]
Temperature, in degrees Celsius	00010	--	--	Field
Specific conductance (μS/cm)	00095	USGS Method I-1780-78	1	Field
pH	00400	USGS Method I-1586-78	--	Field
Alkalinity, in mg/L as $CaCO_3$	00410	USGS Method I-1030-78	--	Field
Total ammonia, in mg/L as N	00610	USEPA Method 350.1	0.02	PaDER
Total nitrate, in mg/L as N	00620	USEPA Method 353.2	.04	PaDER
Total nitrite, in mg/L as N	00615	USEPA Method 353.2	.004	PaDER
Total ammonia and organic (kjeldahl) nitrogen, in mg/L as N	00625	USEPA Method 351.2	.2	PaDER
Total phosphorus, in mg/L as P	00665	USEPA Method 365.4	[3].01-.02	PaDER
Orthophosphate, in mg/L as P	70507	USEPA Method 365.1	[3].002-.02	PaDER
Ametryne, in μg/L	82184	USGS Method 0-3106-83	.1	NWQL
Alachlor, in μg/L	77825	USGS Method 0-3106-03	[3].1-.2	NWQL
Atrazine, in μg/L	39630	USGS Method 0-3106-03	.1	NWQL
Bromacil, in μg/L[4]	30234	USGS Method 0-3106-03	.2	NWQL
Butachlor, in μg/L[4]	30235	USGS Method 0-3106-03	.1	NWQL
Butylate, in μg/L[4]	30236	USGS Method 0-3106-03	.1	NWQL
Carboxin, in μg/L[4]	30245	USGS Method 0-3106-03	.2	NWQL
Cyanazine, in μg/L	81757	USGS Method 0-3106-03	[3].1-.2	NWQL
Cycloate, in μg/L[4]	30254	USGS Method 0-3106-03	.1	NWQL
Deethylatrazine, in μg/L	75981	USGS Method 0-3106-03	[3].1-.2	NWQL
Deisopropylatrazine, in μg/L	75980	USGS Method 0-3106-03	[3].1-.2	NWQL
Diphnamid, in μg/L[4]	30255	USGS Method 0-3106-03	.1	NWQL
Hexazinone, in μg/L[4]	30264	USGS Method 0-3106-03	[3].1-.2	NWQL
Metolachlor, in μg/L	82612	USGS Method 0-3106-03	[3].1-.2	NWQL
Metribuzin, in μg/L	82611	USGS Method 0-3106-03	.1	NWQL
Prometon, in μg/L	39056	USGS Method 0-3106-03	[3].1-.2	NWQL
Prometryne, in μg/L	39057	USGS Method 0-3106-03	.1	NWQL
Propazine, in μg/L	39024	USGS Method 0-3106-03	.1	NWQL
Simazine, in μg/L	39055	USGS Method 0-3106-03	.1	NWQL
Simetryne, in μg/L	39054	USGS Method 0-3106-03	.1	NWQL
Triazines, in μg/L as atrazine	34757	By immunoassay	.1	PA
Terbacil, in μg/L[4]	30311	USGS Method 0-3106-03	.2	NWQL
Trifluralin, in μg/L	39030	USGS Method 0-3106-03	.1	NWQL
Vernolate, in μg/L[4]	30324	USGS Method 0-3106-03	.1	NWQL

[1] The smallest measured concentration of a constituent that may be reliably reported using a given analytical method.

[2] PaDER is Pennsylvania Department of Environmental Resources, Bureau of Laboratories; NWQL is U.S. Geological Survey National Water Quality Laboratory; PA is U.S. Geological Survey Pennsylvania District Laboratory.

[3] Range of minimum reporting levels during the study period.

[4] Constituent determined in samples collected February 11, 1991, and thereafter.

Quality-assurance data for determinations of herbicide concentrations by gas chromatography included three pairs of sequential field replicate samples, one atrazine standard, and two field blanks composed of deionized water. Twelve sequential replicate samples also were analyzed at the USGS Methods Research Development Laboratory by a separate method that included solid-phase extraction and analysis by use of liquid chromatography (T.S. Steinheimer, U.S. Department of Agriculture, and M.G. Ondrus, University of Wisconsin-Stout, written commun., 1990). Herbicide residues were not detected in field blanks (Appendix 2), an indication that sample bottles and sample handling and shipping procedures probably were not a source of contamination. Nearly identical atrazine and deethylatrazine (DEA) concentrations in sequential replicate samples indicate representative sampling methods and good laboratory precision (table 3). An atrazine standard having a concentration of 1 µg/L was prepared at the Pennsylvania District Laboratory and analyzed at the NWQL. The concentration reported by the NWQL (0.8 µg/L) was within the required accuracy for the determinations. Twelve pairs of sequential replicate samples were analyzed by separate laboratories for atrazine, DEA, and deisopropylatrazine (DIA) (table 4). These data indicate good to excellent interlaboratory precision of atrazine and DEA determinations. Lack of coincidence of positive detections of DIA between laboratories indicates that determinations of DIA may not be accurate or precise at the low concentrations in samples from springs.

Quality-assurance data for determinations of herbicides by ELISA included (1) comparisons of ELISA results to NWQL results for sequential field-replicate samples and (2) comparison of triplicate ELISA analyses done routinely for each sample. Triazine compounds were detected by use of ELISA methods in each of 79 water samples from springs and 42 of 50 ground-water samples from wells. The possibility of false positive results by use of the ELISA method was not evaluated because atrazine was detected in each of the 49 samples that were analyzed by both ELISA and conventional methods. However, qualitative comparisons of triazine residue concentrations from ELISA methods and atrazine concentrations from conventional analytical methods indicate that higher triazine residue concentrations were obtained by ELISA methods. The apparent bias has been observed and has been quantified in other studies (Thurman and others, 1990; Pomes and Thurman, 1990). Apparent bias was not quantified as part of this study because the narrow range of atrazine concentrations determined is not amenable to regression analysis and because triazine compounds other than atrazine (that display some cross-reactivity with the antibody used in the ELISA method) also were present in most water samples. Laboratory replicate analyses by ELISA were generally within 5 percent of the mean value.

Acknowledgments

The USGS gratefully acknowledges the cooperation of the Wyrick, Sysak, Shriner, Thurston, Graf, and Kuhn families for providing access to the springs and spring creeks. Appreciation is also extended to David Bingaman of the Pennsylvania Department of Agriculture for providing pesticide-use and land-use data from farms in the study area. Additionally, the USGS is grateful for the support of Marty G. Ondrus of the University of Wisconsin-Stout and Thomas R. Steinheimer of the U.S. Department of Agriculture (formerly with the USGS Methods Research and Development Program) for additional determinations of herbicide concentrations.

Table 3.—Summary of determinations of atrazine, deethylatrazine, and deisopropylatrazine concentrations in sequential replicate samples

[µg/L, microgram per liter; <, less than; ND, not determined]

Spring number	Date of sampling	Atrazine			Deethylatrazine			Deisopropylatrazine		
		Result 1 (µg/L)	Result 2 (µg/L)	RPD[1] (percent)	Result 1 (µg/L)	Result 2 (µg/L)	RPD[1] (percent)	Result 1 (µg/L)	Result 2 (µg/L)	RPD[1] (percent)
Sp-17	10-16-90	0.2	0.2	0	0.5	0.6	18	< 0.1	< 0.1	ND
Sp-17	02-11-91	.2	.2	0	.3	.3	0	<.2	<.2	ND
Sp-17	04-02-91	.2	.2	0	.6	.5	18	.1	<.1	ND

[1] RPD is the relative percentage difference between results; it is the absolute value of the difference in concentrations between replicates divided by the mean, in percent.

Table 4.—Summary of interlaboratory determinations of atrazine, deethylatrazine, and deisopropylatrazine concentrations in sequential replicate samples

[All concentrations are in micrograms per liter; NWQL, result obtained by use of liquid-liquid extraction and dual column gas chromatography at the U.S. Geological Survey National Water Quality Laboratory, Arvada, Colo.; MRDL, result obtained by use of solid-phase extraction and liquid chromatography at the U.S. Geological Survey Methods Research and Development Laboratory, Arvada, Colo.; RPD, the relative percentage difference between results. It is the absolute value of the difference in results divided by the mean, in percent; <, less than; ND, not determined]

Spring number	Date of sampling	Atrazine			Deethylatrazine			Deisopropylatrazine		
		NWQL	MRDL	RPD	NWQL	MRDL	RPD	NWQL	MRDL	RPD
Sp-17	05-10-90	0.2	0.2	0	0.6	0.4	40	<0.1	0.4	ND
Sp-17	05-21-90	.2	.2	0	.1	.4	120	<.1	.5	ND
Sp-17	05-21-90	.2	.2	0	.3	.5	50	<.1	.4	ND
Sp-17	05-22-90	.2	.2	0	.5	.4	22	<.1	.4	ND
Sp-16	05-10-90	.2	.4	67	.4	.3	29	.1	<.1	ND
Sp-16	05-21-90	.2	.3	40	.4	.4	0	<.1	<.1	ND
Sp-16	05-21-90	.2	.7	111	.2	.4	67	<.1	<.1	ND
Sp-16	05-22-90	.2	.2	0	.2	.4	67	<.1	<.1	ND
Sp-33	05-10-90	.2	.2	0	.4	.4	0	.1	<.1	ND
Sp-33	05-21-90	.2	.2	0	.4	.8	67	<.1	<.1	ND
Sp-33	05-21-90	.2	.3	40	.3	.6	67	<.1	<.1	ND
Sp-33	05-22-90	.2	.2	0	.3	.4	29	<.1	<.1	ND

DESCRIPTION OF THE STUDY AREA

The following sections briefly describe the location and physical setting, soils, and land use and agricultural practices in the study area. The hydrogeology of the study area is described in a later section because parts of the description are based on data collected as part of this investigation.

Location and Physical Setting

The study area is in Cumberland County, west of Carlisle (fig. 1). It is in the Great Valley Section of the Valley and Ridge Province (Berg and others, 1984). The part of the Great Valley that extends from the Susquehanna River west and south to the Pennsylvania and Maryland border is also referred to as the "Cumberland Valley." In the immediate vicinity of the study area, the Cumberland Valley trends southwest to northeast, and it is approximately 12 mi wide. The Cumberland Valley is bounded on the southeast by South Mountain (the northern terminus of the Blue Ridge Mountains) and on the northwest by Blue Mountain (the first of several elongated ridges in the Appalachian Mountains).

The Cumberland Valley in Cumberland County is drained in part by Yellow Breeches and Conodoguinet Creeks, which flow into the Susquehanna River. The central part of the valley is drained by spring creeks, including Alexanders and Mount Rock Spring Creeks. The study area is inclusive of that part of the Alexanders Spring and Mount Rock Spring Creek Basins that extends from the gaged reaches of the spring creeks south to the watershed divide between the Yellow Breeches and Conodoguinet Creeks watersheds. The east and west boundaries were arbitrarily defined, because surface-drainage areas are questionable (owing to the undulating surface topography in the center of the valley) and because no ground-water flow boundaries separating Alexanders and Mount Rock Springs from adjacent karst springs were identified.

Soils

Soils have formed from fine-grained residuum by weathering of underlying carbonate bedrock. Upland areas are underlain by deep (generally greater than 5 ft) moderate- to well-drained silt-loam soils of the Duffield-Hagerstown Association (Zarichansky, 1985, p. 7). Dry valleys are underlain mostly by deep, well-drained Huntington silt loam, and areas adjacent to the spring creeks are underlain by deep, well- to poorly-drained Melvin and Lindside silt loam. Excavations along roads and in quarries reveal that the combined thickness of soil and residual materials ranges from 0 to 40 ft. The thickness of residual materials is related to the configuration of the underlying bedrock surface; therefore, little or no residuum is retained over bedrock pinnacles, and thick accumulations of residuum have formed in closed surface depressions, swales, and dry valleys. In parts of the area, nearly continuous belts of limestone pinnacles and ridges rise 10 to 30 ft above adjacent soil-covered areas. These ridges are classified and mapped by the U.S. Department of Agriculture as the Hagerstown-Rock outcrop complex (Zarichansky, 1985, p. 53-55).

In the central part of the Cumberland Valley, much of the agricultural land used for crop production is underlain by soils of the Duffield-Hagerstown Association. A relative rating of nitrate and pesticide leaching potentials developed for major soil series in Pennsylvania indicates "intermediate" nitrate and pesticide leaching potentials for Duffield soils and "nominal" nitrate and pesticide leaching potentials for Hagerstown soils (Pennsylvania State University, 1991, p. 11-12).

Land Use and Agricultural Practices

Much of the area is composed of agricultural land, either cropland or pasture, and lesser areas of forested and developed land. Developed land includes single-family residential areas and paved roads. Most residential areas have been built along existing roads rather than in subdivisions. Land-use changes are associated with increases in population; for example, forest and cropland have been developed for additional residential housing. No community water or sewer services are provided for these homes and farms. They are served instead by individual wells and septic systems.

Agricultural land includes pasture for dairy and livestock grazing, fields cultivated for animal feed and seed production, and fallow areas. Cropland in Cumberland County is planted in forage and small-grain crops such as alfalfa, wheat, oats, and barley, and in row crops, primarily corn and soybeans (Gunn, 1991). Estimates of crop acreage for Cumberland County and the Alexanders and Mount Rock Spring Creek watersheds are summarized in table 5. Although row crops are planted in only 20 percent of the land area of Cumberland County, they cover nearly half of the land in the study area.

Crop production systems used include conventional tillage, minimum tillage, and no-till planting systems. In conventional-tillage systems, moldboard plowing is followed by either disking or harrowing to prepare fields for planting. Conventional tillage is used in areas of flat to gentle slopes and deep soils containing few rocks or rock outcrops. In minimum-tillage systems, either a chisel plow, a field cultivator, or a heavy disk is used to prepare fields for planting. No-till systems require no mechanical cultivation of fields before planting. Minimum-tillage and no-till systems are better suited for crop production in fields where soils are susceptible to erosion or are stony. Reduced tillage systems also are favored because production costs are lower than for conventional tillage (Pennsylvania State University, 1991).

Most of the herbicides used are applied to cropland. In general, herbicides are used to control the growth and spread of weeds so that weeds will not (1) adversely affect the use and the value of cropland, (2) reduce the yield or the quality of crops, or (3) increase the costs of production and harvest. Agricultural herbicide use in the study area was characterized on the basis of (1) herbicide-use surveys in Pennsylvania from 1979 to 1990, (2) current recommendations of the Pennsylvania State University College of Agriculture, and (3) an unpublished herbicide-use survey in 1989 of cropland in the Alexanders and Mount Rock Spring watersheds.

Table 5.—Cropped area of Cumberland County and the Alexanders Spring Creek and Mount Rock Spring Creek watersheds, near Carlisle, Pa.

[--, not determined]

	Cumberland County	Alexanders Spring Creek Watershed	Mount Rock Spring Creek Watershed
Total land area, in acres	355,200	12,300	15,700
Cropland, in acres	[1]126,300	8,700	13,200
Percent of land area	36	[2]71	[2]84
Land in forage and small-grain crops, in acres	[1]57,000	3,250	5,340
Percent of land area	16	[2]26.5	[2]34
Land in row crops, in acres	[1]69,300	5,450	7,860
Percent of land area	20	[2]44.5	[2]50
Planted in corn, in acres	[1]64,900	--	--
Percent of row crops	94	--	--
Planted in soybeans, in acres	[1]4,400	--	--
Percent of row crops	6	--	--

[1] Gunn, 1991.

[2] McCarty and Aulenbacher, 1987.

The bulk of herbicide applications in Pennsylvania is to row crops, especially corn (Hartwig and others, 1980; Hanthorn and others, 1982; Gianessi and Puffer, 1988; Pennsylvania Agricultural Statistics Service, 1986; Knopf, 1991). Pasture and fallow cropland are maintained with little herbicide use except for periodic applications of selective herbicides to control the growth and spread of noxious weeds such as wild onion and Canada thistle. Cover crops generally receive fewer herbicide applications than do row crops. Good stands of most forage and small-grain crops are highly competitive and do not require applications of herbicides for additional weed control. Some forage and small-grain crops receive preplant or preemergent applications of nonselective herbicides to control most weeds before establishment of the crop or postemergent applications of selective herbicides to control noxious weeds such as Canada thistle. Herbicides are commonly applied one or more times to most row crops, including preplant applications of selective or nonselective herbicides and preemergent and postemergent applications of selective herbicides.

Information on past herbicide use may be as important as information on current use because trace quantities of persistent herbicides and herbicide-soil metabolites may be retained in the soil and aquifer for several years after application. Comparisons of agricultural herbicide-use data from surveys during 1979-90 indicate that one or more herbicides have been applied to most plantings of corn, and that changes in the products and application rates have been minor (Hartwig and others, 1980; Hanthorn and others, 1982; Gianessi and Puffer, 1988; Pennsylvania Agricultural Statistics Service, 1986; Knopf, 1991) (table 6). Surveys during 1979-90 indicate that a combination of atrazine and either alachlor or metolachlor was applied to most corn acreage. Beginning in the mid-1980's, metolachlor has been applied more frequently than alachlor. Use of simazine statewide has decreased, and use of cyanazine has increased.

In 1989, the Pennsylvania Department of Agriculture surveyed pesticide use on 769 acres of cropland in the watersheds of Alexanders and Mount Rock Springs (table 7). These data indicate a higher ratio of row crops to cover crops in the drainage areas upslope from the spring heads than was estimated by McCarty and Aulenbacher (1987) for the whole watersheds. The Pennsylvania Department of Agriculture survey indicates that cyanazine, atrazine, and the chloroacetanilide herbicides metolachlor and alachlor were the main herbicides applied in 1989 to corn acreage in the watersheds (about 90 percent by weight of documented agricultural herbicide use in the basin). The pesticide-use data for corn indicate the percentage of crop acreage with applications of alachlor, atrazine, dicamba, and metolachlor are similar to those of recent statewide surveys listed in tables 6 and 7. The percentage of corn acreage to which cyanazine was applied, as well as the application rates of cyanazine, paraquat, and 2,4-D, were larger than reported in previous surveys. The reasons for these differences are not known.

Table 6.—Summary of selected surveys of herbicide use on corn acreage in Pennsylvania

[<, less than]

Herbicide	Corn acreage treated (percent)	Application rate per crop year (pounds per acre)
Statewide survey in 1979[1]		
Alachlor	37	1.68
Atrazine	92	1.14
Butylate	14	6.37
Cyanazine	16	1.65
Dicamba	10	.32
Paraquat	9	1.52
Glyphosate	<1	2.72
Metolachlor	15	2.40
Simazine	10	1.56
2,4-D	7	.12
Statewide survey in 1980[2]		
Alachlor	24	1.75
Atrazine	74	1.57
Cyanazine	18	1.57
Dicamba	3.6	.50
Metolachlor	8	1.71
Paraquat	3.6	.40
Simazine	6.5	1.85
Statewide survey from 1982 through 1985[3]		
Alachlor	25	3.00
Atrazine	81	2.00
Cyanazine	40	2.00
Metolachlor	8	2.50
2,4-D	6	.40
Survey of three watersheds in southeastern Pennsylvania in 1985[4]		
Alachlor	29-41	1.39-1.54
Atrazine	79-90	1.02-1.26
Butylate	0-1.2	0-1.57
Cyanazine	11-40	1.51-1.62
Dicamba	5-12	.24-.36
Paraquat	3.8-9.8	.24-.34
Metolachlor	36-66	1.20-1.42
Simazine	0-1.6	0-1.21
2,4-D	3.9-9.4	.18-.54
Statewide survey in 1990[5]		
Alachlor	17	1.57
Atrazine	83	1.27
Cyanazine	20	1.49
Dicamba	12	.38
Metolachlor	47	1.71

[1] Hartwig and others, 1980. Application rates are for Lancaster County, Pa.

