Ground-Water Resources and the Hydrologic Effects of Petroleum Occurrence and Development, Warren County, Northwestern Pennsylvania

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In cooperation with the
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Conversion Factors and Datum

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m^2)
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
barrel (bbl), (petroleum, 1 barrel = 42 gal)	0.1590	cubic meter (m^3)
gallon (gal)	3.785	liter (L)
Flow rate		
gallon per minute (gal/min)	0.06309	liter per second (L/s)
gallon per day (gal/d)	0.003785	cubic meter per day (m^3/d)
million gallons per day (Mgal/d)	0.04381	cubic meter per second (m^3/s)
Specific capacity		
gallon per minute per foot [(gal/min)/ ft)]	0.2070	liter per second per meter [(L/s/m]
Hydraulic gradient		
foot per mile (ft/mi)	0.1894	meter per kilometer (m/km)
Transmissivity*		
foot squared per day (ft^2/d)	0.09290	meter squared per day (m^2/d)

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = (°F - 32) / 1.8$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Horizontal coordinate information is referenced to the North American Datum of 1988 (NAVD 88).

Altitude, as used in this report, refers to distance above the vertical datum.

*Transmissivity: The standard unit for transmissivity is cubic foot per day per square foot times foot of aquifer thickness [(ft^3/d)/ft^2]ft. In this report, the mathematically reduced form, foot squared per day (ft^2/d), is used for convenience.

Specific conductance is expressed in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25°C).

Concentrations of chemical constituents in water are expressed either in milligrams per liter (mg/L) or micrograms per liter (µg/L). Concentrations of radionuclides in water are given in pico-curies per liter (pCi/L).

Wells and springs listed in this report are identified by unique numbers assigned by the USGS. The prefix "Wr" in the well numbers indicates the wells are in Warren County. The prefix "Wr SP" in the spring numbers indicates the springs ("SP") are in Warren County. Well and spring numbers are assigned when the sites are initially inventoried and are not necessarily sequential.

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Abstract

Most of the northern half of Warren County is in the Northwestern Glaciated Plateau Section of the Appalachian Plateaus Physiographic Province. The remainder of the county is in the High Plateau Section. The glacial outwash sand and gravel hydrogeologic unit is the most extensively used unconsolidated unit for water supply in Warren County because it is capable of yielding large amounts of water to wells and it is situated in populated valleys. The median well yield for 47 specific-capacity tests was 25 gal/min (gallons per minute); well yields ranged from 2 to 1,600 gal/min. Acceptable well yields for domestic supply also are available from other unconsolidated hydrogeologic units including alluvium, colluvium, glacial drift, ice-contact stratified sand and gravel, and undifferentiated alluvium and glacial lacustrine. The median well yields during specific-capacity tests of wells in these five hydrogeologic units ranged from 8 to 18 gal/min.

A comparison of the median specific capacities for wells in the unconsolidated and bedrock hydrogeologic units indicates that wells completed in the outwash sand and gravel hydrogeologic unit had the highest median specific capacity of 6.0 (gal/min)/ft (gallons per minute per foot); specific capacities for wells completed in the outwash sand and gravel unit ranged from 0.14 to 300 (gal/min)/ft. For wells completed in the bedrock hydrogeologic units, their corresponding median specific capacities are Pottsville Group, 0.5 (gal/min)/ft; Shenango Formation, 0.44 (gal/min)/ft; Cuyahoga Formation, 0.24 (gal/min)/ft; Knapp Formation, 0.45 (gal/min)/ft; Corry Sandstone through Riceville Formation, 0.67 (gal/min)/ft; Riceville Formation, 1.5 (gal/min)/ft; Oswayo Formation, 0.07 (gal/min)/ft; Venango Formation, 1.0 (gal/min)/ft; and Chadakoin Formation, 0.71 (gal/min)/ft.

Annual precipitation at Warren for the years 1984-87 was above the long-term mean. The 4-year average of the annual hydrologic balance for 1984 indicated 40 percent of the precipitation was lost to evapotranspiration. Ground-water discharge, commonly defined as base flow, accounted for about 29 percent of precipitation, and surface runoff made up 31 percent. During 1984-87, ground-water discharge made up from 47 to 50 percent of total runoff or streamflow. In 1990, ground-water withdrawals made up only 1.3 percent [13.8 Mgal/d (million gallons per day)] of the total withdrawals for the county. However, ground water is the predominant source for domestic, municipal, and industrial water supplies in Warren County outside of the larger cities.