[2] Hanthorn and others, 1982.

[3] Gianessi and Puffer, 1988.

[4] Pennsylvania Agricultural Statistics Service, 1986.

[5] Knopf, 1991.

Table 7.—Summary of pesticide use on cropland in part of the Alexanders and Mount Rock Spring Creek watersheds, near Carlisle, Pa.

[Survey in 1989 by the Pennsylvania Department of Agriculture (David D. Bingaman, Pennsylvania Department of Agriculture, written commun., 1991); --, not determined]

CROP (acreage) Pesticide	Percentage of crop acreage treated	Application rate per crop year (pounds active ingredient applied per crop acre)
ROW CROPS (643 acres, 84 percent of crop acreage)		
CORN (613 acres, 80 percent of crop acreage)		
Alachlor	13	2.00
Atrazine	82	1.16
Cyanazine	74	3.50
Dicamba	7.2	.31
Paraquat	14	3.02
Linuron	4.9	.50
Metolachlor	55	1.46
2,4-D	5.4	1.50
SOYBEANS (30 acres, 4 percent of crop acreage)		
Alachlor	100	4.00
Linuron	100	1.00
FORAGE AND SMALL-GRAIN CROPS (126 acres, 16 percent of crop acreage)		
ALFALFA (15 acres, 2 percent of crop acreage)		
Dimethoate	100	1.50
BARLEY (22 acres, 3 percent of crop acreage)		
--	--	--
WHEAT (18 acres, 2 percent of crop acreage)		
--	--	--
SORGHUM-SUDAN GRASS (71 acres, 9 percent of crop acreage)		
--	--	--

HYDROGEOLOGY

The flow characteristics and aqueous geochemistry of karst springs provide valuable insights into aquifer characteristics and ground-water quality of the carbonate-rock terrane. In studies of karst, researchers have made extensive use of spring data to develop conceptual models of carbonate-rock aquifers (White, 1969, 1977, 1988; White and White, 1974; Atkinson, 1977; Drake and Harmon, 1973; Thrailkill, 1986; Schuster and White, 1971, 1972; Smart and Hobbs, 1986) and to devise monitoring strategies that account for at least some of the complexities of ground-water flow in these terranes (Quinlan and Ewers, 1985; Quinlan and Alexander, 1987; Mull and others, 1988; Quinlan, 1989). The discussion of flow characteristics and aqueous geochemistry is provided so that the data and interpretations in this report can be compared with results from similar studies in other areas underlain by carbonate-rock aquifers.

The study area is underlain by marine sedimentary rocks of Lower Paleozoic age. These rocks are part of the Cumberland Valley Sequence, a succession of 12 separate formations estimated to be 15,000 ft thick. A detailed description of the geology of the Cumberland Valley in Cumberland County is given by Stose (1953) and Becher and Root (1981). The part of the Cumberland Valley Sequence that crops out is primarily composed of limestone and dolomite. The Cumberland Valley Sequence was metamorphosed, folded, and faulted during the Taconic and Allegheny Orogenies and tilted northwest as part of the South Mountain anticlinorium during the Allegheny Orogeny (Becher and Root, 1981). Formations crop out from southwest to northeast; the generally steep dip of bedding and the frequent reversals of dip reflect several orders of folding. The area that includes the Cumberland Valley has been subjected to subaerial weathering and erosion since Mesozoic time.

Karst Features

The hydrogeologic setting of the central part of the Cumberland Valley that includes the study area has been described as a regolith-mantled carbonate-rock aquifer system (Chichester, 1991). The topography consists of broad, undulating upland surfaces that are dissected by a combination of dry valleys and spring-fed creeks. The mostly northward-flowing spring-fed creeks that drain the central part of the Cumberland Valley are widely spaced (many 2 to 4 mi apart) so that the stream density of this terrane is the lowest in any part of Pennsylvania. Much of the precipitation that falls on upland areas either recharges the regional aquifer or returns to the atmosphere by evaporation and transpiration processes. Numerous karst features (topographically closed depressions and sinkholes) in upland areas are points of direct recharge to the carbonate-rock aquifer (Kochanov, 1989).

The study area includes two valleys that lack stream channels and a locality where Mount Rock Spring Creek disappears abruptly along a rock outcrop. These features can be explained on the basis of the hydrogeology of the area.

Valleys in karst terranes that lack stream channels are referred to as dry valleys. A dry valley is one without surface drainage, though the catchment area is ordinarily large enough to generate streamflow. Also associated with these dry valleys are a lack of substantial runoff in upland areas that would generate stormflows and deep ground-water levels that do not ordinarily intersect the land surface to form seeps and springs. A dry valley having a branched network about 4 mi in length joins Mount Rock Spring Creek at about 1 mi from its mouth (fig. 2). A second dry valley about 3.5 mi in length joins Alexanders Spring Creek 0.3 mi below the spring head.

A 0.25-mi section of the valley containing Mount Rock Spring Creek is also dry because the stream is diverted into a sinkhole 0.3 mi downstream from Mount Rock Spring. This type of sinkhole is referred to in karst literature as a "swallow hole." Streamflow that is lost into the swallow hole resurges in springs at the head of the unnamed tributary to Mount Rock Spring Creek. The relation of flow and water quality of Mount Rock Spring and the unnamed tributary to Mount Rock Spring Creek was examined during this study.

Streamflow was sustained in the dry valleys and the dry reach of Mount Rock Spring Creek during June 1972 after Hurricane Agnes and during March and April 1993 after severe winter storms. Both the hurricane and the winter storms caused large rises in ground-water levels (locally more than 30 ft after

Hurricane Agnes and more than 70 ft after the 1993 winter storms) that caused streams and ponds to form in the dry valleys. The discharge of Mount Rock Spring exceeded the inflow capacity of the swallow hole and caused Mount Rock Spring Creek to flow through the normally dry reach. Ground-water discharges sustained these streams in the dry valleys and the higher rates of discharge at the karst springs.

Recharge and Ground-Water Flow

Average annual recharge to the carbonate-rock terrane of the Conodoguinet Creek Basin has been estimated to be 15 in. of precipitation, or about 36 percent of the average annual precipitation (Becher and Root, 1981, p. 11-12). Ground water in the regolith-mantled carbonate-rock aquifer is present in intergranular pores of the regolith and in partings, fractures, and solutional openings in carbonate bedrock.

In upland areas, depths of static water levels in wells can exceed 100 ft below land surface. Static water levels measured in 47 domestic water wells in the study area ranged from 11 to 141 ft below land surface. The median water level was 59 ft below land surface.

The position of major ground-water divides and the general directions of ground-water flow in the carbonate-rock terrane of Cumberland County are given in a ground-water-level contour map (based on a combination of stream elevations and depths to static water-level data in widely spaced wells collected November 1972) by Becher and Root (1981). The map indicates a well-defined ground-water divide about 3 mi south of Alexanders and Mount Rock Springs that roughly coincides with the surface watershed boundary between the Yellow Breeches and Conodoguinet Creeks. The spacing and orientation of ground-water-level contours indicate a hydraulic gradient of 40 to 60 ft/mi in upland parts of the study area and regional ground-water flow in a northeasterly direction toward Alexanders and Mount Rock Springs and Conodoguinet Creek. Water-level contours partially envelop areas upgradient from Alexanders and Mount Rock Springs. This configuration of water-level contours is indicative of an area where convergent ground-water flow is toward the springs.

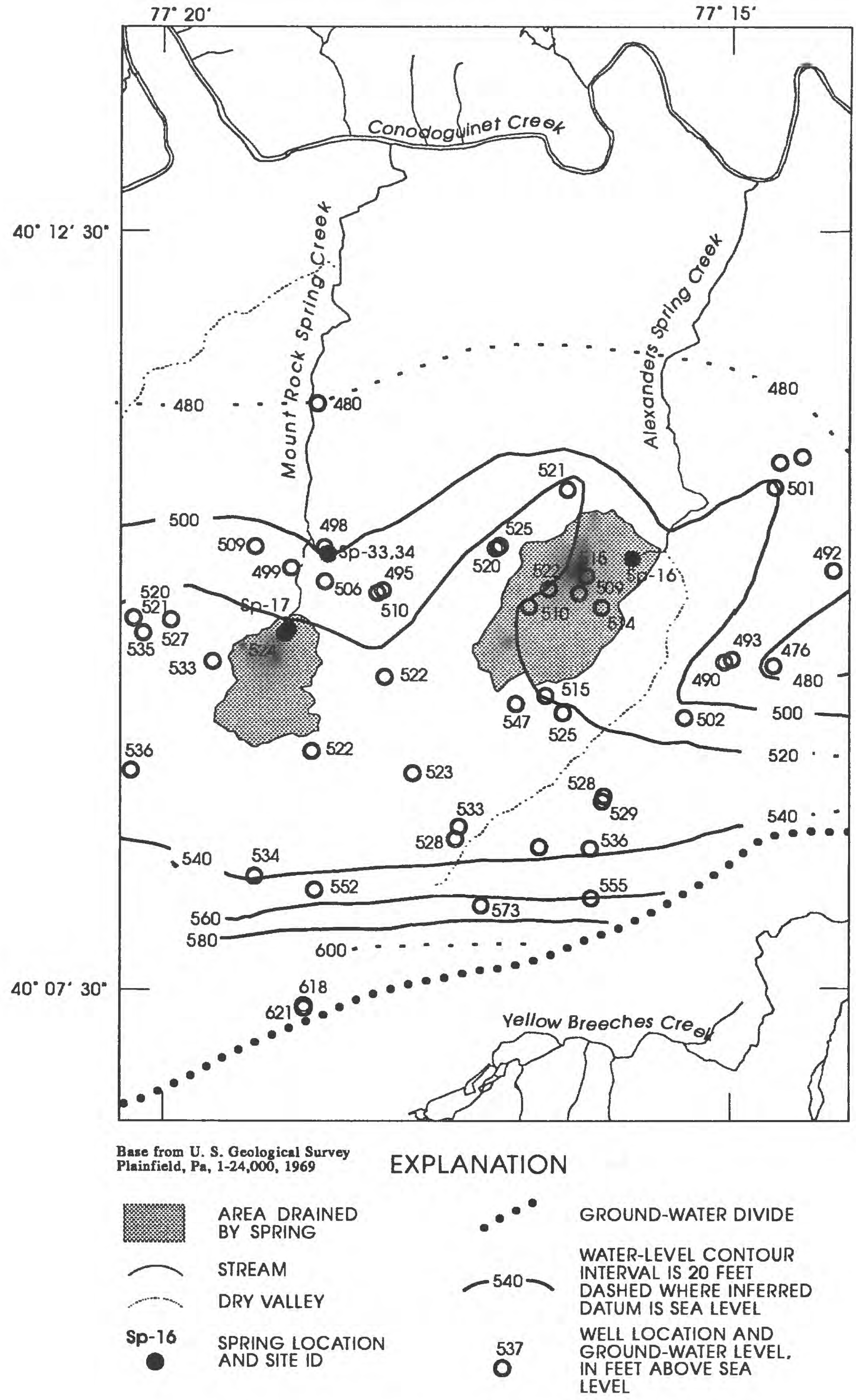
A water-level map from more closely spaced data may provide a basis for estimating the recharge areas to the springs. Ground-water-level data were collected from 47 domestic water wells in the study area during March 1991 for use in plotting a water-level contour map having greater control than the previously published map (fig. 3).

The configuration of water-level contours does not indicate a well-defined area of convergent ground-water flow to Alexanders or Mount Rock Springs (fig. 3). Figure 3 and the Becher and Root map (1981) indicate an apparent north-south trending ground-water divide that separates the spring heads of Mount Rock and Alexanders Springs. However, the apparent ground-water basin southeast of Mount Rock Spring on the Becher and Root map is shown in figure 3 as a broad area of negligible hydraulic gradient. The apparent area of recharge to Alexanders Spring that included the dry valley southeast of the spring (Becher and Root, 1981) was not indicated by ground-water-level data collected as part of this study; water-level contours on the east side of the dry valley are not closed.

Although ground-water-level contours do not provide direct evidence for estimating the recharge areas to Mount Rock and Alexanders Springs, they do indicate that the surface-drainage areas to these springs and the area for which pesticide-use data were collected are upgradient from the spring heads. The surface-drainage areas to each spring opening were determined from USGS 7-1/2 minute topographic maps having 10 ft contour intervals. The surface-drainage areas to Alexanders and Mount Rock Springs are 1.2 and 0.58 mi^2. Although the analysis of discharge data demonstrates that the surface-drainage areas to the springs provide an insufficient catchment area to account for the discharges from the springs, there is sufficient land area between the spring heads and the regional ground-water divide to account for these discharges.

Discharge Characteristics of Springs

A comparison of the quantity of herbicides and herbicide-soil metabolites in spring discharge to the quantity of herbicides applied requires estimates of the recharge area that contributes ground-water flow to each spring. The quantity of herbicides applied may then be estimated from a combination of land-use



Base from U. S. Geological Survey
Plainfield, Pa, 1-24,000, 1969

Figure 3.—Ground-water levels near Carlisle, Pa., March 1991.

and herbicide-use data and from the areal extent or size of the recharge area. The recharge area to a spring is herein defined as the land area that has the same horizontal extent as that part of an aquifer from which ground-water flow is diverted to the spring opening.

Discharge characteristics for the three gaged sites were similar during the period of data collection (table 8). The mean daily discharges from May 1990 through April 1991 were nearly identical at 3.7 to 3.8 ft^3/s. However, the absolute range and relative standard deviation of daily mean discharges for the site on Alexanders Spring Creek were less than for the other sites. The maximum daily discharges for each spring—8.1 ft^3/s from Alexanders Spring and 10 ft^3/s from Mount Rock Spring and the unnamed tributary to Mount Rock Spring Creek—were measured in January 1991 (fig. 4). The minimum daily discharges were 1.8 ft^3/s from Alexanders Spring in October 1990, less than 0.01 ft^3/s at Mount Rock Spring during part of September and October 1990, and 0.1 ft^3/s from the unnamed tributary to Mount Rock Spring Creek during part of August, September, and October 1990. Mount Rock Spring and the unnamed tributary to Mount Rock Spring nearly ceased to flow during late summer and early fall of dry years.

Substantial increases in discharge (more than 1 ft^3/s) occurring several times during the study were related to periods of precipitation or snowmelt that caused appreciable ground-water recharge (fig. 4). An initial increase in discharge was usually observed on the same day as the onset of precipitation or snowmelt. However, a lag time of 2 to 5 days was observed between the onset of precipitation and the peak discharge. The lag time may coincide with the time period over which deep percolation of recharge causes a rise in the water-table altitude of the carbonate-rock aquifer. Recession curves of discharge hydrographs are either straight or convex and upward sloping, indicative of constant or accelerated reductions in discharge with time.

Table 8.—Monthly and total discharge and precipitation from May 1990 through April 1991 at sites near Carlisle, Pa.

[mi^2, square mile; ft^3/s-days, cubic foot per second days; in., inch; Precip., discharge as a percentage of precipitation in the surface drainage area above gaging station]

Date	Total discharge at streamflow-gaging station									Precipitation gage; weather station at Shippensburg, Pa.; total precipitation	
	Alexanders Spring Creek near Plainfield, Pa. (01569775) Surface-drainage area is 1.2 mi^2			Mount Rock Spring Creek at Mount Rock, Pa. (01569730) Surface-drainage area is 0.58 mi^2			Unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa. (01569740) Surface-drainage area is 2.9 mi^2				
	ft^3/s-days	in.	Precip.	ft^3/s-days	in.	Precip.	ft^3/s-days	in.	Precip.	Actual (in.)	Departure[1] (in.)
1990											
May	99.1	3.1	57	22.2	1.4	26	35.9	0.46	8.5	5.41	1.83
June	114	3.6	260	75.9	4.9	360	111	1.4	100	1.38	-2.55
July	90.7	2.9	73	43.0	2.8	71	33.7	.43	11	3.97	.58
August	82.6	2.6	55	25.9	1.7	36	15.1	.19	4.0	4.74	1.49
September	74.8	2.4	132	13.2	.8	44	15.0	.19	10	1.81	-1.65
October	87.8	2.8	35	54.2	3.5	44	53.5	.68	8.6	7.89	5.16
November	102	3.2	200	112	7.2	460	100	1.3	83	1.57	-1.54
December	111	3.5	55	117	7.5	120	118	1.5	24	6.31	3.19
1991											
January	176	5.5	200	223	14	520	242	3.1	110	2.70	-.10
February	167	5.3	430	237	15	1,200	252	3.2	260	1.23	-1.30
March	147	4.6	120	232	15	410	232	3.0	81	3.69	.08
April	143	4.5	190	211	14	590	190	2.4	100	2.38	-.96
Total	1,390	44	100	1,370	88	200	1,390	18	42	43.08	4.28

[1] Departures from monthly average precipitation for 62 years of record beginning in 1929 (U.S. Department of Commerce, 1991, 1992).

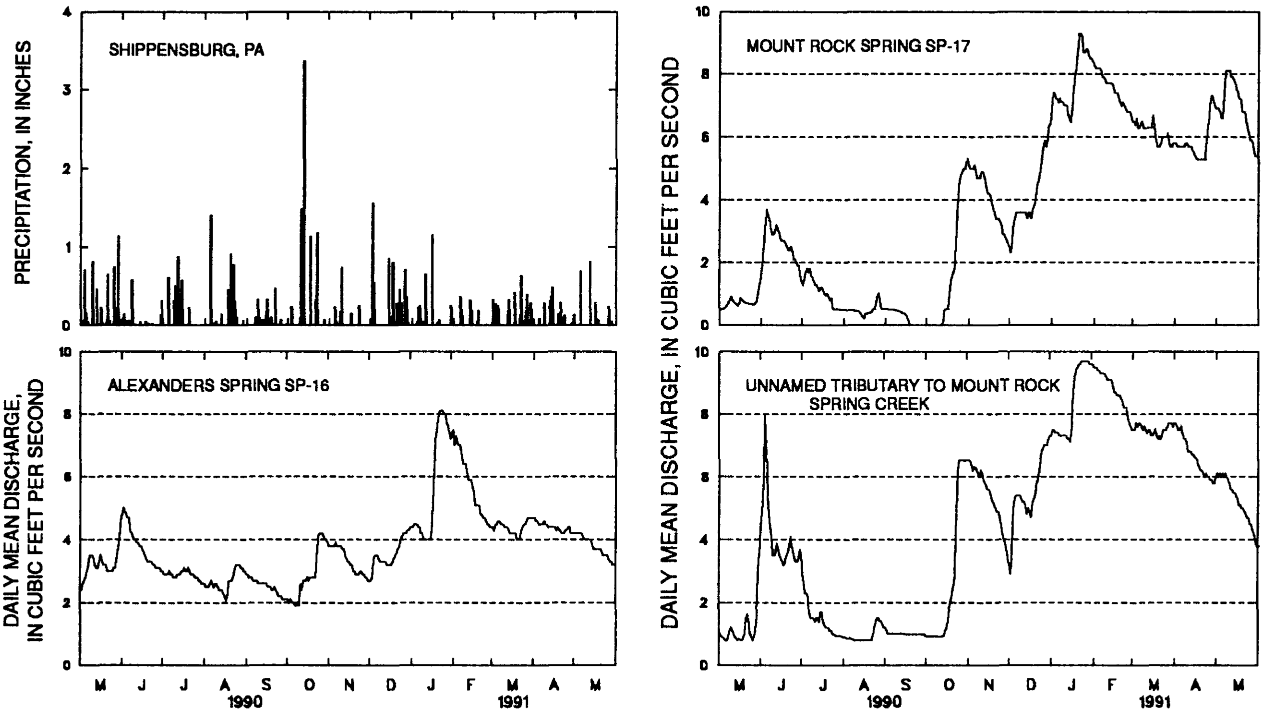


Figure 4.—Precipitation at Shippensburg, Pa., and daily mean discharge from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

Total discharge from Alexanders and Mount Rock Springs equaled or exceeded precipitation volumes in the surface-drainage areas to the springs. Total discharge at Alexanders Spring from May 1990 through April 1991 is equivalent to 44 in. of precipitation in the 1.2-mi^2 surface-drainage area to the spring (table 8). Total discharge at Mount Rock Spring for this period is equivalent to 88 in. of precipitation in the 0.58-mi^2 drainage area to the spring. Total discharges from Alexanders and Mount Rock Springs for this 12 months is equal to 100 and 200 percent of the 43.08 in. of precipitation recorded during the same time period at the nearest weather station at Shippensburg, Pa. (U.S. Department of Commerce, 1990, 1991). Because a substantial part of the total precipitation is returned to the atmosphere through evaporation and transpiration, the recharge areas to these springs must exceed the size of their surface-drainage basins.