Concentrations of dissolved iron exceeded the U.S. Environmental Protection Agency (USEPA) Secondary Maximum Contaminant Level (SMCL) of 300 µg/L (micrograms per liter) in 95 of the 266 wells sampled (36 percent). The Riceville Formation is the only hydrogeologic unit in which ground-water samples did not exceed the SMCL for dissolved iron. Median concentrations of dissolved iron ranged from 50 µg/L in samples from the Shenango and Riceville Formations to 2,350 µg/L in samples from the alluvium and glacial lacustrine, undifferentiated unit. Concentrations of dissolved manganese exceeded the USEPA SMCL in samples from 155 of the 260 wells sampled (60 percent). Samples from at least 40 percent of the wells in each hydrogeologic unit exceeded the SMCL for dissolved manganese, indicating a widespread problem in the county. The median concentrations of dissolved manganese ranged from 25 µg/L in the glacial outwash sand and gravel, the Cuyahoga Formation, and the Riceville Formation to 450 µg/L in the alluvium and glacial lacustrine, undifferentiated.

Concentrations of total dissolved solids exceeded the USEPA SMCL of 500 mg/L in samples from 9 of the 257 wells sampled (3.5 percent). The median concentrations ranged from 66 mg/L in samples from the Pottsville Group to 308 mg/L in samples from the Catskill and Venango Formations. Most samples contained less than 1,000 mg/L total dissolved solids and were classified as fresh water. Samples from only three wells had concentrations classified as slightly saline (2,140, 1,440, and 1,730 mg/L).

Samples collected from 233 water wells were analyzed for arsenic, and 38 samples (16 percent) exceeded the USEPA Maximum Contaminant Level (MCL) of 10 µg/L. Twenty-two of the water wells with arsenic concentrations exceeding the MCL were domestic supply wells. Twenty-five of these 38 wells (66 percent) were completed in the glacial outwash sand and gravel hydrogeologic unit.

In Warren County, ground water moves within and through two general flow systems—a shallow, local aquifer system with active flow, and a deeper, regional aquifer system

at flow rates that are slow relative to the circulation of water in the shallow system. In the glaciated area, the upper part of the local flow system is made up of saturated unconsolidated deposits. About 95 percent of the ground-water circulation in the county takes place within the local flow system. The depth of the active local flow system is variable, however, as the bottom of the system parallels the bedrock surface and is about 150 to 175 feet beneath the land surface. The base of the regional aquifer system is unknown. Ground-water flow patterns in the unglaciated area are similar to flow patterns in the glaciated area. In the unglaciated plateau, however, bedrock hillsides and hilltops are covered with colluvium instead of till and other glacial deposits.

Topographic position affects the water levels in wells. Hilltops are areas of aquifer recharge, and valley bottoms are areas of aquifer discharge. Water levels ranged from above land surface in some valley wells to more than 200 feet below land surface in hilltop wells. The average depth to water was 25-30 feet below land surface in a valley wells to about 50 feet below land surface for hilltop wells. Hydrographs from monitor wells in the county illustrated seasonal variation in the water levels. Water levels generally declined during the summer and early fall as a result of evapotranspiration and continuing ground-water discharge from the aquifer.

The development of ground water in Warren County for domestic and municipal use has been difficult because of very shallow petroleum reservoirs in parts of the ground-water system. Analysis of water samples from wells in the Tidioute area indicated poor water quality that would require costly treatment prior to use. Excessive concentrations of iron, manganese, aluminum, chloride, dissolved solids, and methane negated the use of these wells for public supply.

In Pleasant Township, a major subsurface natural gas migration in 1983 resulted in high concentrations of natural gas observed in water wells, a spring, lake, and tributary stream of Chapman State Park. Although natural gas concentrations in ground-water diminished over time in ground water, several wells continued to experience severe natural-gas contamination in 1986. A well containing water that was saturated with natural gas was reported to have exploded, and another well suddenly discharged water from a vent pipe after pumping. Samples from wells in this area had elevated levels of arsenic and barium. Thirty-two of 68 samples collected in this area equalled or exceeded the USEPA MCL of 10 µg/L for arsenic. Barium concentrations ranged from 40 to 1,660 µg/L but were below the USEPA MCL of 2,000 µg/L. It is not know if these elevated concentrations were the result of gas migrations, but the concentrations were higher than those reported for samples collected from other wells in the county that draw water from the same hydrogeologic units.

Introduction

Ground water[1] is the predominant source of domestic, municipal, and industrial water supplies in Warren County, northwestern Pennsylvania. Several incidents of ground-water contamination in Warren County during the 1970s and early 1980s promoted an awareness of the importance of ground water to the citizens of the county. Data on the quality of ground water and a description of the hydrogeologic units tapped for water supply were lacking for extensive areas of Warren County. To address these data and information needs, a cooperative study was initiated in 1984 by the Warren County Commissioners, the Pennsylvania Department of Conservation and Natural Resources (PaDCNR) Bureau of Topographic and Geologic Survey, and the U.S. Geological Survey (USGS) to investigate the ground-water resources of Warren County.

Purpose and Scope

This report describes and evaluates the hydrogeology and ground-water resources of Warren County, Pa. Special emphasis is placed on the comparison of the results of laboratory analyses of ground-water samples collected throughout the county to drinking-water standards. Data and interpretation in part of this report are devoted to increasing the understanding of ground-water quality as it is affected by development of oil and gas resources in the county. Information in this report will assist in the development and management of the ground-water resources in Warren County.

Ground-water data were collected from 1984 through 1987. Water samples collected from mostly domestic water wells and springs throughout Warren County were analyzed for major anions, cations, and trace elements. Well yields and specific capacities reported by well drillers were compiled and statistically analyzed. Water-level recorders were installed on several water wells tapping different **aquifers** to monitor responses to precipitation and to examine seasonal changes in ground-water levels. To accurately delineate aquifers, the geologic mapping of surficial deposits and **bedrock** was revised and updated by field observations and interpretation of geophysical logs and aerial photographs. At several sites having ground-water contaminants at concentrations above drinking-water standards, data collection was expanded to include geophysical logging, **aquifer testing**, and collection of periodic samples to assess changes in ground-water quality with time. The quality/composition of water from wells and springs in oil and gas fields was compared to that of ground water outside oil and gas fields to determine the effect of oil and gas development on ground-water quality. In addition, brines from oil wells were analyzed, and concentrations of constituents of **dissolved** natural gas were measured in water samples from domestic water wells. The fresh and saline ground water in abandoned oil wells

[1]Bold text is defined in the glossary.

were analyzed for a wide variety of constituents including volatile organic compounds (VOCs). Reconnaissance sampling of ground water for analyses of radionuclides—including radon, radium, and uranium—was conducted in 1987 at a limited number of water wells, springs, and abandoned oil and gas wells; the results of these analyses were compared to drinking-water standards.

Previous Investigations

A cursory evaluation of the ground-water resources of northwestern Pennsylvania including Warren County was performed by Leggette (1936). In this report, rudimentary chemical analyses of ground-water samples from six water wells in Warren County tapping gravel (four wells), sandstone (one well), and shale (one well) indicated concentrations of total **dissolved solids** less than 200 parts per million and concentrations of iron ranging from 0.02 to 0.84 parts per million. In Grand Valley in southwestern Warren County, a compilation of depths of salt water obtained from drillers of oil and gas wells shows many observations of salt water encountered at depths less than 300 ft below land surface (Leggette, 1936).

Adjacent to Warren County, the ground-water resources of the Allegheny River Basin in Chautauqua and Cattaraugus Counties, N.Y., were described by Frimpter (1974) with specific attention given to the determination of perennial yields of water from major aquifers. Southeast of Warren County, in the Clarion River Basin, ground-water resources were evaluated in two reports by Buckwalter and others (1979, 1981).

The effects of natural gas and oil production on ground water in western New York were described by Crain (1969). The findings generally are applicable to Warren County because of similar petroleum reservoirs and common oil and gas production practices. Crain (1969, p. 6) discusses crude oil and associated salt water contaminating ground water from leaking production and abandoned wells, pipelines, and oil separation tanks. Crain (1969, p. 13) suggested that crude oil and salt water problems in the ground-water system generally were undocumented and unnoticed because oil field areas were either unpopulated or lightly populated, with little ground-water development. In valleys with few domestic water wells, Crain (1969, p. 10-13) noted that the **casing** of water wells completed in deep **water-bearing zones** in unconsolidated deposits probably cased off any crude oil floating on the shallow **water table** and little, if any, oil would enter the water supply. Crain (1969, p. 8) also stated that because salt water and natural gas are so widely distributed at depth in western New York, it commonly is difficult to tell how much of the pollution from salt water and gas is a naturally occurring phenomenon and how much has been facilitated by gas-well drilling and production.