Water balances of individual watersheds in the study area were not determined as part of this study. However, Becher and Root (1981) determined annual water balances for a 7-year period for the Conodoguinet and Yellow Breeches Creek Basins. The average annual yield of ground water from carbonate rocks of the Conodoguinet Creek Basin over the 7-year period was 1.33 (ft^3/s)/mi^2 (Becher and Root, 1981, p. 12). The estimated recharge areas to Alexanders and Mount Rock Springs on the basis of this annual yield are 2.8 mi^2.

Several assumptions are made to estimate recharge areas to springs on the basis of components of the water balance of the carbonate-rock terrane as a whole, and in turn, to estimate the crop acreage and herbicide usage in these recharge areas. The most important of these assumptions are that (1) climate, especially precipitation, is not substantially different for the period over which components of the regional water balance were determined and the period when ground-water discharges were determined for springs; (2) change in the quantity of water stored in unsaturated materials and the carbonate rock aquifer over the two data-collection periods is not substantial; (3) the recharge areas are of fixed areal extent, without substantial inputs of water other than precipitation, or outputs other than ground-water discharges to springs; and (4) cropping intensity and herbicide use in the recharge areas are not substantially different from cropping intensity of the watershed as a whole and from herbicide use on farms near the springs.

Because precipitation was similar in the two study periods, the differences should not be a large source of error in estimating the recharge areas to the springs. From May 1990 through April 1991, the total precipitation at Shippensburg, Pa., was 102 percent of the average annual precipitation for the period used to determine the water balance for the carbonate-rock terrane of the Conodoguinet Creek Basin (Becher and Root, 1982, p. 11).

Changes in the quantity of water stored in unsaturated materials and the carbonate-rock aquifer are probably insignificant in the 7-year period used to determine the water balance for the carbonate rocks of the Conodoguinet Creek Basin, but may be a source of error in estimating recharge areas to the springs, given the shorter (1-year) period of data collection. Although data were not collected as part of this investigation to directly assess changes in quantity of water stored in unsaturated materials or in the aquifer, increased rates of ground-water discharge from springs at the end of the investigation indicate an increase in the quantity of water stored in the aquifer. If storage is assumed to be unchanged, then the estimated recharge areas to the springs will be less than if an increase in storage were factored into the water balance.

The third set of assumptions on the nature of the recharge areas may be a substantial source of error in estimates of size, crop acreage, and herbicide use in the recharge areas to the springs. Efforts to approximate the recharge areas on the basis of the surface-drainage areas and configuration of ground-water-level contours were not successful. No evidence of inputs other than precipitation (such as from diversion of streams) was found in areas upgradient from the springs. The quantity of underflow of ground water as an output from the recharge area is not known. If underflow relative to discharge at the springs is appreciable, then the recharge areas to the springs and herbicide use in the recharge areas will be underestimated.

In comparing the quantities of herbicides in ground-water discharge to springs with the quantities of herbicide applied annually to cropland, it was assumed that the cropping intensity and herbicide use in the recharge areas are not substantially different from cropping intensity of the watershed as a whole and the herbicide use on farms near the springs. Any substantial differences in cropping intensity or herbicide use would cause errors in estimation.

Aqueous Geochemistry

The aqueous geochemistry of spring discharges and water from wells, as well as the variation in those properties through time, provides useful information for determining recharge areas, ground-water-flow paths, and ground-water residence times. The geochemical data collected for the project are summarized in three parts: (1) selected physical properties, (2) major-ion chemistry, and (3) geochemical models of carbonate equilibria.

Selected Physical Properties

Temperature, pH, specific conductance, and alkalinity of water discharged from Alexanders Spring, Mount Rock Spring, Sp-33, Sp-34, and the unnamed tributary to Mount Rock Spring (Appendix 3) were measured periodically. During March 1991, temperature, pH, and specific conductance of water were measured at 50 wells (Appendix 1). Measurements of water quality for each spring and for the 50 wells are summarized in table 9.

The ranges in measurements of water quality at Alexanders and Mount Rock Springs were smaller than ranges at the two springs (Sp-33 and Sp-34) that feed the unnamed tributary to Mount Rock Spring Creek. These differences may be related to physical differences in the network of fractures and solution openings that transmit ground water to the springs.

The median water temperatures for each spring and for all water wells were nearly equal to the mean annual air temperature (11.3°C) at the nearest weather station, in Shippensburg, Pa. (U.S. Department of Commerce, 1991). Water temperature was fairly constant at Alexanders and Mount Rock Springs

Table 9.—Summary of selected physical properties of ground water near Carlisle, Pa.

[°C, degree Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter]

Measurement	Number of observations	Median	Range	RSD[1] (percent)
Alexanders Spring (Sp-16)				
Water temperature (°C)	38	11.3	11.2-11.3	0.4
Specific conductance (µS/cm)	41	573	545-600	2.5
pH	39	7.2	7.1-7.5	1.5
Alkalinity (mg/L as $CaCO_3$)	37	232	214-247	3.1
Mount Rock Spring (Sp-17)				
Water temperature (°C)	39	11.1	10.8-11.8	1.3
Specific conductance (µS/cm)	42	535	495-551	2.0
pH	40	7.4	7.1-7.6	1.5
Alkalinity (mg/L as $CaCO_3$)	37	207	196-218	2.4
Unnamed tributary to Mount Rock Spring Creek (Sp-33)				
Water temperature (°C)	35	11.9	9.2-14.3	11
Specific conductance (µS/cm)	38	537	471-620	5.2
pH	35	7.7	7.1-8.1	2.6
Alkalinity (mg/L as $CaCO_3$)	33	209	190-242	4.3
Unnamed tributary to Mount Rock Spring Creek (Sp-34)				
Water temperature (°C)	25	11.1	10.1-11.9	3.6
Specific conductance (µS/cm)	26	594	540-658	5.0
pH	26	7.3	7.1-7.7	2.5
Alkalinity (mg/L as $CaCO_3$)	24	230	212-257	4.9
Water wells				
Water temperature (°C)	50	11.4	8.9-12.4	6.0
Specific conductance (µS/cm)	50	657	203-1,860	41
pH	50	7.4	7.0-7.9	3.1

[1] Relative standard deviation is the standard deviation of the sample divided by the mean of the sample, in percent.

as compared to temperatures at springs Sp-33 and Sp-34 (fig. 5). Much of the variation in water temperature was seasonal and was most apparent at springs Sp-33 and Sp-34 (Appendix 3). Schuster and White (1971) used the magnitude of seasonal changes in chemistry of water in the field to discern diffuse-flow from conduit-flow springs in the folded Appalachians of Pennsylvania. On the basis of the seasonal variation in water temperature and other measurements in the field, Alexanders and Mount Rock Springs would be classified as diffuse-flow springs, whereas springs Sp-33 and Sp-34 would be classified as conduit-flow springs.

The median specific conductance of water from wells in the study area was substantially greater than that of water discharged from springs (table 9). The variation in specific conductance of water samples collected from wells also was substantially greater than that of water discharged from each of the springs. The broad range of specific conductance of water from wells is probably due to a combination of natural spatial variation in mineral content of ground water, as well as local increases in mineral content from anthropogenic sources such as septic systems, barnyards, and fertilizer and soil additives applied to cropland.

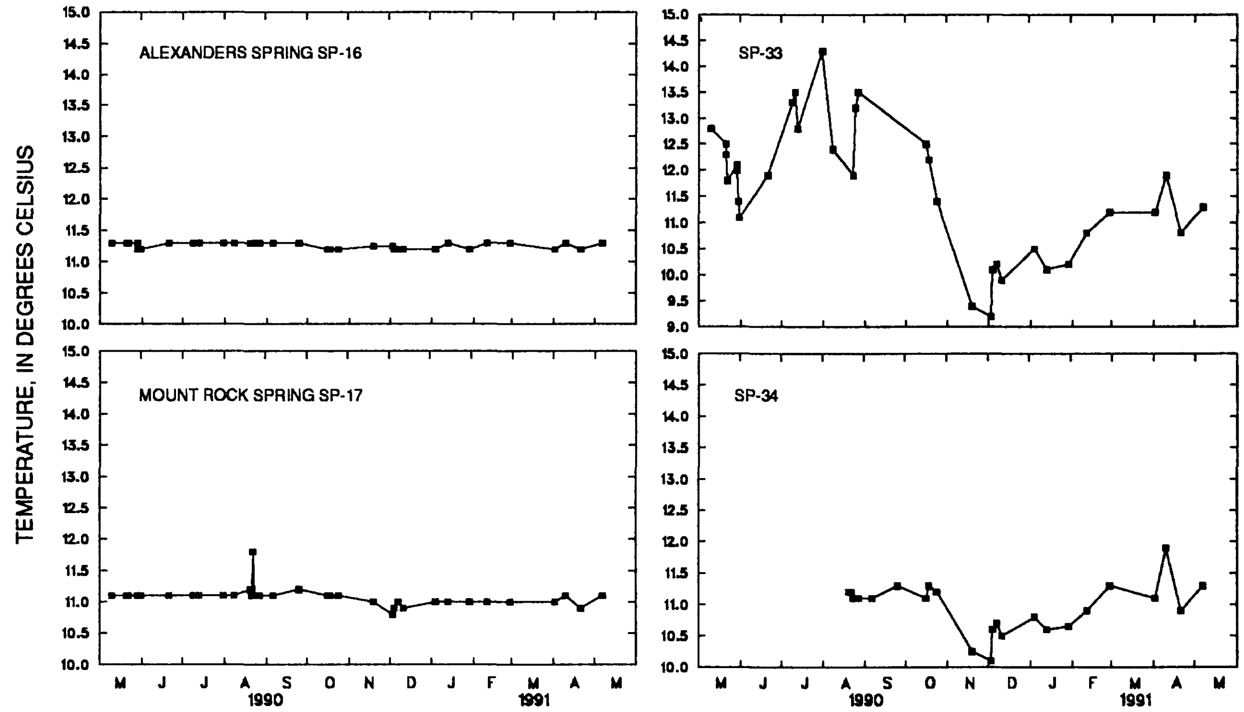


Figure 5.—Temperature of water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

Temporal changes in specific conductance of water discharged from springs were related to changes in streamflow, so that specific conductance usually increased during periods of increased discharge (figs. 4 and 6). This response is opposite that observed in karst springs that receive a substantial proportion of ground-water recharge through open sinkholes. Recharge waters that pass through these karst features generally have a lower mineral content than ground water that has already equilibrated with aquifer materials; the result is a reduction in specific conductance of spring discharges after periods of precipitation. Increases in specific conductance of discharges from springs has been observed after periods of precipitation at several springs in Cumberland County. Becher and Root (1981, p. 18) attributed this response to addition of soluble salts from the unsaturated zone displaced by meteoric recharge. This response is also consistent with displacement of high-conductivity ground water by meteoric recharge (C.J. Taylor, U.S. Geological Survey, oral commun., 1993).

Specific-conductance measurements at Mount Rock Spring and spring Sp-33 were similar for much of the study, except when discharge from Mount Rock Spring was low. The similarity of specific-conductance measurements (as well as nutrient and herbicide concentrations) of Mount Rock Spring and spring Sp-33 indicates that the spring is the point of resurgence of Mount Rock Spring Creek.

Water collected from wells and springs in the study area was neutral to slightly alkaline. The pH of water samples from wells and springs ranged from 7.0 to 8.1. The pH of water discharged from spring Sp-33 was higher than that of the other springs. The higher pH is probably the result of a shift in carbonate equilibria from degassing of dissolved carbon dioxide.

The temporal variation in alkalinity of water discharged from springs is similar to the temporal variation in specific-conductance measurements (fig. 6). This similarity is expected because bicarbonate ion is the primary source of alkalinity and a major dissolved constituent in ground water in the study area.

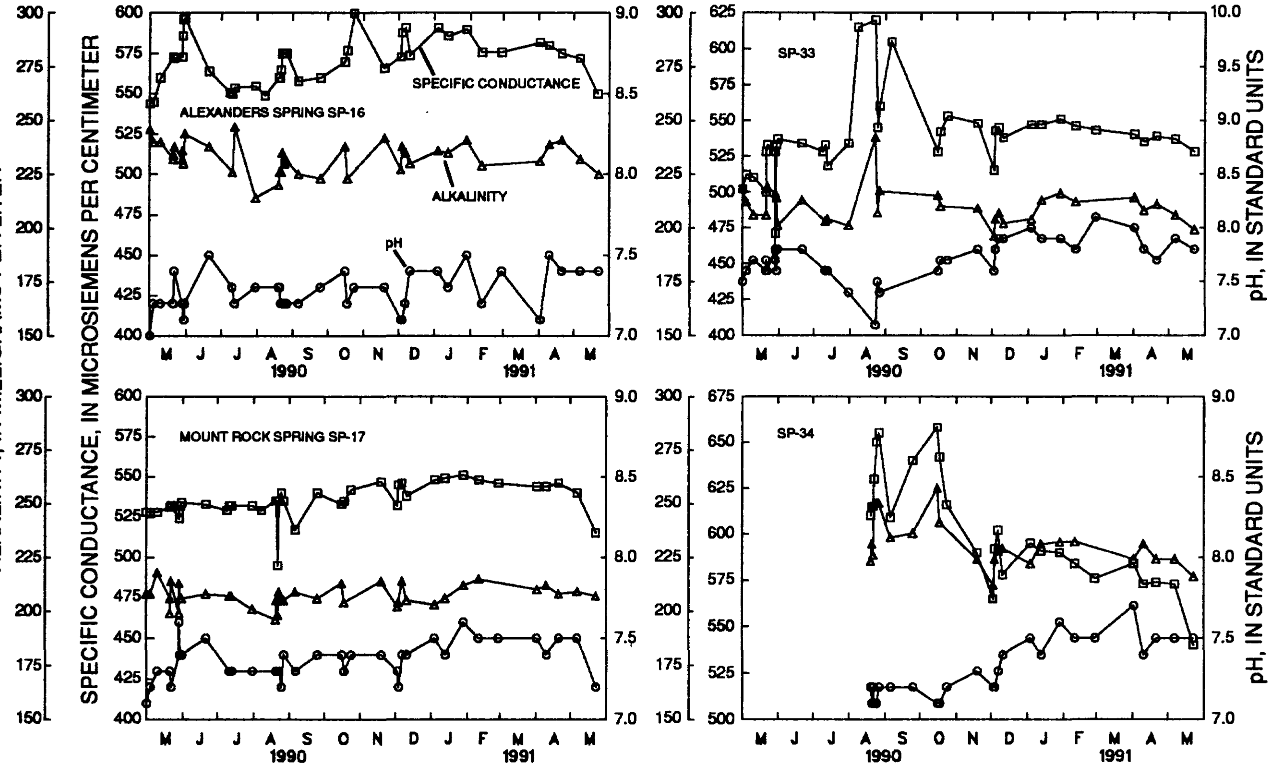


Figure 6.—Specific conductance, pH, and alkalinity of water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

Major-Ion Chemistry

The four springs were sampled once to determine the major-ion chemistry of ground water discharged from each of the sites. Additional chemical data collected from the sites by Becher and Root (1981) also were examined.

Chemical quality of ground water discharged from each of the four springs is similar (table 10). The dissolved-solids concentration of ground water discharged from the four sites, determined as the sum of constituents, ranged from 430 mg/L at spring Sp-33 to 460 mg/L at Alexanders Spring. Calcium and bicarbonate are the dominant dissolved ions in water discharged at each of the sites; the water contains lesser concentrations of dissolved magnesium, nitrate, and sulfate. Compared to Alexanders Spring, the other springs had lower concentrations (on a milliequivalent basis) of bicarbonate and lower combined concentrations of calcium and magnesium.

Variation in the molar ratios of calcium to magnesium (Ca^{2+}/Mg^{2+}) in discharges from springs may reflect different lithologies in the contributing areas to the springs. The Ca^{2+}/Mg^{2+} ratio typical of ground water in aquifer materials composed of dolomite is near 1 (Meisler and Becher, 1967). The Ca^{2+}/Mg^{2+} ratios of ground water in limestone aquifers generally range from 3 to 10; the ratios generally range from 1.5 to 3 for ground water in mixed sequences of dolomite and limestone (Meisler and Becher, 1967; White, 1988). The Ca^{2+}/Mg^{2+} ratio of spring flows from Alexanders Spring and spring Sp-34 (4.1 and 3.2) indicate that the aquifer material is primarily limestone. The Ca^{2+}/Mg^{2+} ratios of spring flows from Mount Rock Spring and spring Sp-33 (2.6 and 2.5) indicate that the aquifer material contains a mix of limestone and dolomite. Because limestone and mixed-carbonate lithologies are interbedded near the springs, recharge areas to the springs could not be delineated on the basis of the observed Ca^{2+}/Mg^{2+} ratios.

Table 10.—Major-ion chemistry of water from springs near Carlisle, Pa., April 4, 1991

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

Constituent	Alexanders Spring (Sp-16)		Mount Rock Spring (Sp-17)		Sp-33		Sp-34	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Calcium, dissolved	87	4.3	73	3.6	69	3.4	80	4.0
Magnesium, dissolved	13	1.1	18	1.5	17	1.4	15	1.2
Sodium, dissolved	6.9	.30	5.9	.26	5.9	.26	7.0	.30
Potassium, dissolved	1.9	.05	1.8	.05	1.8	.05	1.9	.05
Bicarbonate, total	282	4.6	265	4.3	261	4.3	273	4.5
Sulfate, dissolved	23	.48	25	.52	25	.52	25	.52
Nitrate, total[1]	26	.41	28	.45	28	.45	28	.45
Chloride, dissolved	14	.39	12	.34	12	.34	15	.42
Silica, dissolved	8.8	--	8.8	--	8.4	--	8.5	--
Sum of constituents	460	11.6	440	11.0	430	10.7	450	11.4

[1] Reported as nitrate (NO_3).

Carbonate Equilibria

The equilibrium between ground water and the major rock-forming minerals in the carbonate-rock aquifer, as well as the equilibrium partial pressure of carbon dioxide in ground water, provide additional insights into ground-water flow systems. The geochemical model WATEQ4F (Ball and others, 1987) was used to determine the degree of saturation of quartz, calcite, aragonite, and dolomite in water samples collected April 4, 1991. The geochemical model was also used to determine the equilibrium partial pressure of carbon dioxide in discharges from the spring.