As part of the National Water-Quality Assessment, the USGS, in cooperation with the Kentucky Geological Survey and the University of Kentucky, completed an investigation of the effects of oil production on surface-water and ground-water resources in the Kentucky River Basin (Evaldi and Kipp, 1991). This research has transfer value because the hydrogeologic setting in the Kentucky River Basin is similar in some respects to that in Warren County, as are some of the oil-production practices. Discharge of oil-field brines from oil separators was suspected to be a major source of dissolved constituents to streams that drain oil-production areas in the Kentucky River Basin. Increases in concentrations of barium, bromide, chloride, sodium, and strontium in the main stem of the Kentucky River Basin downstream of river mile 270 are attributed to drainage from oil-production watersheds. Ground-water samples obtained from the oil-production watersheds, however, indicated shallow ground water in valley **alluvium** was probably not widely affected by oil-production activities (Evaldi and Kipp, 1991, p. 54). The discharge of bromide into surface water used as sources of public supply is of particular concern because of the possible role of bromide in the formation of carcinogenic trihalomethanes that can form during the disinfection of water supplies with chlorine (Evaldi and Kipp, 1991, p. 40).

Several reports have included data on the quality of ground-water samples collected in Warren County. In a report for the Pennsylvania Department of Environmental Resources (PaDER) entitled "Subsurface Gas Blowouts in Pennsylvania and Elsewhere," Walker (1984) describes the subsurface gas blowout at Chapman State Park and vicinity in Warren County in 1983. Descriptions of gas explosions and concentrations of methane in ground water are noted. In another report for PaDER, Waite and Blauvelt (1983) describe several case histories of ground-water contamination in Warren County, including crude-oil contamination in three water wells in Glade Township, chloride contamination of ground water in Triumph Township, and leakage of crude oil and brines from abandoned oil wells beneath the surface and near the shoreline of Allegheny Reservoir. Detailed chemical analyses of five samples of brine from Upper Devonian oil sands in Warren County are included in a thesis by Dresel (1985) concerning the geochemistry of oil field brines from western Pennsylvania; these brine analyses are presented in a later section of this report.

Description of the Study Area

Geography

Warren County is an area of 885 mi^2 in northwestern Pennsylvania (fig. 1). The population in 2000 was 43,863 (U.S. Census Bureau, 2005). Warren is the county seat. There are 6 boroughs (fig. 1) and 22 townships (appendix) in Warren County. The largest borough in population is Warren Borough (10,259), followed by Sugar Grove (1,870), Youngsville (1,834), Tidioute (792), Clarendon (564), and Bear Lake (193) (U.S. Census Bureau, 2005). The names and locations of the 7½-minute quadrangles for Warren County are shown in figure 2.

Winters are cold and summers are mild in Warren County. December, January, and February temperatures average below

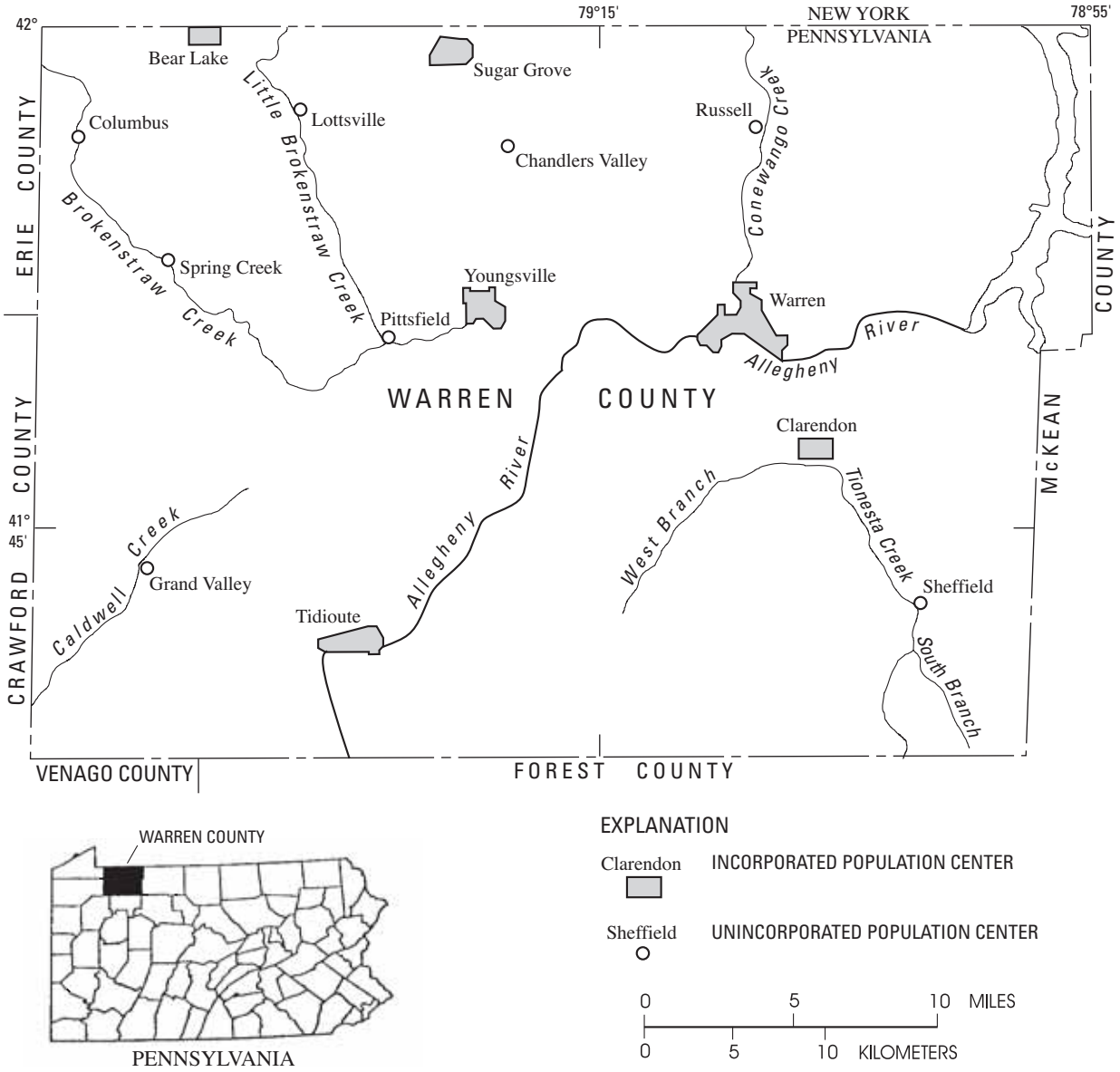


Figure 1. Population centers, boroughs, and major streams in Warren County, Pennsylvania.