The degree of saturation of water with respect to constituents among rock-forming minerals is commonly reported in terms of a saturation index (S.I.). The S.I. is a unitless number defined as the log of the ion activity product for dissociation of the mineral divided by the solubility product constant for the mineral. An S.I. near zero (typically from -0.1 to 0.1) indicates that mineral phases are in equilibrium with the solution. A positive S.I. indicates a solution is oversaturated with respect to a mineral phase (the mineral will tend to precipitate from solution), whereas a negative S.I. indicates that a solution is undersaturated with respect to a mineral phase (if the mineral phase is present, it will tend to dissolve).

Water samples from each of the springs were oversaturated with respect to quartz, but their degrees of saturation varied with respect to carbonate minerals (table 11). Alexanders Spring is the only site where ground-water discharges were undersaturated with respect to all of the rock-forming carbonate minerals. Water from the other springs ranged from equilibrium to oversaturated with respect to the high-calcium minerals calcite and aragonite. However, the observed differences in the S.I. cannot be easily explained because numerous environmental factors affect carbonate equilibria; for example, (1) spatial and temporal variation in the chemical composition of ground-water recharge, (2) spatial variation in the chemical composition of the unsaturated zone and aquifer materials, (3) residence time of ground water relative to rates of dissolution of the geologic materials, (4) changes in chemical composition of water due to mixing along a ground-water-flow path, and (5) changes in the partial pressure of carbon dioxide along a ground-water-flow path.

Water discharged from Alexanders Spring had the highest equilibrium partial pressure of carbon dioxide among waters from the four springs; the median enrichment relative to the earth's atmosphere was 47 (table 12). The relative standard deviation in carbon dioxide partial pressures for samples of water discharged from Mount Rock Spring was similar to that for Alexanders Spring, but median enrichment of carbon dioxide relative to the earth's atmosphere was lower. The largest relative standard deviations in carbon dioxide partial pressures were for samples from springs Sp-33 and Sp-34 (table 12). Relations between Mount Rock Spring and spring Sp-33 described earlier indicate that higher S.I.'s from Mount Rock Spring water compared to spring Sp-33 water are best explained by degassing of carbon dioxide from water to the atmosphere in the reach upstream of the swallow hole and in the conduit system that connects the swallow hole to the point of resurgence. The low calcite and aragonite S.I.'s at Alexanders Spring might be due to less degassing of carbon dioxide near the spring head than at the other sites.

The chemical characteristics of water at the spring sites were similar to those of karst water derived from various hydrogeologic settings in the Nittany and Lebanon Valleys of Pennsylvania (Drake and Harmon, 1973). Carbon dioxide partial pressures and other geochemical data from the spring sites indicate that chemical characteristics of ground-water discharge from Alexanders Spring, Mount Rock Spring, and spring Sp-34 are similar to the chemical characteristics of water from wells and diffuse flow springs. Drake and Harmon (1973, p. 955) suggest that diffuse spring and well waters "... are derived primarily from seepage recharge to the deep carbonate aquifers." The chemical characteristics of ground-water discharge from spring Sp-33 (positive saturation indices and low carbon dioxide pressures) are similar to the chemical characteristics of basin surface discharge during periods of base flow (Drake and Harmon, 1973, p. 955).

Table 11.—Saturation indices of quartz, calcite, aragonite, and dolomite in water from springs near Carlisle, Pa., April 4, 1991

Spring name	Saturation index[1]			
	Quartz	Calcite	Aragonite	Dolomite
Alexanders Spring (Sp-16)	0.36	-0.18	-0.34	-1.7
Mount Rock Spring (Sp-17)	.36	.14	-.01	-.85
Sp-33	.34	.58	.43	.09
Sp-34	.35	.36	.21	-.47

[1] Saturation index = log (ion activity product/solubility product).

Table 12.—Equilibrium partial pressures of carbon dioxide in water from springs near Carlisle, Pa.

[Partial pressures of carbon dioxide (CO_2) are expressed as a unitless ratio of the equilibrium partial pressure of CO_2 in ground-water discharge to the global mean partial pressure of CO_2 in the earth's atmosphere (3.4×10^{-4} atmospheres)]

Spring name	Number of observations	Median	Range	RSD[1] (percent)
Alexanders Spring (Sp-16)	37	47	25-62	25
Mount Rock Spring (Sp-17)	37	33	18-55	26
Sp-33	33	13	6.4-29	41
Sp-34	24	41	15-67	41

[1] Relative standard deviation is the sample standard deviation divided by the sample mean, in percent.

HERBICIDES AND NUTRIENTS IN GROUND WATER AND SPRINGS

Triazine herbicides, atrazine-soil metabolites, nitrogen, and phosphorus were detected in water discharged from each of the four springs investigated. Triazine herbicide residues and nutrients also were detected in water from most wells sampled.

Discharge (in pounds per day) of selected herbicides, herbicide-soil metabolites, and nutrients were estimated for Alexanders and Mount Rock Springs. Constituent discharges were not estimated for the unnamed tributary to Mount Rock Spring Creek because accurate estimates of the flow from each of the springs could not be obtained. Results of chemical analyses of spring water were of acceptable precision and accuracy to estimate constituent discharges of atrazine, DEA, nitrate, and total phosphorus. The discharge of prometon for Alexanders Spring Creek was estimated for two periods of precipitation. Daily constituent concentrations were determined by interpolation between measured concentrations according to graphical methods described by Porterfield (1972). Constituent discharges were determined for each day on the basis of estimated daily constituent concentrations and daily mean discharge data.

Herbicides and Herbicide-Soil Metabolites

Four triazine herbicides and two atrazine-soil metabolites were detected in discharges from springs. The triazine herbicides detected were atrazine, simazine, hexazinone, and prometon. The atrazine-soil metabolites DEA and DIA also were detected in discharge from the springs. None of the samples of spring discharge contained concentrations of cyanazine or the chloroacetanilide herbicides alachlor and metolachlor that were above the MRL's (Appendix 2).

Atrazine concentrations in water samples from each spring (fig. 7) were less than or equal to 0.3 µg/L. The median concentration of atrazine in samples from each of the springs was 0.2 µg/L (table 13). At times, atrazine concentrations in samples from spring Sp-34 and Alexanders Spring were 0.1 µg/L above or below the median concentration of 0.2 µg/L. Atrazine concentrations in water samples from spring Sp-33 and Mount Rock Spring were nearly invariant at 0.2 µg/L. Increases in herbicide concentrations in spring water after application to nearby cropland were not observed (no "spring flush" of herbicides through the ground-water system seems to have occurred).

The two soil metabolites of atrazine were detected in samples collected from each of the springs. DEA and DIA were detected in 100 and 20 samples, respectively, of the 101 samples analyzed by use of gas chromatography (table 13). An additional soil metabolite of atrazine, hydroxyatrazine, was determined in 12 interlaboratory samples by use of liquid chromatography. Hydroxyatrazine was not detected at an MRL of 0.1 µg/L in any of the 12 samples (T.R. Steinheimer, U.S. Department of Agriculture and M.G. Ondrus, University of Wisconsin-Stout, written commun., 1990). DEA was detected in samples from each of the springs during much of the sampling period. Concentrations of DEA were, on average, twice that of atrazine, the parent compound. The highest concentrations of DEA were in water samples collected after rains in late August and November 1990; the concentrations were slightly below or above 1 µg/L (fig. 7). DIA was only rarely detected in samples collected from spring Sp-33, Alexanders Spring, and Mount Rock Spring; however, 10 of the 18 water samples from spring Sp-34 contained detectable concentrations of DIA. The maximum concentration of DIA was 0.8 µg/L in a water sample collected from spring Sp-33. This was the only sample for which the concentration of DIA exceeded that of DEA or atrazine.

The detection or nondetection of selected pesticide-soil metabolites and the relative proportion of these soil metabolites to parent compounds in water may be indicative of the source and flow path by which these compounds enter ground water and surface water. Adams and Thurman (1991) suggest that the molar ratios of DEA to atrazine, referred to as the "deethylatrazine to atrazine ratio (DAR)," in ground-water samples may be useful in differentiating nonpoint sources from point sources of atrazine. On the basis of their observations that deethylatrazine is produced by the metabolic activity of soil bacteria and fungi and that mobility and persistence of DEA and atrazine in ground water are similar, Adams and Thurman (1990) have shown that DAR's are commonly higher for ground-water samples containing atrazine leached through soils from applications to cropland than for ground-water samples containing atrazine introduced directly into the aquifer from point sources. Low DAR's are also likely in ground water where recharge pathways bypass the soil matrix, as in sinkholes. Thurman and others (1992)

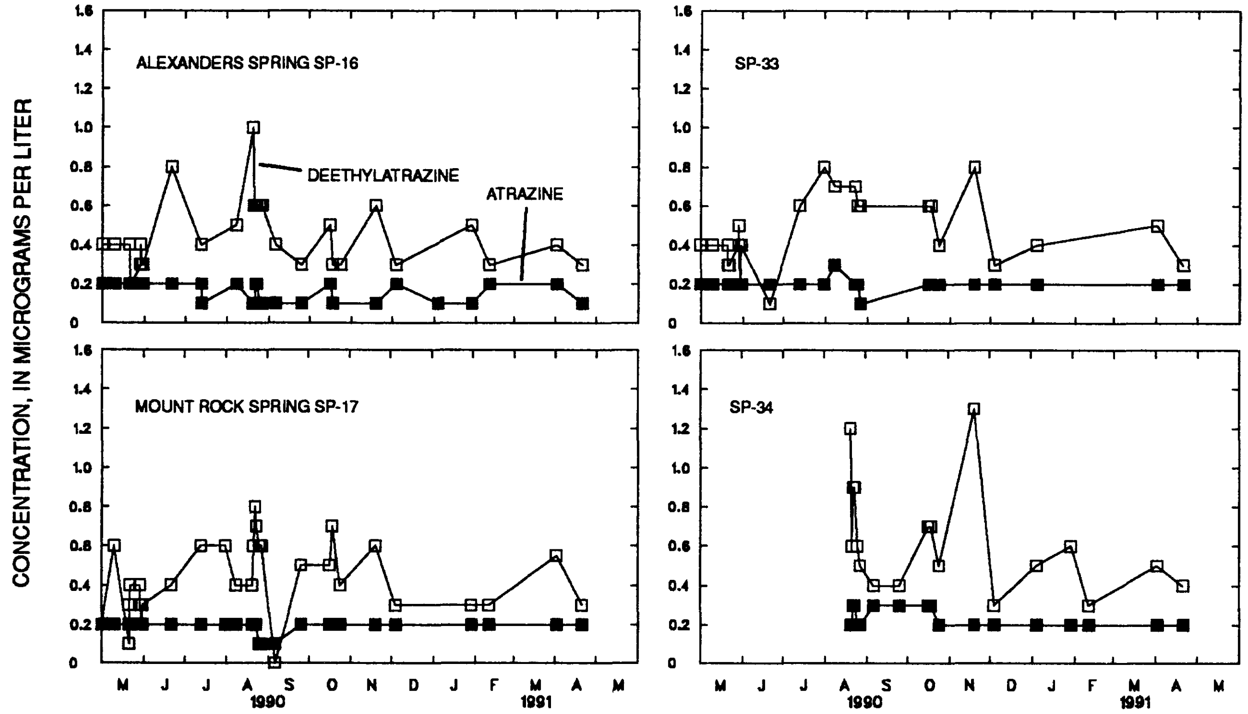


Figure 7.--Atrazine and deethylatrazine concentrations in water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

indicate that because the atrazine-soil metabolite DIA persists in soils for less time than atrazine and DEA, DIA is commonly detected in surface runoff but not in ground water. Similarly, the detection or nondetection of DIA in a carbonate-rock aquifer may also be an indicator of whether or not recharge through sinkholes is a major pathway for migration of agricultural chemicals through the unsaturated zone.

The DAR's in spring discharges were about 2 for much of the study period; thus, the molar quantity of DEA was typically twice that of atrazine. These observed DAR's are higher than the DAR's measured in surface runoff (much less than 1) and in stormflow (less than 0.1) measured in agricultural areas of the Midwestern United States (Adams and Thurman, 1991; Squillace and others, 1991; Thurman and others, 1992). The high DAR's in spring discharges may indicate 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. The low percentage of DIA detections in discharges from Alexanders and Mount Rock Springs also may mean that much of the atrazine is leached through soils.

Further evaluation of the use of ratios of herbicide-soil metabolites and soil metabolite to parent compound in the carbonate-rock terranes of the Cumberland and Lancaster Valleys of Pennsylvania may be of merit, given their potential for use in determining how herbicide-use practices introduce herbicides into ground water and the pathways by which herbicides reach ground water.

Prometon was the herbicide detected at the highest concentration (1.2 µg/L), and it was second only to atrazine in the number of detections (table 13). Thirteen of the 14 water samples containing detectable prometon were collected from Alexanders Spring (fig. 8); the remaining sample was collected from Mount Rock Spring. Prometon was only detected in samples collected up to 17 days after substantial rainfall. The brief lag time between precipitation and detection of prometon in spring discharge and the subsequent disappearance of prometon in spring discharge within a few weeks indicate that the prometon may have leached from a location near the spring outlet.

Table 13.—Summary of herbicide-concentration data for water from springs and wells near Carlisle, Pa.

[µg/L, microgram per liter; <, less than; --, not determined]

Constituent	Number of observations	Median (µg/L)	Range (µg/L)	RSD[1] (percent)
	Alexanders Spring (Sp-16)			
Atrazine	29	0.2	0.1-0.2	29
Prometon	29	<.1	<.1-1.2	--
Simazine	29	<.1	--	--
Deethylatrazine	29	.4	.2-1.0	41
Deisopropylatrazine	29	<.1	<.1-.2	--
Triazines by immunoassay	21	.4	.2-.7	36
	Mount Rock Spring (Sp-17)			
Atrazine	30	.2	.1-.2	16
Prometon	30	<.1	<.1-.2	--
Simazine	30	<.1	--	--
Deethylatrazine	30	.4	<.1-.8	[2]41
Deisopropylatrazine	30	<.1	<.1-.1	--
Triazines by immunoassay	20	.5	.2-.7	33
	Sp-33			
Atrazine	23	.2	.1-.3	15
Prometon	23	<.1	--	--
Simazine	23	<.1	--	--
Deethylatrazine	23	.4	.1-.8	41
Deisopropylatrazine	23	<.1	<.1-.8	--
Triazines by immunoassay	18	.5	.2-.7	33
	Sp-34			
Atrazine	18	.2	.2-.3	22
Prometon	18	<.1	--	--
Simazine	18	<.1	<.1-.1	--
Deethylatrazine	18	.6	.3-1.3	44
Deisopropylatrazine	18	.1	<.1-.4	[2]83
Triazines by immunoassay	20	.5	.2-.8	34
	Water wells			
Triazines by immunoassay	50	.5	<.1-3.5	113

[1] Relative standard deviation is the sample standard deviation divided by the sample mean, in percent.

[2] Samples whose concentrations were less than the minimum reporting level were replaced by concentrations of 0.05 mg/L for estimation of the relative standard deviation.

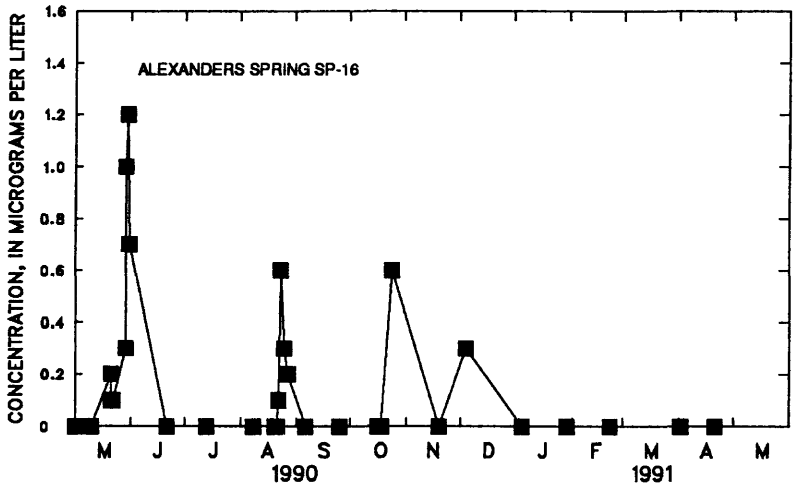


Figure 8.–Prometon concentrations in water from Alexanders Spring, near Carlisle, Pa.

Simazine was detected in only 4 of the 101 water samples collected from spring sites, although trace concentrations of simazine below the MRL were indicated in each sample analyzed by gas chromatography. The four samples containing detectable amounts of simazine were collected in August and October 1990 from spring Sp-34. Simazine concentrations in the four samples were at the MRL of 0.1 µg/L.

Hexazinone was detected in only one sample (Appendix 2) that was collected from Alexanders Spring in the morning of May 21, 1990, after a rainfall. The sample had a hexazinone concentration at the MRL of 0.2 µg/L. A sample collected from Alexanders Spring later that day did not contain a detectable concentration of hexazinone.

Triazine herbicide residues were detected in each of 79 spring discharge samples analyzed by ELISA methods (Appendix 2). Triazine compounds also were detected in ground water from 42 of 50 wells that were sampled (Appendix 1). The data are summarized in table 13. No substantial seasonal differences in concentrations of triazine herbicide residue were indicated for ground-water discharges from the four springs (fig. 9). The median concentration of triazine compounds in water samples from 50 wells in the study area (0.5 µg/L) is nearly identical to concentrations measured in ground-water discharges at springs (table 13). However, the range and relative standard deviation of triazine concentrations were substantially larger for ground-water samples from wells than for samples from springs. The wide spatial distribution of wells that produced water containing detectable triazine herbicide residues indicates that these residues are present in ground water throughout much of the area west of Carlisle.

None of the concentrations of atrazine, prometon, simazine, or hexazinone in 101 water samples collected during the study exceeded either USEPA lifetime health advisory levels or maximum contaminant levels (MCL) for public drinking-water supplies (U.S. Environmental Protection Agency, 1991). Advisory levels have not been established for atrazine-soil metabolites or for triazine concentrations determined by ELISA methods. Belluck and others (1991) have suggested that, until additional data on soil metabolite toxicology are available, the additive concentrations of atrazine, DEA, and DIA may be compared to existing atrazine health advisory levels for risk assessment and policy development. The additive concentrations of atrazine, DEA, and DIA in ground-water discharges from springs also did not exceed the USEPA MCL of 3.0 µg/L for atrazine (U.S. Environmental Protection Agency, 1991).

Herbicide residues in discharges from springs can be toxic to fish, aquatic invertebrates, algae, and aquatic vascular plants. Although fauna commonly are not as sensitive to the toxic effects of herbicides as aquatic plants are, any herbicide-induced effects on aquatic plants is likely to affect faunal habitats

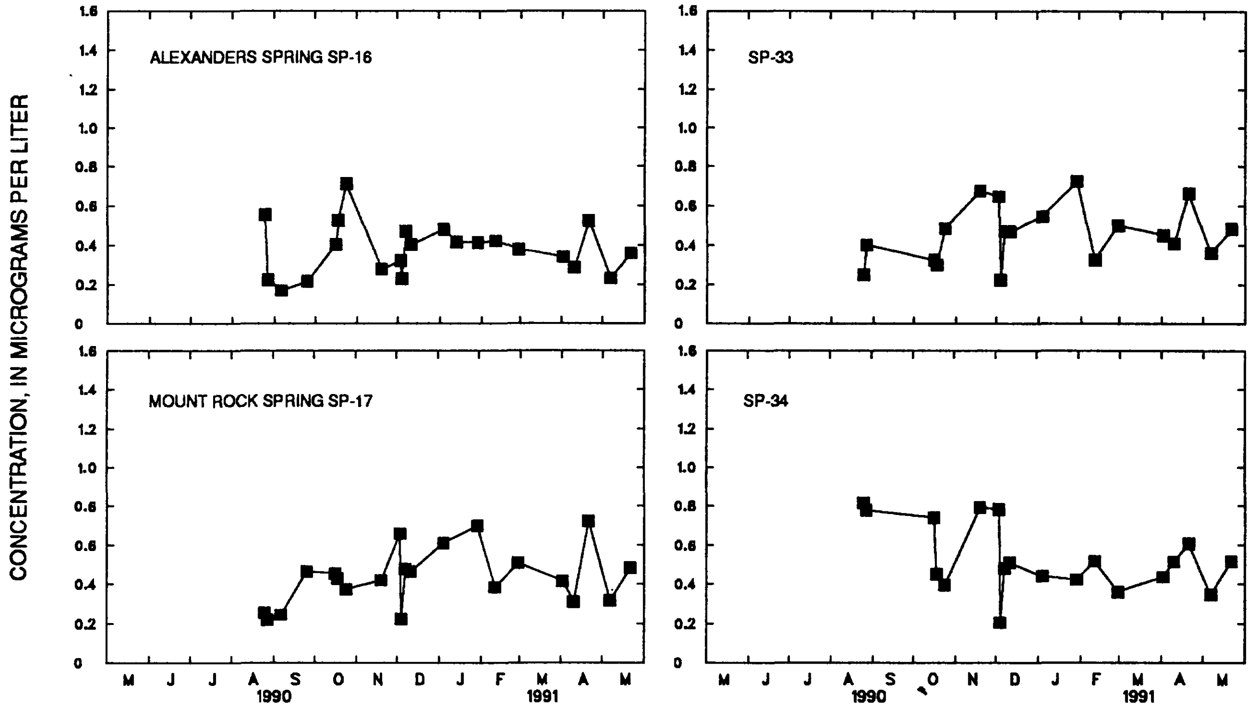


Figure 9.--Triazine-residue concentrations in water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

substantially. However, atrazine concentrations measured in spring discharges are lower than threshold concentrations demonstrated to cause a direct adverse effect on survival, growth, and reproduction of aquatic vertebrates and invertebrates (Eisler, 1989; Trotter and others, 1990). Studies cited by Eisler (1989) and Trotter and others (1990) indicate that atrazine concentrations ranging from 1 to 5 µg/L can adversely affect algal growth and succession and can affect photosynthetic processes of mature aquatic vascular plants. Environment Canada has proposed a maximum acceptable concentration for atrazine of 2.0 µg/L for protection of freshwater aquatic life (Trotter and others, 1990). The U.S. Fish and Wildlife Service has proposed a maximum acceptable concentration of 5 µg/L of atrazine for protection of "sensitive" aquatic plants and 11 µg/L for most aquatic plants and animals (Eisler, 1989). Concentrations of atrazine detected in Alexanders and Mount Rock Spring Creeks were nearly an order of magnitude lower than these proposed criteria. Potential effects of atrazine soil metabolites or combinations of herbicides on aquatic ecosystems are not currently known.

The daily and cumulative discharges of atrazine and DEA are nearly identical for Alexanders and Mount Rock Spring Creeks (table 14). The median daily discharges of atrazine in Alexanders and Mount Rock Springs were 0.003 and 0.004 lb, respectively. The median daily discharges of DEA were about twice that of atrazine--0.007 and 0.009 lb for Alexanders and Mount Rock Springs, respectively. The cumulative discharges of atrazine and DEA were 1.2 and 3.0 lb in Alexanders Spring, and 1.5 and 3.2 lb in Mount Rock Spring.

Table 14.—Summary of daily concentration, daily discharge, and cumulative discharge of selected constituents from springs near Carlisle, Pa., May 1, 1990, through April 30, 1991

[mg/L, milligram per liter; μg/L, microgram per liter; <, less than; --, not determined]

Constituent	Daily concentration		Daily discharge		Cumulative discharge (pounds)
	Median	Range	Median (pounds)	Range (pounds)	
Alexanders Spring (Sp-16)					
Atrazine	0.2 μg/L	0.1-0.2 μg/L	0.003	0.0007-0.007	1.2
Deethylatrazine (DEA)	.4 μg/L	.1-1.0 μg/L	.007	.002-.02	3.0
Prometon					
May 21-June 6, 1990	--	<.1-1.2 μg/L	--	0-.03	.13
Aug. 21-Sept. 6, 1990	--	<.1-.6 μg/L	--	0-.01	.05
Nitrate nitrogen, as N	5.2 mg/L	3.2-6.3 mg/L	94	38-240	39,000
Phosphorus, as P	.02 mg/L	<.01-.03 mg/L	.3	0-1.3	120
Mount Rock Spring (Sp-17)					
Atrazine	.2 μg/L	.1-.3 μg/L	.004	0-.01	1.5
Deethylatrazine (DEA)	.4 μg/L	<.1-.8 μg/L	.009	0-.02	3.2
Nitrate nitrogen, as N	5.7 mg/L	3.5-7.0 mg/L	94	0-370	43,000
Phosphorus, as P	.02 mg/L	<.01-.04 mg/L	.2	0-1.6	130

Daily mean discharges of atrazine and DEA from Alexanders Spring were steady during the study, whereas discharges of atrazine and DEA from Mount Rock Spring increased part way through the study (fig. 10). At Mount Rock Spring, the greater part of the total discharge of atrazine and DEA was from November 1990 through April 1991, primarily because of an increase in flow during that part of the study. Periodic changes in DEA discharge resulted from changes in DEA concentrations and spring discharge. Several years of data are desirable for full assessment of seasonality of herbicide concentrations and discharges; however, available data indicate little seasonal variation in herbicide concentrations but potentially larger seasonal variation in herbicide discharges. Most of the seasonal variation in herbicide discharges is attributed to changes in rates of ground-water discharge, so that herbicide discharges may be larger during winter and early spring than at other times. Thus, the period of greatest herbicide discharge to streams from ground water in this carbonate-rock terrane may be as long as 6 to 10 months after the typical herbicide-application period during May and June.

The discharge of prometon from Alexanders Spring was estimated for the duration of two periods of increased spring flow after rainstorms in May and August 1990. Estimates of the discharge of prometon for the two periods was possible because intensive sampling provided sufficient data for estimation of prometon concentrations over the rise and fall of the discharge hydrograph (fig. 8). For the first intensive sampling period, the maximum prometon concentration was 1.2 μg/L, and the maximum daily discharge of prometon was 0.03 lb (table 14). For the second intensive sampling period, the maximum prometon concentration was 0.6 μg/L, and the maximum daily discharge of prometon was 0.01 lb. The total discharges of prometon for these two intensive sampling periods were 0.13 and 0.05 lb.

Nutrients

Nitrate was the major form of nitrogen in spring discharges and in water from wells. Ammonium and nitrite were only rarely detected in water samples collected from the spring sites, and ammonium plus organic nitrogen concentrations were at or below the MRL of 0.2 μg/L as N. Nitrate concentrations for 119

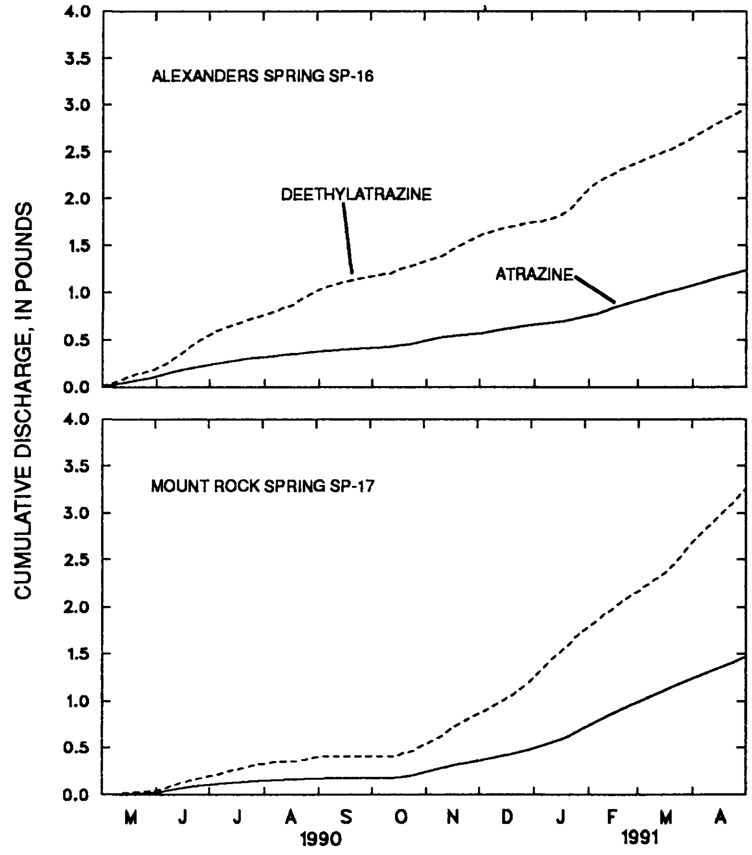


Figure 10.--Cumulative discharge of atrazine and deethylatrazine from Alexanders Spring and Mount Rock Spring, near Carlisle, Pa.

water samples from the four spring sites ranged from 2.9 to 6.7 mg/L, and median nitrate concentrations for the four sites ranged from 5.3 mg/L at Alexanders Spring to 5.8 mg/L at spring Sp-34 (table 15). No seasonality was noted in nitrate concentrations in samples from springs (fig. 11). The minimum nitrate concentrations for each spring were in samples collected in October 1990. The cause of these lower concentrations is not known. Nitrate was also the major form of nitrogen in water from wells (table 15). The median concentration of nitrate in water samples from 50 wells in the study area, 6.6 mg/L, was from 14 to 26 percent greater than the median nitrate concentrations of ground water discharged from each of the spring sites.

Total phosphorus, the sum of all forms of phosphorus in unfiltered samples, was detected at concentrations near the MRL's of 0.01 and 0.02 mg/L as P in most of the samples from springs (fig. 12). The median concentration of total phosphorus was 0.02 mg/L at each of the spring sites; the concentrations ranged from less than 0.01 to 0.04 mg/L as P (table 15). Concentrations of total phosphorus were below the MRL in most samples collected in August, October, November, and December 1990 and January 1991 (fig. 12). The reason for the decrease in total phosphorus is not known.

Phosphorus was also detected in water samples from each of the 50 wells. Concentrations of total phosphorus in water samples from wells were comparable to concentrations in ground water discharged from spring sites (table 15). The median concentration of total phosphorus was at the MRL of 0.02 mg/L as P.

Table 15.—Summary of nutrient-concentration data for springs and wells near Carlisle, Pa.

[mg/L, milligram per liter; <, less than; –, not determined]

Constituent	Number of observations	Median (mg/L)	Range (mg/L)	RSD[1] (percent)
Alexanders Spring (Sp-16)				
Nitrite, as N	35	<0.004	<0.004-0.010	–
Nitrate, as N	35	5.3	3.3-6.1	11
Ammonia plus organic nitrogen, as N	35	.33	<.20-.88	43
Ammonia, as N	35	<.02	<.02-.03	–
Total phosphorus, as P	35	.02	<.01-.03	24
Orthophosphate, as P	35	.008	<.002-.017	38
Mount Rock Spring (Sp-17)				
Nitrite, as N	34	<.004	<.004-.007	–
Nitrate, as N	34	5.6	3.4-6.7	11
Ammonia plus organic nitrogen, as N	34	.33	<.20-.90	50
Ammonia, as N	34	<.02	<.02-.03	–
Total phosphorus, as P	34	.02	<.01-.04	50
Orthophosphate, as P	34	.01	<.002-.027	50
Sp-33				
Nitrite, as N	29	<.004	<.004-.008	–
Nitrate, as N	29	5.4	3.8-6.5	12
Ammonia plus organic nitrogen, as N	29	.39	<.20-1.11	48
Ammonia, as N	29	<.02	<.02-.04	–
Total phosphorus, as P	29	.02	<.01-.04	33
Orthophosphate, as P	29	.01	<.002-.022	45
Sp-34				
Nitrite, as N	21	<.004	<.004-.007	–
Nitrate, as N	21	5.8	2.9-6.5	12
Ammonia plus organic nitrogen, as N	21	.30	<.20-.73	49
Ammonia, as N	21	<.02	<.02-.03	–
Total phosphorus, as P	21	.02	<.01-.03	24
Orthophosphate, as P	21	.008	.003-.015	38
Water wells				
Nitrite, as N	50	<0.004	<0.004-0.006	–
Nitrate, as N	50	6.6	.68-35	68
Ammonia plus organic nitrogen, as N	50	.45	<.20-1.3	55
Ammonia, as N	50	<.02	<.02-.05	–
Total phosphorus, as P	49	.02	<.02-.04	19
Orthophosphate, as P	49	<.02	<.02-.02	–

[1] Relative standard deviation is the standard deviation of the sample divided by the mean of the sample, in percent.

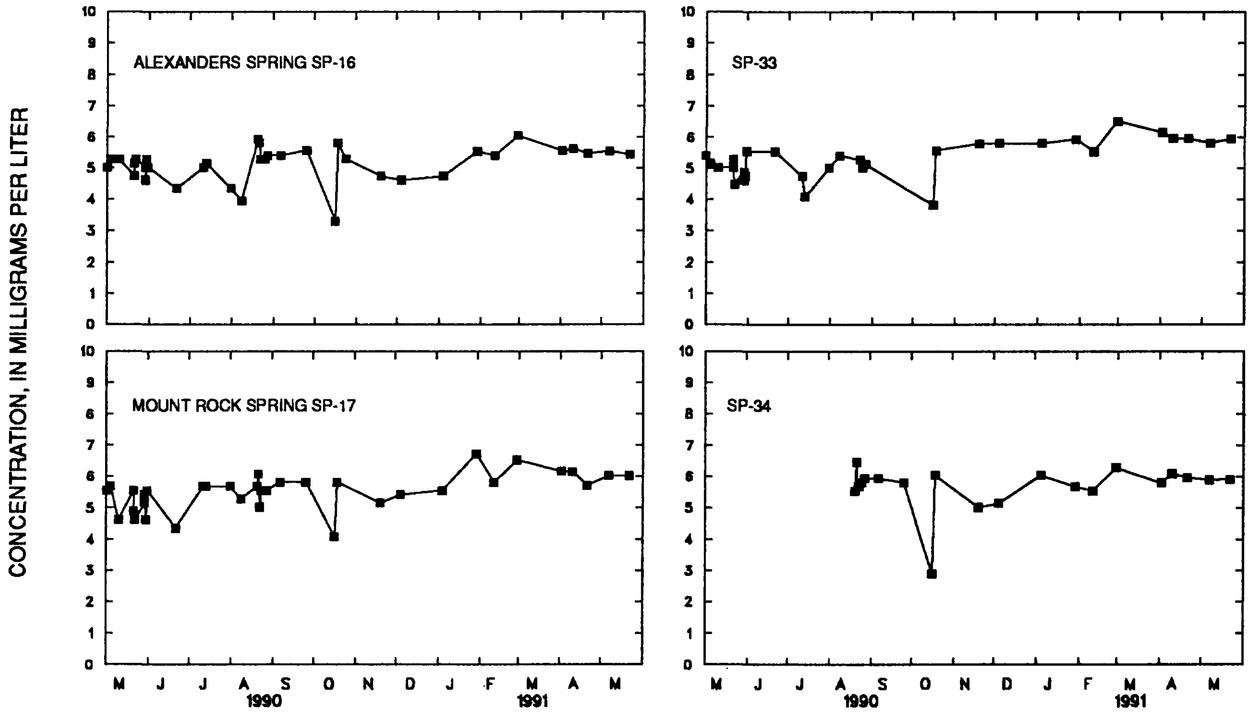


Figure 11.--Nitrate-nitrogen concentrations of water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

Neither nitrate nor nitrite concentrations in ground-water discharges from springs exceeded the USEPA MCL's for public drinking-water supplies. Ground water from 8 of the 50 wells sampled, however, did contain nitrate at concentrations that exceed the MCL. The MCL is primarily for the protection of human infants; however, young poultry, swine, horses, sheep, and cattle and adult horses, sheep, and cattle can also be affected by nitrate in drinking water (Shuval and Gruener, 1972; Fan, Willhite, and Book, 1987; Shearer and others, 1972; Mansouri, 1985; Young and Mancl, 1985).

The observed nutrient concentrations may be conducive for development of eutrophic conditions in lakes, reservoirs, and streams given certain physical and hydrologic conditions. There is, however, no simple predictor of threshold nitrogen and phosphorus concentrations that will lead to eutrophication. Commonly cited thresholds for eutrophication of lakes and streams are 0.3 mg/L of inorganic nitrogen (including nitrite, nitrate, and ammonia) and from 0.01 to 0.1 mg/L of phosphorus (McKee and Wolf, 1963; MacKenthun, 1969; Vollenweider, 1968; Harms and others, 1974; U.S. Environmental Protection Agency, 1986). Thus, nitrate concentrations in ground-water discharges to the limestone-spring creeks are in excess of, and phosphorus concentrations are in the range of, commonly cited thresholds for development of eutrophic conditions.

From May 1990 through April 1991, the median daily discharge of nitrate at both Mount Rock and Alexanders Springs was 94 lb (table 10). The cumulative discharge of nitrate in Mount Rock Spring (43,000 lb) was slightly greater than that of Alexanders Spring (39,000 lb).

The discharge of nitrate in Mount Rock and Alexanders Springs increased part way through the study period (fig. 13). Two progressive increases in daily nitrate discharges occurred at Mount Rock Spring, one in November 1990 and the other in January 1991. The increase in daily nitrate discharges in Alexanders Spring occurred in January 1991. Changes in nitrate discharge in the two springs are primarily related to changes in rates of ground-water discharge and not to changes in nitrate concentration.

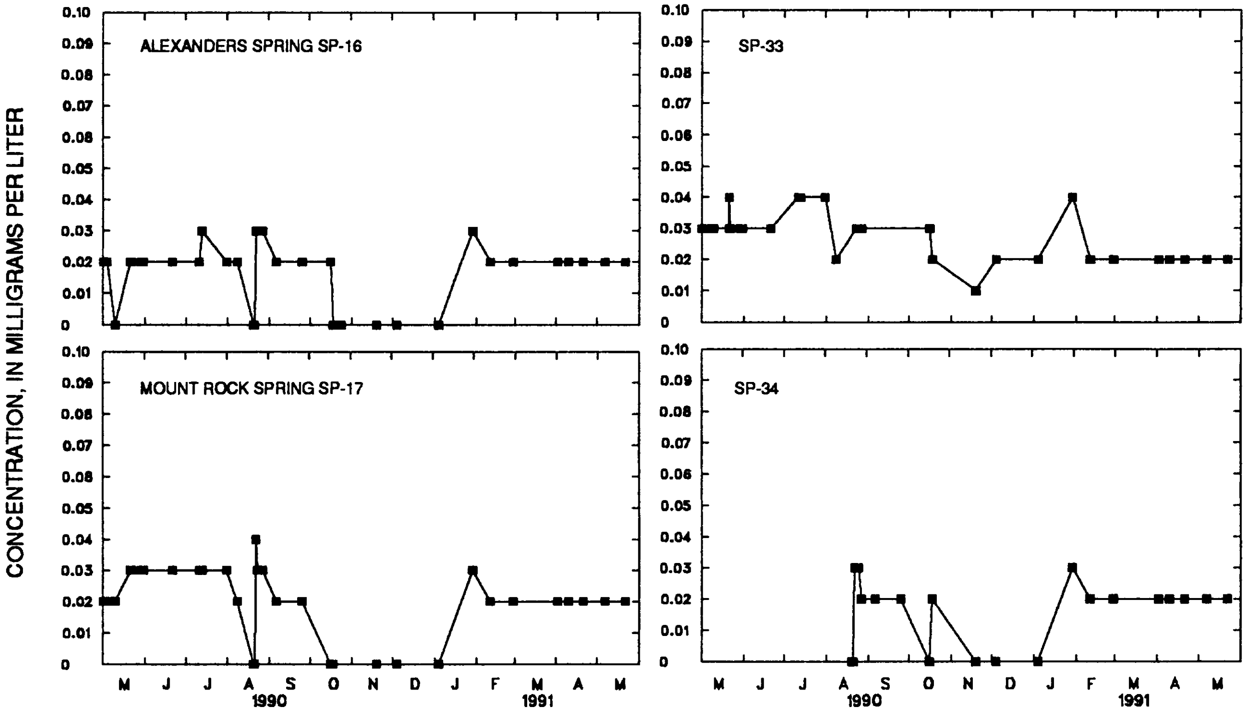


Figure 12.--Total phosphorus concentrations of water from Alexanders Spring, Mount Rock Spring, and springs discharging to the unnamed tributary to Mount Rock Spring Creek, near Carlisle, Pa.

Phosphorus concentrations were near the MRL of 0.02 mg/L for most of the investigation. Median daily discharges of phosphorus from Alexanders and Mount Rock Springs were 0.3 and 0.2 lb; total discharges over the study period were 120 and 130 lb. Quantities of phosphorus discharged from Alexanders and Mount Rock Springs varied during the study (fig. 14). The temporal variation in phosphorus discharge is related to changes in phosphorus concentrations and to changes in rates of ground-water discharge. The most substantial change in phosphorus discharges in Alexanders and Mount Rock Spring Creeks began in January 1991 because phosphorus concentrations increased from less than the MRL to 0.02 mg/L and the spring discharges were at the maximum for the study. Several years of data with fewer censored data points would be desirable for a thorough assessment of seasonality of phosphorus concentrations and discharges. However, available data indicate some seasonal variation in phosphorus concentrations and large seasonal variation in phosphorus discharges.

Results of this study indicate that nutrient discharges from ground water are greatest during the winter and early spring. Because riparian vegetation and aquatic plants are dormant during these seasons, most of the nutrients from ground-water discharges may be transported to successively larger streams with little assimilation.

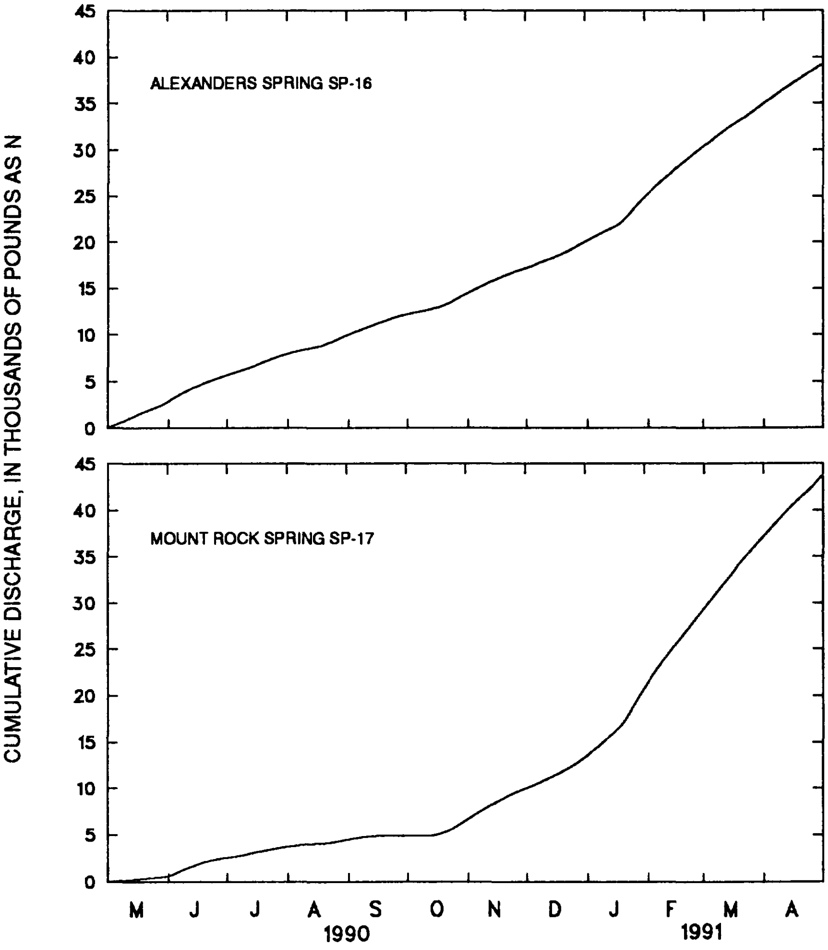


Figure 13.--Cumulative nitrate-nitrogen discharge from Alexanders Spring and Mount Rock Spring, near Carlisle, Pa.

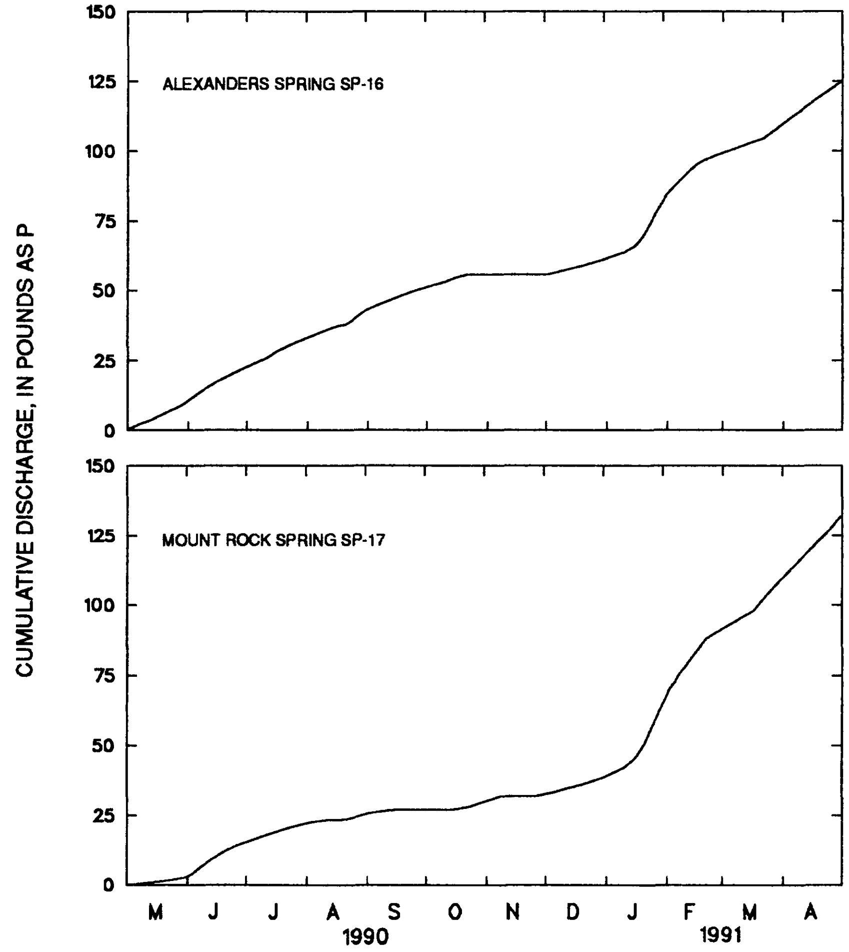


Figure 14.--Cumulative phosphorus discharge from Alexanders Spring and Mount Rock Spring, near Carlisle, Pa.

RELATION OF WATER QUALITY TO LAND USE AND AGRICULTURAL PRACTICES

This section describes the relation of ground-water quality to land use and agricultural practices in the study area. Included are discussions of (1) a statistical evaluation of triazine-residue concentrations, nitrate concentrations, and specific conductances of water from wells in agricultural and residential areas; (2) comparisons of herbicide compounds applied to agricultural land in the study area with the herbicides detected in discharge from Alexanders and Mount Rock Springs; and (3) estimates of the quantities of selected herbicides used in the study area relative to the quantities of herbicides and herbicide-soil metabolites discharged from the springs.

Water From Wells

The objective of the analysis of quality of water from selected wells in the study area was to determine whether ground-water quality differs significantly between areas of agricultural and residential land use. The 50 wells sampled were designated as representing either residential or agricultural land use at the first visit to each site. The designation was made on the basis of a combination of land use and activities on the property containing the well and on adjoining properties. Wells that were designated "agricultural" included wells on farms that were currently engaged in crop production and domestic wells where land in crop production was immediately adjacent to the property. Wells that were designated "residential" included wells on farms that were no longer engaged in crop production and domestic wells in residential areas where cropland was not immediately adjacent to the site. Of the 50 water wells sampled, 13 were agricultural and 37 were residential.

Triazine herbicide residue concentrations, nitrate concentrations, and specific conductances were evaluated. Five separate hypotheses were evaluated by use of two separate statistical tests:

> Hypothesis I.--There is no significant difference in the distribution of detectable triazine herbicide residues in ground water between areas of agricultural and residential land use.
>
> Hypothesis II.--There is no significant difference in the triazine herbicide concentrations of ground water between areas of agricultural and residential land use.
>
> Hypothesis III.--There is no significant difference in the nitrate concentrations of ground water between areas of agricultural and residential land use.
>
> Hypothesis IV.--There is no significant difference in the presence of nitrate in excess of 10 mg/L as N in ground water between areas of agricultural and residential land use.
>
> Hypothesis V.--There is no significant difference in the specific conductance of ground water between areas of agricultural and residential land use.

The statistical tests used to evaluate the data were a chi-square test and a Mann-Whitney U test. The chi-square test was used to evaluate whether there is a significant difference in the incidence of detectable triazine herbicides and nitrate concentrations of greater than 10 mg/L as N in ground water from the agricultural and residential wells sampled (hypotheses I and IV). The Mann-Whitney U test was used to evaluate whether there is a significant difference in the triazine herbicide concentrations, nitrate concentrations, and specific conductances of ground water from the agricultural and residential wells sampled (hypotheses II, III, and V). All statistical tests were evaluated for significance at the 95-percent confidence level (p less than or equal to 0.05).

Triazine herbicide residues were detected at 0.1 μg/L (by use of ELISA) in samples from 30 of 37 residential wells and 12 of 13 agricultural wells sampled (Appendix 1). Triazine herbicide residues were detected at only slightly greater frequency in the agricultural wells sampled. From the sampled population, a chi-square test of hypothesis I indicates no significant difference ($p = 0.73$) in the distribution of detectable triazine herbicide residues in ground water from areas of agricultural and residential land use.

Samples from the agricultural and residential wells also had similar concentrations of triazine herbicide residues (table 16). A Mann-Whitney U test of hypothesis II indicates no significant difference ($p = 0.38$) in the concentrations of triazine herbicide residues in ground water from areas of agricultural and residential land use.

Median nitrate concentration in water from agricultural wells was slightly higher than for the residential wells (table 16). However, a Mann-Whitney U test of hypothesis III by use of these data indicates no significant difference ($p = 0.14$) in nitrate concentrations in ground water from areas of agricultural and residential land use.

Nitrate concentrations exceeded 10 mg/L as N (the USEPA MCL) in water from 4 of 37 residential wells and 3 of 13 agricultural wells (table 16). Water from a larger proportion of agricultural wells exceeded this MCL. However, a chi-square test of hypothesis IV indicates no significant difference ($p = 0.30$) in the presence of nitrate concentrations greater than 10 mg/L in ground water from areas of agricultural and residential land use.

Specific conductances of water from agricultural wells were appreciably higher than from residential wells (table 16). A Mann-Whitney U test of hypothesis V indicates that the specific conductance of ground water from areas of agricultural land use is significantly higher than that from areas of residential land use ($p = 0.045$). Because specific conductance is directly related to dissolved mineral content, it may be inferred that dissolved mineral content of ground water in areas of agricultural land use also is higher than in areas of residential land use, although determination of differences in the major-ion chemistry of ground water between the two land-use areas would be the most desirable means of verifying such a relation.

Table 16.—Summary of selected water-quality data for agricultural and residential land uses adjacent to wells, near Carlisle, Pa.

[µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligram per liter; µg/L, microgram per liter]

Land use adjacent to well	Number of observations	Median	Range	RSD[1] (percent)
		Specific conductance, in µS/cm		
All wells	50	657	203-1,860	41
Residential	37	617	203-1,030	31
Agricultural	13	810	359-1,860	46
		Nitrate, in mg/L as N		
All wells	50	6.6	.68-35	68
Residential	37	6.3	.68-16	47
Agricultural	13	7.3	1.6-35	89
		Triazines by immunoassay, in µg/L as atrazine		
All wells	50	.5	<.1-3.5	113
Residential	37	.4	<.1-3.5	115
Agricultural	13	.5	<.1-3.2	111

[1] Relative standard deviation is the standard deviation of the sample divided by the mean of the sample, in percent.

Water From Springs

Atrazine is the only herbicide detected in discharge from the springs that was reported in common use on row crops in the study area (table 7). No apparent seasonality was noted for atrazine concentrations in ground water discharged at the springs, such as a "spring flush" that occurs in many agricultural watersheds after herbicide applications at the beginning of the growing season (Thurman and others, 1991). Instead, atrazine was discharged from each of the springs in a narrow range of concentrations from 0.1 to 0.3 μg/L. These findings indicate that atrazine is persistent at trace concentrations in the ground-water resources of the study area and that current concentrations of atrazine may have resulted from many years of use in the area rather than from a single period of herbicide application. Atrazine-soil metabolite concentrations indicate a nonpoint source of atrazine that has reached the carbonate-rock aquifer by leaching through soil rather than by direct inflows of surface runoff through sinkholes.

The absence of any observable spring flush of agricultural chemicals in ground-water discharge at the springs may be due to (1) the large volume of water in the regolith and the aquifer relative to the annual fluxes of ground water through the aquifer, (2) the dominance of diffuse recharge, and (3) diffuse ground-water flow in the aquifer.

The herbicides cyanazine, alachlor, and metolachlor have been applied to corn acreage but were not detected in discharge at the springs. This finding indicates that either detectable concentrations of these compounds were not transported to the carbonate-rock aquifer on a basinwide scale or, if appreciable quantities were transported to the aquifer, they were not transported to the springs that were monitored. These observations also may indicate differences in the persistence and leachability of the various herbicides applied to agricultural land in the carbonate terrane of the Cumberland Valley.

Simazine was present at the MRL of 0.1 μg/L in a number of samples from spring Sp-34 and traces of simazine below the MRL were indicated in samples from each spring. The trace concentrations of simazine in all samples may also be from its past use in the area. The source of detectable concentrations of simazine in selected samples from spring Sp-34 is not known. Pesticide-use surveys indicate that simazine has been used on a low percentage of the total corn acreage in Pennsylvania (table 6). The use of simazine was not reported on agricultural land in the study area (table 7); however, the compound is recommended for control of annual grasses on corn acreage (Pennsylvania State University, 1991).

Hexazinone was detected in one sample of ground water discharged from Mount Rock Spring. The source of hexazinone in the sample is not known. The use of hexazinone in the study area was not reported, however, the compound is recommended for control of annual broadleaf weeds on alfalfa acreage (Pennsylvania State University, 1991). Hexazinone is also used on nonagricultural land. Pennsylvania Department of Transportation has used hexazinone along highways for control of thistles (Ed Meyers, Pennsylvania Department of Transportation, oral commun., 1991).

Prometon was detected in more than half of the samples collected from Alexanders Spring and in one sample collected from Mount Rock Spring. The use of prometon on agricultural land in the study area was not reported. Use of prometon on agricultural land is unlikely because it is a highly persistent, nonselective herbicide. However, prometon is licensed for industrial weed control in a formulation containing 25 percent active ingredient, and it is also packaged for residential use in a dilute formulation containing 1 to 2 percent active ingredient. Applications to residential areas or to road surfaces before paving are potential sources of prometon detected in water discharged at the spring sites. The association of prometon detections with water samples collected after periods of rainfall indicates that the prometon in the ground water may be from sources near the spring openings.

To estimate pesticide use, the land use and cropping patterns in the recharge areas to each spring head were assumed to be the same as for the whole surface watershed of the spring creeks (table 5). The percentages of row crops planted in corn and soybeans is assumed to be equal to countywide percentages (table 5). Herbicide use on row crops in the recharge areas to the springs, including the types of herbicide used and their application rates, was assumed to be the same as herbicide use on farms near the springs (table 7). Estimates of crop acreage and pesticide use in the ground-water recharge areas to Alexanders and Mount Rock Springs are summarized in table 17.

The total discharges of atrazine from Alexanders and Mount Rock Springs from May 1990 through April 1991, including the atrazine equivalent weights of DEA, are 4.6 and 5.2 lb. The atrazine discharge from Alexanders Spring is about 0.5 percent of the quantity applied annually to cropland in the recharge area to the spring (table 18). The atrazine discharge from Mount Rock Spring is about 0.6 percent of the quantity applied annually to cropland in the recharge area to the spring. From May 1990 through April 1991, the yields of nitrate nitrogen per acre of land in the recharge areas to Alexanders and Mount Rock Springs were 22 and 24 lb/acre. For the same period, yields of phosphorus per acre of land in the recharge areas to Alexanders and Mount Rock Springs were only 0.07 and 0.08 lb/acre.

Table 17.—Estimates of cropland acreage and herbicide use in the recharge areas to Alexanders and Mount Rock Springs, near Carlisle, Pa.

	Alexanders Spring	Mount Rock Spring
Recharge area (acres)	1,800	1,800
Cropland (acres)		
Planted in row crops	810	900
Planted in corn	770	850
Planted in soy beans	49	54
Herbicide use on row crops (pounds)		
Alachlor	400	440
Atrazine	730	810
Cyanazine	2,000	2,200
Dicamba	17	19
Paraquat	320	360
Linuron	68	80
Metolachlor	610	680
2,4-D	62	69
Total	4,207	4,658

Table 18.—Estimates of yield of nitrate, phosphorus, and atrazine to ground water in the recharge areas to Alexanders and Mount Rock Springs, near Carlisle, Pa.

[lb/acre, pound per acre]

Constituent	Alexanders Spring	Mount Rock Spring
Nitrate nitrogen, as N (lb/acre)	22	24
Phosphorus, as P (lb/acre)	.07	.08
Atrazine (lb/acre)	.002	.003
Percent of atrazine applied	.5	.6

SUMMARY AND CONCLUSIONS

Land use in the study area is a combination of agricultural, forested, and residential areas. Agricultural land is used for dairy, livestock, and crop production. Herbicides are used primarily for corn production; applications of cyanazine, atrazine, metolachlor, and alachlor account for about 90 percent of the total herbicide use in the study area.

Discharges from springs in the area vary seasonally and after rainfall or snowmelt. Discharge commonly increased within a day of receiving appreciable precipitation, but peak discharges often lagged the precipitation by 2 to 5 days. Discharge was greatest after precipitation during winter and early spring. Direct surface runoff to streamflow was minimal in the gaged reaches of area streams, so streamflow was composed of ground-water discharge at the spring openings. Median daily discharges at Alexanders Spring Creek, Mount Rock Spring Creek, and the unnamed tributary to Mount Rock Spring Creek were 3.8, 3.7, and 3.8 ft^3/s. Total discharge for a 1-year period from May 1990 through April 1991 was 1,390, 1,370, and 1,390 ft^3/s-days. Total discharge from Alexanders and Mount Rock Springs was 100 and 200 percent of total precipitation in the surface drainage areas to the springs, evidence that recharge areas to the springs exceed the surface drainage areas.

Temperature of water in springs and wells was near the mean annual air temperature, 11.3°C. Temperatures of ground-water discharge from Alexanders Spring and Mount Rock Spring ranged from 10.8 to 11.8°C, whereas temperatures of ground-water discharge from springs Sp-33 and Sp-34 ranged from 9.2 to 14.3°C. Temperature data indicate that Alexanders Spring and Mount Rock Spring are diffuse-flow springs and springs Sp-33 and Sp-34 are conduit-flow springs.

Specific conductance of discharge from Alexanders Spring increased slightly after precipitation. Discharge from Mount Rock Spring was variable because specific conductance increased after some storms and decreased after others. Specific-conductance data indicate that, for periods of appreciable discharge from Mount Rock Spring, spring Sp-33 is the point of resurgence of streamflow of Mount Rock Spring Creek. However, for periods of minimal flow, water quality of spring Sp-33 approaches that of spring Sp-34.

The pH of water from springs and wells ranged from 7.0 to 8.1. The pH of water from spring Sp-33 was typically higher than that for the other spring sites because of possible shifts in carbonate equilibria associated with degassing of carbon dioxide.

Total alkalinity of spring discharges was appreciable; the median concentrations in spring samples ranged from 209 mg/L at spring Sp-33 to 232 mg/L at Alexanders Spring. After precipitation, most changes in alkalinity of spring discharges were similar to changes in specific conductances.

The dissolved-solids concentration (sum of constituents) of water samples collected from each of the spring sites on April 4, 1991, ranged from 430 mg/L at spring Sp-33 to 460 mg/L at Alexanders Spring. Waters from the springs are similar in chemical composition; calcium and bicarbonate are the dominant ions, and magnesium, sulfate, nitrate, and chloride are present in lesser concentrations.

Calcium to magnesium molar ratios of discharge from Alexanders Spring and spring Sp-34 are indicative of aquifer materials consisting mostly of limestone, whereas calcium to magnesium ratios of discharge from Mount Rock Spring are indicative of aquifer materials consisting of a mixed sequence of limestone and dolomite.

Carbonate equilibria (carbonate mineral saturation indices and equilibrium partial pressures of carbon dioxide) of discharge from Alexanders Spring, Mount Rock Spring, and spring Sp-34 are typical of values for diffuse-flow springs and wells in other karst areas of Pennsylvania. Carbonate equilibria of spring Sp-33 are similar to base-flow samples from streams in other karst areas.

Four triazine herbicides and two atrazine soil metabolites were detected in spring discharges. Atrazine and the soil metabolite DEA were detected in discharge from each of the spring sites for the duration of the study period. Prometon and hexazinone were detected in discharge after some periods of precipitation. Simazine and the soil metabolite DIA were detected in a few spring-discharge samples. Atrazine concentrations did not vary appreciably in discharges from springs. A spring flush of atrazine was not observed in discharges from springs that followed atrazine applications. Median atrazine and DEA concentrations in samples from Alexanders Spring were 0.2 and 0.4 µg/L. Median atrazine and DEA concentrations in samples from Mount Rock Spring and spring Sp-33 also were 0.2 and 0.4 µg/L. Median concentrations of atrazine, DEA, and DIA in samples from spring Sp-34 were 0.2, 0.6, and 0.1 µg/L.

Triazine herbicide residues were detected in ground water from 42 of 50 wells sampled and analyzed by use of ELISA methods. The median concentration of triazine herbicides in ground-water samples from wells was similar to concentrations measured during the study period at each of the springs.

None of the samples analyzed contained concentrations of herbicides that exceeded the USEPA MCL's for lifetime exposure in public drinking water. The combined concentration of atrazine and atrazine soil metabolites were less than published guidelines for protection of sensitive aquatic plants.

Water-quality data were of acceptable precision and accuracy to estimate constituent discharges of atrazine, DEA, nitrate, and total phosphorus. Discharges of prometon from Alexanders Spring were estimated for two periods of record after precipitation.

The discharge of atrazine and its soil metabolite DEA were nearly constant at Alexanders Spring and increased at Mount Rock Spring during the study. The median daily discharge of DEA was twice that of its parent compound in both Alexanders Spring and Mount Rock Spring. Total discharge of atrazine and DEA at Alexanders Spring was 1.2 and 3.0 lb. Total discharge of atrazine and DEA at Mount Rock Spring was 1.5 and 3.2 lb. The discharge of prometon from Alexanders Spring was 0.18 lb and followed two periods of precipitation. Most changes in discharge of herbicide and metabolite from Alexanders and Mount Rock Springs were the result of changes in spring discharge and not changes in constituent concentrations. The greatest part of the atrazine and DEA discharge was in the winter and early spring rather than during the growing season.

Nitrate is the primary nitrogen-containing nutrient in ground water in the study area. Median nitrate concentration in water samples from Alexanders Spring, Mount Rock Spring, Sp-33, Sp-34, and wells were 5.3, 5.6, 5.4, 5.8, and 6.6 mg/L as N. Nitrate concentrations observed in spring discharge did not vary appreciably during the investigation. The median nitrate concentration of water samples from wells was greater than the median concentrations of samples from the springs.

Phosphorus was detected in all the springs at concentrations at or below the MRL for total phosphorus. The median concentration of total phosphorus in samples collected for each of the spring sites and for 50 water wells, was 0.02 mg/L as P.

In none of the water samples collected from springs did the concentration of nitrate exceed the USEPA MCL for public drinking-water supplies, however, ground water from 8 of 50 wells sampled exceeded this MCL. Nitrate concentrations in ground-water discharges to the limestone spring creeks are in excess of, and phosphorus concentrations are in the range of, commonly cited threshold levels for possible development of eutrophic conditions in lakes and streams.

The median daily discharge of nitrate from Alexanders and Mount Rock Springs was 94 lb as N, for each of the springs. Total discharge of nitrate from Alexanders Spring was 39,000 lb and from Mount Rock Spring was 43,000 lb. Increases in nitrate discharge at Mount Rock Spring were related to increases in discharge, not to increases in constituent concentration.

The median daily discharge of total phosphorus from Alexanders Spring and Mount Rock Spring was 0.3 and 0.2 lb as P. Total discharge of phosphorus from Alexanders and Mount Rock Springs was 120 and 130 lb. Slight variations in phosphorus discharge were related to both changes in phosphorus concentration and spring discharge.

Atrazine was the only herbicide in common use that was detected in spring discharges. The herbicides cyanazine, metolachlor, and alachlor are applied to agricultural land in the recharge areas to the springs but were not detected in water discharged from the springs. The use of hexazinone and simazine were not documented, but these herbicides have been recommended for weed control on some crops. Prometon is not normally applied to cropland, but it is available for use in nonselective control of vegetation in residential and industrial areas and roadways.

No physical or hydrologic boundaries accurately delineate recharge areas to the springs. Recharge areas were estimated from an available water balance. The estimated recharge area to each spring is about 1,800 acres. Corn acreage in the recharge areas to Alexanders and Mount Rock Springs is 770 and 850 acres. Total herbicide use in the recharge area to Alexanders Spring is estimated to be 4,200 lb, including 730 lb of atrazine. Total herbicide use in the recharge area to Mount Rock Spring is estimated to be 4,700 lb, including 810 lb of atrazine.

The combined atrazine and DEA discharges from Alexanders Spring from May 1990 through April 1991 are about 0.5 percent of the estimated quantity of atrazine applied annually to cropland in the recharge area to the spring. The combined atrazine and DEA discharges from Mount Rock Spring for the same period are about 0.6 percent of the estimated quantity of atrazine applied annually to cropland in the recharge area to the spring.

Yields of nitrate in the recharge areas to Alexanders and Mount Rock Springs are 22 and 24 lb/acre. Yields of total phosphorus in the recharge areas to these springs are 0.07 and 0.08 lb/acre.

There was no significant difference in either the distribution or the concentration of triazine herbicide residues in water from wells in areas of residential and agricultural land use. There also was no significant difference in nitrate concentrations and presence of nitrate in excess of 10 mg/L as N in water from wells in areas of residential and agricultural land use.

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APPENDIXES

Appendix 1.—Record of wells and springs near Carlisle, Pa.

[DDMMSS, degrees, minutes, and seconds; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; µg/L, micrograms per liter; H, hilltop; V, valley; F, flat; S, hillside; A, agricultural well site; R, residential well site; 371ELBK, Elbrook Formation; 371SDGV, Shadygrove Formation; 371ZLGR, Zullinger Formation; 367RCKR, Rockdale Run Formation; 367SFRS, Stoufferstown Formation; 367SNNG, Stonehenge Formation; --, no data]

USGS well or spring number	Latitude (DDMMSS)	Longitude (DDMMSS)	Township or borough	Aquifer code	Altitude of land surface (feet)	Topo-graphic setting	Land use near well	Depth of well (feet)	Bottom of casing (feet)	Date of site visit	Water level (feet)	Temper-ature (°C)	Specific conductance (µS/cm)	pH	Triazines by immunoassay (µg/L as atrazine)
							Wells								
461	400919	0771808	Dickinson	371SDGV	615	H	A	215	--	03-13-1991	92.6	11.7	886	7.3	0.3
549	401032	0771437	Dickinson	367RCKR	560	H	A	--	--	03-11-1991	59.0	11.9	572	7.6	3.2
838	400922	0771506	Dickinson	371ZLGR	545	F	R	80	--	03-11-1991	55.0	11.2	846	7.2	.5
839	400953	0771639	Dickinson	371SDGV	575	F	R	150	79	03-11-1991	52.5	11.9	574	7.5	.4
840	401011	0771705	Dickinson	367SNNG	575	F	R	113	--	03-12-1991	49.3	11.6	617	7.6	.5
841	401010	0771707	Dickinson	367RCKR	570	F	R	355	63	03-12-1991	49.5	11.8	433	7.4	.3
842	401033	0771628	Dickinson	367RCKR	555	F	R	300	--	03-12-1991	33.6	11.6	587	7.5	.1
843	400946	0771650	Dickinson	371SDGV	580	H	R	93	--	03-12-1991	70.0	11.3	483	7.7	<.1
844	400754	0771848	Penn	371ELBK	645	F	R	198	162	03-12-1991	93.0	10.8	251	7.9	.1
845	400708	0771855	Penn	371ELBK	650	F	R	144	125	03-12-1991	31.5	11.8	505	7.6	<.1
846	400707	0771855	Penn	371ELBK	650	F	R	246	120	03-12-1991	28.7	11.8	423	7.5	.1
847	400938	0771900	Dickinson	371SDGV	560	H	R	125	52	03-12-1991	35.9	11.8	585	7.7	<.1
848	400809	0771647	Dickinson	371ELBK	645	H	A	80	--	03-13-1991	--	10.8	531	7.7	.2
849	400808	0771620	Dickinson	371ELBK	590	F	R	--	--	03-13-1991	53.6	10.5	203	7.6	1.7
850	400829	0771612	Dickinson	371ELBK	620	H	R	180	109	03-13-1991	92.0	11.5	608	7.5	.5
851	400827	0771613	Dickinson	371ELBK	620	H	R	226	190	03-13-1991	90.7	11.0	478	7.6	.9
852	400813	0771732	Dickinson	371ELBK	610	F	R	360	108	03-13-1991	82.0	10.7	757	7.4	1.9
853	400818	0771730	Dickinson	371ELBK	600	H	R	288	20	03-13-1991	66.7	10.7	687	7.5	1.2
854	400838	0771602	Dickinson	371ELBK	610	F	R	108	--	03-13-1991	72.5	10.7	541	7.6	.2
855	400840	0771754	Dickinson	371ZLGR	665	H	A	350	--	03-13-1991	141.2	10.3	966	7.3	2.1
856	400945	0771611	Dickinson	371SDGV	555	H	A	--	--	03-14-1991	40.7	11.3	810	7.3	.2
857	401004	0771857	West Pennsboro	367SNNG	530	H	R	--	--	03-13-1991	30.7	11.1	577	7.7	.2
858	400958	0771839	West Pennsboro	367SNNG	555	H	R	123	100	03-14-1991	48.4	10.9	344	7.5	.5
859	401012	0771839	West Pennsboro	367SNNG	510	F	A	125	--	03-14-1991	11.3	8.9	359	7.5	.6
860	401110	0771841	West Pennsboro	367RCKR	500	F	A	170	--	03-14-1991	20.0	11.4	1,857	7.4	<.1
861	401013	0771916	West Pennsboro	367SNNG	550	F	R	98	57	03-14-1991	40.5	10.3	845	7.4	.3
862	400850	0771848	Penn	371ZLGR	655	H	R	212	156	03-14-1991	132.6	9.3	670	7.4	<.1

Appendix 1.—Record of wells and springs near Carlisle, Pa.--Continued

USGS well or spring number	Latitude (DDMMSS)	Longitude (DDMMSS)	Township or borough	Aquifer code	Altitude of land surface (feet)	Topo-graphic setting	Land use near well	Depth of well (feet)	Bottom of casing (feet)	Date of site visit	Water level (feet)	Temper-ature (°C)	Specific conductance (µS/cm)	pH	Triazines by immunoassay (µg/L as atrazine)
							Wells--Continued								
863	400800	0771920	Penn	371ELBK	625	V	A	150	–	03-14-1991	90.2	10.6	550	7.9	0.8
864	401005	0771321	South Middleton	367SFRS	540	F	R	150	83	03-20-1991	62.8	11.4	660	7.3	<.1
865	401008	0771332	South Middleton	367SNNG	540	F	R	600	–	03-20-1991	46.4	12.0	690	7.1	<.1
866	400958	0771407	Dickinson	367SFRS	550	F	R	–	–	03-20-1991	57.7	11.6	1,026	7.1	1.7
867	400923	0771502	Dickinson	371ZLGR	555	S	A	112	100	03-20-1991	61.7	11.6	748	7.5	.4
868	400920	0771440	Dickinson	371ZLGR	595	S	R	242	100	03-20-1991	118.7	11.6	498	7.6	2.5
869	400951	0771623	Dickinson	371SDGV	550	F	R	160	80	03-20-1991	40.2	11.0	488	7.7	1.4
870	400927	0771940	West Pennsboro	371SDGV	605	F	A	200	–	03-20-1991	72.0	12.0	1,408	7.1	3.2
871	400944	0772002	West Pennsboro	367SNNG	570	F	A	150	–	03-20-1991	42.6	11.3	896	7.0	1.5
872	400945	0772022	West Pennsboro	367RCKR	560	F	R	112	40	03-20-1991	38.1	12.2	630	7.4	.6
873	400939	0772017	West Pennsboro	367SNNG	575	S	A	150	–	03-20-1991	39.5	11.8	1,295	7.2	.5
874	400958	0771619	Dickinson	367SNNG	555	F	R	148	60	03-20-1991	39.9	12.0	526	7.4	.3
875	400746	0771719	Dickinson	371ELBK	650	H	R	150	128	03-21-1991	76.3	11.4	902	7.2	.5
876	400845	0772039	Penn	371ZLGR	585	F	R	100	50	03-21-1991	48.2	10.6	733	7.1	.3
877	400954	0771808	West Pennsboro	367SNNG	590	H	R	–	–	03-21-1991	94.8	11.9	908	7.0	3.5
878	400907	0771658	Dickinson	371ZLGR	650	H	R	375	38	03-21-1991	102.9	11.2	1,015	7.3	.2
879	400910	0771642	Dickinson	371SDGV	610	H	R	200	140	03-21-1991	94.6	12.4	829	7.4	2.4
880	400903	0771633	Dickinson	371ZLGR	615	S	R	198	140	03-21-1991	90.0	11.2	522	7.6	.9
881	400900	0771528	Dickinson	371ZLGR	585	F	R	275	168	03-21-1991	83.0	11.2	828	7.2	.9
882	401042	0771434	Dickinson	367RCKR	550	F	R	90	70	03-22-1991	–	11.9	653	7.3	<.1
883	401044	0771422	Dickinson	367RCKR	540	F	R	–	–	03-22-1991	–	10.8	833	7.0	.3
884	400748	0771620	Dickinson	371ELBK	615	H	A	232	–	03-21-1991	60.0	11.4	782	7.2	.2
885	400953	0771811	West Pennsboro	367SNNG	580	H	R	500	–	03-21-1991	69.3	11.8	944	7.0	1.1
							Springs								
Sp-16	401003	0771553	Dickinson	367SNNG	505	V	–	–	–	02-28-1991	–	11.3	576	7.4	
Sp-17	400941	0771859	West Pennsboro	371SDGV	525	V	–	–	–	02-28-1991	–	11.0	546	7.5	
Sp-33	401009	0771840	West Pennsboro	367SNNG	505	V	–	–	–	02-28-1991	–	11.2	543	8.1	
Sp-34	401009	0771840	West Pennsboro	367SNNG	505	V	–	–	–	02-28-1991	–	11.3	576	7.5	

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.

[All values are in micrograms per liter; Regular, regular sample; Interlab, interlaboratory quality-assurance sample, Sqrep, sequential replicate quality-assurance sample; standard, 1 microgram per liter atrazine standard; blank, double-distilled water blank; <, less than; --, not analyzed

Date of sampling	Type of sample	Ametryne, total	Alachlor, total recov-erable	Atrazine, total	Bromacil, water, whole, recov-erable	Butachlor, water, whole, recov-erable	Butylate, water, whole, recov-erable	Carboxin, water, whole, recov-erable	Cyanazine, total	Cycloate, water, whole recov-erable	Deethyl-atrazine, water, whole, total	Deisopropyl-atrazine water, whole, total	Diphenamid water, whole, recov-erable
							Mount Rock Spring (Sp-17)						
05-01-90	Regular	<0.10	<0.10	0.20	–	–	–	–	<0.10	–	0.2	<0.1	–
05-10-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
05-10-90	Interlab	–	–	.20	–	–	–	–	–	–	.4	.4	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.1	<.1	–
05-21-90	Interlab	–	–	.20	–	–	–	–	–	–	.4	.5	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-21-90	Interlab	–	–	.20	–	–	–	–	–	–	.5	.4	–
05-22-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-22-90	Interlab	–	–	.20	–	–	–	–	–	–	.5	.4	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-30-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.2	<.1	–
05-31-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
06-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
07-13-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
07-31-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
08-08-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
08-20-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
08-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
08-22-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.8	<.1	–
08-23-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.7	<.1	–
08-25-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
08-27-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
09-06-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	<.1	<.1	–
09-25-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
10-16-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
10-16-90	Seqrep	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
10-18-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.7	<.1	–
10-24-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
11-19-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
12-03-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-04-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
12-07-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-11-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
01-04-91	Regular						Low surrogate recovery						
01-29-91	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
02-11-91	Regular	<.10	<.20	.20	<0.2	<0.1	<0.1	<0.2	<.20	<0.1	.3	<.2	<0.1
02-11-91	Seqrep	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.3	<.2	<.1
02-28-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Hexazinone, water, whole, recoverable	Metolachlor, water, whole, total recoverable	Metribuzin, water, whole, total recoverable	Prometon, total	Prometryne, total	Propazine, total	Simazine, total	Simetryne, total	Terbacil, water, whole, recoverable	Trifluralin, total recoverable	Vernolate, water, whole, recoverable	Triazines, total, by immunoassay
				Mount Rock Spring (Sp-17)							
–	<0.1	<0.1	<0.1	<0.1	<0.10	<0.10	<0.1	–	<0.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	.2	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.3
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.3
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	–	–	–	–	–	–	–	–	–	–	.7
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	–	–	–	–	–	–	–	–	–	–	.5
–	–	–	–	–	–	–	–	–	–	–	.5
				Low surrogate recovery							.6
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.7
<0.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<0.2	<.10	<0.1	.4
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	–
–	–	–	–	–	–	–	–	–	–	–	.5

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Date of sampling	Type of sample	Ametryne, total	Alachlor, total recoverable	Atrazine, total	Bromacil, water, whole, recoverable	Butachlor, water, whole, recoverable	Butylate, water, whole, recoverable	Carboxin, water, whole, recoverable	Cyanazine, total	Cycloate, water, whole recoverable	Deethylatrazine, water, whole, total	Deisopropylatrazine water, whole, total	Diphenamid water, whole, recoverable
						Mount Rock Spring (Sp-17)–Continued							
04-02-91	Regular	<0.10	<0.20	0.20	<0.2	<0.1	<0.1	<0.2	<0.20	<0.1	0.6	<0.2	<0.1
04-02-91	Seqrep	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.5	<.2	<.1
04-21-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.3	<.2	<.1
05-07-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
05-22-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
						Alexanders Spring (Sp-16)							
05-01-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-10-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	.1	–
05-10-90	Interlab	–	–	.40	–	–	–	–	–	–	.3	<.1	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-21-90	Interlab	–	–	.30	–	–	–	–	–	–	.4	<.1	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.2	<.1	–
05-21-90	Interlab	–	–	.70	–	–	–	–	–	–	.4	<.1	–
05-22-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.2	<.1	–
05-22-90	Interlab	–	–	.20	–	–	–	–	–	–	.4	<.1	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-30-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-31-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
06-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.8	<.1	–
07-13-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
07-31-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.4	<.1	–
08-08-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
08-20-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	1.0	.2	–
08-21-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	.1	–
08-22-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	.1	–
08-23-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
08-25-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
08-27-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
09-06-90	Regular						Low surrogate recovery						
09-06-90	Seqrep	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
09-25-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.3	<.1	–
10-16-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
10-18-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.3	<.1	–
10-24-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
11-19-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
12-03-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-04-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
12-07-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-11-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
01-04-91	Regular						Low surrogate recovery						
01-13-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Hexazinone, water, whole, recov-erable	Metolachlor, water, whole, total recov-erable	Metribuzin, water, whole, total recov-erable	Prometon, total	Prometryne, total	Propazine, total	Simazine, total	Simetryne, total	Ter-bacil, water, whole, recov-erable	Trifluralin, total recov-erable	Vernolate, water, whole, recov-erable	Triazines, total, by immuno-assay
Mount Rock Spring (Sp-17)–Continued											
<0.2	<0.2	<0.1	<0.2	<0.1	<0.10	<0.10	<0.1	<0.2	<0.10	<0.1	0.4
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	–
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.7
–	–	–	–	–	–	–	–	–	–	–	.3
–	–	–	–	–	–	–	–	–	–	–	.5
Alexanders Spring (Sp-16)											
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
.2	<.1	<.1	.2	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	.3	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	1.0	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	1.2	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	.7	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	.6	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	.3	<.1	<.10	<.10	<.1	–	<.10	–	.6
–	<.1	<.1	.2	<.1	<.10	<.10	<.1	–	<.10	–	.2
				Low surrogate recovery							.2
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.5
–	<.1	<.1	.6	<.1	<.10	<.10	<.1	–	<.10	–	.7
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	–	–	–	–	–	–	–	–	–	–	.3
–	<.1	<.1	.3	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	–	–	–	–	–	–	–	–	–	–	.5
–	–	–	–	–	–	–	–	–	–	–	.4
				Low surrogate recovery							.5
–	–	–	–	–	–	–	–	–	–	–	.4

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Date of sampling	Type of sample	Ametryne, total	Alachlor, total recov-erable	Atrazine, total	Bromacil, water, whole, recov-erable	Butachlor, water, whole, recov-erable	Butylate, water, whole, recov-erable	Carboxin, water, whole, recov-erable	Cyanazine, total	Cycloate, water, whole recov-erable	Deethyl-atrazine, water, whole, total	Deisopropyl-atrazine water, whole, total	Diphenamid water, whole, recov-erable
Alexanders Spring (Sp-16)–Continued													
01-29-91	Regular	<0.10	<0.10	0.10	–	–	–	–	<0.10	–	0.5	<0.1	–
02-11-91	Regular	<.10	<.20	.20	<0.2	<0.1	<0.1	<0.2	<.20	<0.1	.3	<.2	<0.1
02-28-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
04-02-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.4	<.2	<.1
04-21-91	Regular	<.10	<.20	.10	<.2	<.1	<.1	<.2	<.20	<.1	.3	<.2	<.1
05-07-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
05-22-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
Sp-33													
05-01-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-10-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	.1	–
05-10-90	Interlab	–	–	.20	–	–	–	–	–	–	.4	<.1	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-21-90	Interlab	–	–	.20	–	–	–	–	–	–	.8	<.1	–
05-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-21-90	Interlab	–	–	.30	–	–	–	–	–	–	.6	<.1	–
05-22-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
05-22-90	Interlab	–	–	.20	–	–	–	–	–	–	.4	<.1	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
05-29-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
05-30-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.2	<.1	–
05-31-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
06-21-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.1	<.1	–
07-13-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
07-31-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.8	.1	–
08-08-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.7	.1	–
08-23-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.7	.1	–
08-25-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
08-27-90	Regular	<.10	<.10	.10	–	–	–	–	<.10	–	.6	<.1	–
10-16-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
10-18-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
10-24-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.4	<.1	–
11-19-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.1	.8	–
12-03-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-04-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
12-07-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-11-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
01-04-91	Regular	<.10	<.10	<.20	–	–	–	–	<.10	–	.4	<.1	–
01-29-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
02-11-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
02-28-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
04-02-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.5	<.2	<.1
04-21-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.3	<.2	<.1

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Hexazinone, water, whole, recov- erable	Metolachlor, water, whole, total recov- erable	Metribuzin, water, whole, total recov- erable	Prometon, total	Prometryne, total	Propazine, total	Simazine, total	Simetryne, total	Ter- bacil, water, whole, recov- erable	Trifluralin, total recov- erable	Vernolate, water, whole, recov- erable	Triazines, total, by immuno- assay
					Alexanders Spring (Sp-16)–Continued						
–	<0.1	<0.1	<0.1	<0.1	<0.10	<0.10	<0.1	–	<0.10	–	0.4
<0.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<0.2	<.10	<0.1	.4
–	–	–	–	–	–	–	–	–	–	–	.4
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.3
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.5
–	–	–	–	–	–	–	–	–	–	–	.2
–	–	–	–	–	–	–	–	–	–	–	.4
					Sp-33						
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	–	–	–	–	–	–	–	–	–	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.3
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.3
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.3
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.7
–	–	–	–	–	–	–	–	–	–	–	.7
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	–	–	–	–	–	–	–	–	–	–	.5
–	–	–	–	–	–	–	–	–	–	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.6
–	–	–	–	–	–	–	–	–	–	–	.7
–	–	–	–	–	–	–	–	–	–	–	.3
–	–	–	–	–	–	–	–	–	–	–	.5
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.5
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.7

Date of sampling	Type of sample	Ametryne, total	Alachlor, total recov-erable	Atrazine, total	Bromacil, water, whole, recov-erable	Butachlor, water, whole, recov-erable	Butylate, water, whole, recov-erable	Carboxin, water, whole, recov-erable	Cyanazine, total	Cycloate, water, whole recov-erable	Deethyl-atrazine, water, whole, total	Deisopropyl-atrazine water, whole, total	Diphenamid water, whole, recov-erable
						Sp-33–Continued							
05-07-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
05-22-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
						Sp-34							
08-20-90	Regular	<0.10	<0.10	0.20	–	–	–	–	<0.10	–	1.2	0.2	–
08-21-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	.1	–
08-22-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.9	.3	–
08-23-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.9	.4	–
08-25-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	.1	–
08-27-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
09-06-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.4	<.1	–
09-25-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.4	<.1	–
10-16-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.7	.1	–
10-18-90	Regular	<.10	<.10	.30	–	–	–	–	<.10	–	.7	.2	–
10-24-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	<.1	–
11-19-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	1.3	.2	–
12-03-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-04-90	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.3	<.1	–
12-07-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
12-11-90	Regular	–	–	–	–	–	–	–	–	–	–	–	–
01-04-91	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.5	.1	–
01-29-91	Regular	<.10	<.10	.20	–	–	–	–	<.10	–	.6	<.1	–
02-11-91	Regular	<.10	<.20	.20	<0.2	<0.1	<0.1	<0.2	<.20	<0.1	.3	<.2	<0.1
02-28-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
04-02-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.5	<.2	<.1
04-21-91	Regular	<.10	<.20	.20	<.2	<.1	<.1	<.2	<.20	<.1	.4	<.2	<.1
05-07-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
05-22-91	Regular	–	–	–	–	–	–	–	–	–	–	–	–
						Quality-Assurance Samples							
Standard													
09-06-90	QA	<.10	<.10	.80	–	–	–	–	<.10	–	<.1	<.1	–
Blank													
09-06-90	QA	<.10	<.10	<.10	–	–	–	–	<.10	–	<.1	<.1	–
Blank													
02-11-91	QA	<.10	<.20	<.10	<.2	<.1	<.1	<.2	<.20	<.1	<.2	<.2	<.1

Appendix 2.—Herbicide concentrations in water from springs near Carlisle, Pa.–Continued

Hexazinone, water, whole, recov-erable	Metolachlor, water, whole, total recov-erable	Metribuzin, water, whole, total recov-erable	Prometon, total	Prometryne, total	Propazine, total	Simazine, total	Simetryne, total	Ter-bacil, water, whole, recov-erable	Trifluralin, total recov-erable	Vernolate, water, whole, recov-erable	Triazines, total, by immuno-assay
					Sp-33–Continued						
–	–	–	–	–	–	–	–	–	–	–	0.4
–	–	–	–	–	–	–	–	–	–	–	.5
					Sp-34						
–	<0.1	<0.1	<0.1	<0.1	<0.10	<0.10	<0.1	–	<0.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	.10	<.1	–	<.10	–	–
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.8
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.8
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.8
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.8
–	<.1	<.1	<.1	<.1	<.10	.10	<.1	–	<.10	–	.7
–	<.1	<.1	<.1	<.1	<.10	.10	<.1	–	<.10	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.8
–	–	–	–	–	–	–	–	–	–	–	.8
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.2
–	–	–	–	–	–	–	–	–	–	–	.5
–	–	–	–	–	–	–	–	–	–	–	.5
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	.4
<0.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<0.2	<.10	<0.1	.5
–	–	–	–	–	–	–	–	–	–	–	.4
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.4
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	.6
–	–	–	–	–	–	–	–	–	–	–	.4
–	–	–	–	–	–	–	–	–	–	–	.5
					Quality-Assurance Samples						
Standard											
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	1.9
Blank											
–	<.1	<.1	<.1	<.1	<.10	<.10	<.1	–	<.10	–	<.1
Blank											
<.2	<.2	<.1	<.2	<.1	<.10	<.10	<.1	<.2	<.10	<.1	–

Appendix 3.—Selected physical properties of water from springs and unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa.

[°C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 degrees Celsius; mg/L, milligrams per liter; --, not determined]

Date of measurement	Temperature (°C)	Specific conductance (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
		Mount Rock Spring (Sp-17)		
05-01-90	–	528	7.1	208
05-04-90	–	528	7.2	208
05-10-90	11.1	528	7.3	218
05-21-90	11.1	531	7.3	206
05-21-90	11.1	531	7.3	199
05-22-90	11.1	532	7.2	214
05-29-90	11.1	524	7.4	199
05-29-90	11.1	528	7.6	213
05-30-90	11.1	532	7.4	206
05-31-90	11.1	534	7.4	206
06-21-90	11.1	533	7.5	208
07-09-90	11.1	529	–	–
07-11-90	11.1	532	7.3	207
07-13-90	11.1	532	7.3	207
07-31-90	11.1	532	7.3	201
08-08-90	11.1	529	–	–
08-20-90	11.2	535	7.3	196
08-21-90	11.1	535	7.3	205
08-22-90	11.8	495	7.3	198
08-23-90	11.1	535	7.3	209
08-25-90	11.1	540	7.2	205
08-27-90	11.1	535	7.4	205
09-06-90	11.1	517	7.3	209
09-25-90	11.2	540	7.4	206
10-16-90	11.1	533	7.4	213
10-18-90	11.1	535	7.3	204
10-24-90	11.1	542	7.4	–
11-19-90	11.0	547	7.4	214
12-03-90	10.8	532	7.3	202
12-04-90	10.9	545	7.2	204
12-07-90	11.0	546	7.4	214
12-11-90	10.9	538	7.4	205
01-04-91	11.0	548	7.5	203
01-13-91	11.0	549	7.4	206
01-29-91	11.0	551	7.6	212
02-11-91	11.0	548	7.5	215
02-28-91	11.0	546	7.5	–
04-02-91	11.0	544	7.5	–
04-10-91	11.1	544	7.4	212
04-21-91	10.9	546	7.5	208
05-07-91	11.1	540	7.5	209
05-22-91	–	515	7.2	207

Appendix 3.—Selected physical properties of water from springs and unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa.–Continued

Date of measurement	Temperature (°C)	Specific conductance (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
		Alexanders Spring (Sp-16)		
05-04-90	–	545	7.2	240
05-10-90	–	560	7.2	240
05-21-90	11.3	573	7.2	232
05-21-90	11.3	572	7.2	234
05-22-90	11.3	572	7.4	238
05-29-90	11.3	573	7.2	232
05-29-90	11.2	586	7.2	236
05-30-90	11.2	596	7.1	230
05-31-90	11.2	597	7.2	244
06-21-90	11.3	564	7.5	238
07-09-90	11.3	551	–	–
07-11-90	11.3	550	7.3	226
07-13-90	11.3	554	7.2	247
07-31-90	11.3	555	7.3	214
08-08-90	11.3	549	–	–
08-20-90	11.3	560	7.3	220
08-21-90	11.3	560	7.3	226
08-22-90	11.3	565	7.2	226
08-23-90	11.3	575	7.2	235
08-25-90	11.3	575	7.2	230
08-27-90	11.3	575	7.2	231
09-06-90	11.3	558	7.2	225
09-25-90	11.3	560	7.3	223
10-16-90	11.2	570	7.4	238
10-18-90	11.2	577	7.2	223
10-24-90	11.2	600	7.3	–
11-19-90	11.2	566	7.3	242
12-03-90	11.2	573	7.1	227
12-04-90	11.2	588	7.1	238
12-07-90	11.2	591	7.2	235
12-11-90	11.2	574	7.4	230
01-04-91	11.2	591	7.4	236
01-13-91	11.2	586	7.3	235
01-29-91	11.2	590	7.5	241
02-11-91	11.3	576	7.2	229
02-28-91	11.3	576	7.4	–
04-02-91	11.2	582	7.1	231
04-10-91	11.3	580	7.5	239
04-21-91	11.2	575	7.4	241
05-07-91	11.3	572	7.4	232
05-22-91	–	550	7.4	225

Appendix 3.—Selected physical properties of water from springs and unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa.–*Continued*

Date of measurement	Temperature (°C)	Specific conductance (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
		Sp-33		
05-01-90	–	502	7.5	218
05-04-90	–	512	7.6	212
05-10-90	12.8	510	7.7	206
05-21-90	12.5	500	7.6	206
05-21-90	12.3	528	7.7	218
05-22-90	11.8	533	7.6	219
05-29-90	12.1	528	7.8	216
05-29-90	12.0	471	7.7	190
05-30-90	11.4	533	7.6	214
05-31-90	11.1	537	7.8	201
06-21-90	11.9	534	7.8	213
07-09-90	13.3	528	–	–
07-11-90	13.5	533	7.6	203
07-13-90	12.8	518	7.6	204
07-31-90	14.3	534	7.4	201
08-08-90	12.4	615	–	–
08-23-90	11.9	620	7.1	242
08-25-90	13.2	545	7.5	207
08-27-90	13.5	560	7.4	217
09-06-90	11.9	605	–	–
10-16-90	12.5	528	7.6	215
10-18-90	12.2	542	7.7	210
10-24-90	11.4	553	7.7	–
11-19-90	9.40	548	7.8	209
12-03-90	9.20	515	7.6	196
12-04-90	10.1	543	7.8	204
12-07-90	10.2	545	7.9	207
12-11-90	9.90	538	7.9	202
01-04-91	10.5	547	8.0	204
01-13-91	10.1	547	7.9	213
01-29-91	10.2	551	7.9	216
02-11-91	10.8	546	7.8	212
02-28-91	11.2	543	8.1	–
04-02-91	11.2	540	8.0	214
04-10-91	11.9	535	7.8	208
04-21-91	10.8	539	7.7	211
05-07-91	11.3	537	7.9	206
05-22-91	–	528	7.8	199

Appendix 3.—Selected physical properties of water from springs and unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa.–Continued

Date of measurement	Temperature (°C)	Specific conductance (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
		Sp-34		
08-20-90	11.2	610	7.2	223
08-21-90	11.2	615	7.1	231
08-22-90	11.2	615	7.2	226
08-23-90	11.1	630	7.1	250
08-25-90	11.1	650	7.1	250
08-27-90	11.1	655	7.2	250
09-06-90	11.1	609	7.2	234
09-25-90	11.3	640	7.2	236
10-16-90	11.1	658	7.1	257
10-18-90	11.3	642	7.1	241
10-24-90	11.2	616	7.2	–
11-19-90	10.2	590	7.3	224
12-03-90	10.1	565	7.2	212
12-04-90	10.6	592	7.2	224
12-07-90	10.7	602	7.3	228
12-11-90	10.5	578	7.4	229
01-04-91	10.8	595	7.5	222
01-13-91	10.6	591	7.4	231
01-29-91	10.6	590	7.6	232
02-11-91	10.9	584	7.5	232
02-28-91	11.3	576	7.5	–
04-02-91	11.1	584	7.7	224
04-10-91	11.9	573	7.4	231
04-21-91	10.9	574	7.5	224
05-07-91	11.3	573	7.5	224
05-22-91	–	540	7.5	216

Appendix 3.—Selected physical properties of water from springs and unnamed tributary to Mount Rock Spring Creek near Mount Rock, Pa.–Continued

Date of measurement	Temperature (°C)	Specific conductance (µS/cm)	pH	Alkalinity (mg/L as $CaCO_3$)
01569740 - Unnamed tributary to Mount Rock Spring Creek				
05-21-90	12.1	560	–	–
05-22-90	11.6	576	–	–
05-29-90	11.8	552	–	–
05-29-90	11.7	517	–	–
05-30-90	11.3	566	–	–
05-31-90	11.2	571	–	–
06-21-90	12.2	558	–	–
07-09-90	13.7	555	–	–
07-11-90	13.6	560	–	–
07-13-90	12.5	544	–	–
08-14-90	–	600	–	–
08-23-90	–	625	–	–
08-25-90	12.5	620	–	–
08-27-90	12.6	625	–	–
09-06-90	–	607	–	–
10-16-90	12.1	604	–	–
10-18-90	12.4	589	–	–
10-24-90	11.4	579	–	–
11-19-90	9.4	563	–	–
12-03-90	9.2	545	–	–
12-04-90	9.8	555	–	–
12-07-90	9.9	566	–	–
12-11-90	9.7	554	–	–
01-04-91	10.2	562	–	–
01-13-91	9.8	556	–	–
01-29-91	10.1	561	–	–
02-11-91	10.5	559	–	–
02-28-91	11.0	549	–	–
04-02-91	11.1	552	–	–
04-10-91	12.0	549	–	–
04-21-91	10.8	555	–	–
05-07-91	11.4	555	–	–
05-22-91	–	530	–	–