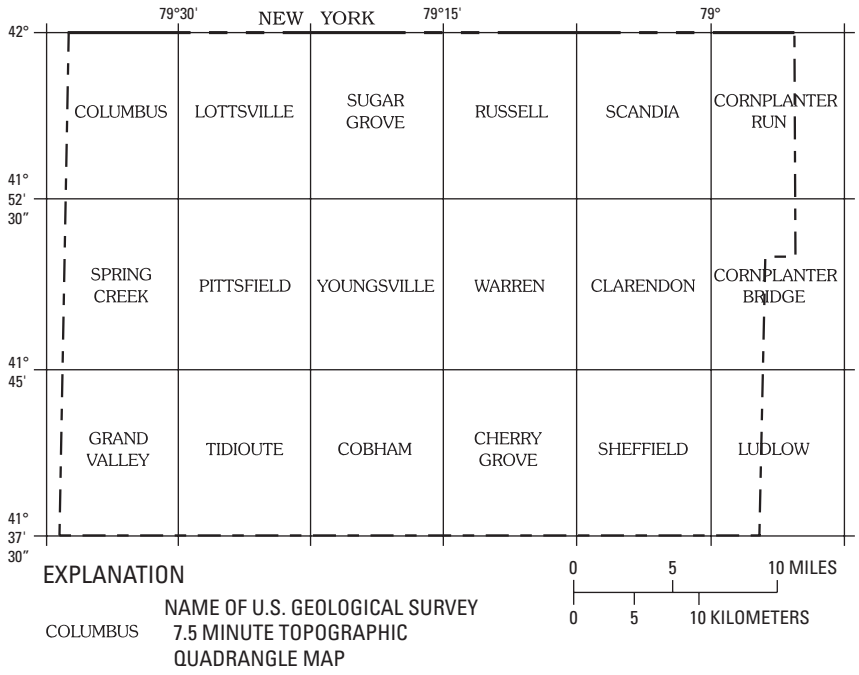


Figure 2. Names and locations of the 7½-minute quadrangle maps in Warren County, Pennsylvania.

freezing (32°F). Average daily temperatures in June, July, and August are above 65°F. From precipitation data compiled during 1926-94 at Warren, the average annual precipitation is 43.7 in. (Pennsylvania State Climatologist, 2005). Northwestern Warren County generally averages slightly more annual precipitation than other areas of Warren County. For northwestern Warren County, precipitation estimates are derived mostly from long-term data collected in adjacent Erie County at the town of Corry, 1.5 mi west of the northwestern boundary of Warren County. Long-term precipitation data from Corry indicate the average annual precipitation is about 46.0 in. In Warren County, precipitation generally occurs during all months. However, the average monthly precipitation is greatest during the summer, followed by spring and fall with about equal quantities of precipitation, and winter months with slightly less precipitation than spring or fall. At Warren, the average seasonal snowfall is 67 in. Heavy rains, which can occur at any time of the year, and severe thunderstorms in summer sometimes cause flash flooding, especially in narrow valleys.

Warren County is drained by the Allegheny River and its tributaries. Tributary streams with large drainage areas in Warren County include Conewango Creek, Brokenstraw Creek, Caldwell Creek, Little Brokenstraw Creek, and West Branch Tionesta Creek (fig. 1). A major feature of northeastern Warren County is the Allegheny Reservoir formed by Kinzua Dam on the Allegheny River 9 mi upstream from Warren. The drainage area of Allegheny Reservoir is 2,180 mi^2. The multipurpose reservoir provides flood control, low-flow augmentation, recreation, and electric power generation. Prior to impoundment, many but not all of the existing oil and gas wells were plugged and sealed to prevent migration of oil, natural gas, and brines to the reservoir.

Soils

Comprehensive information on the soils of Warren County is available from the Soil Conservation Service (U.S. Department of Agriculture, Soil Conservation Service, 1985). The soils in most of the county are acidic, with the exception of a few alkaline soils in valleys. These alkaline soils were formed in glacial outwash or glacial **till**. Parent materials of soils on uplands are mostly acid shale, acid siltstone, and acid sandstone. Soil reaction, which is a measure of acidity or **alkalinity** of a soil expressed in **pH** units, commonly ranged from a pH of 3.6 to 5.5 in upland soils.

Soils may have considerable influence on ground-water systems. Soils and their respective permeability characteristics may limit or promote infiltration of precipitation to the ground-water system. Relatively impermeable zones in the soil horizon, including fragipans, may limit or generally prevent selected contaminants, such as brine from oil wells disposed on land surface, from entering into the ground-water system (Auchmoody and Walters, 1988, p. 280).

A primary characteristic of many of the soils in Warren County is the presence of a fragipan (U.S. Department of Agriculture, Soil Conservation Service, 1985), a loamy, subsurface horizon low in permeability, low to moderate in clay content, and high in silt or very-fine sand content. The very low perme-

ability of fragipans causes perching of water, particularly in the spring and early summer. This condition generally ends by late summer when roots have extracted most of the water during the growing season. In areas of soil fragipans, this perching of ground water may lower the ground-water discharge by raising the **evapotranspiration** component compared to areas with permeable soils.

Hydrologic Setting

Water enters the hydrologic system in Warren County mostly as precipitation or streamflow. A large part of the water entering the hydrologic system moves out of the county within a few days. Significant streamflow inputs to Warren County from New York are the Allegheny River and Conewango Creek (fig. 1).

Streamflow or that part of precipitation that appears in streams has a distinct seasonal variation; the period of highest streamflow generally is late winter or early spring (February to April), and the period of lowest streamflow is late summer and early fall (August to October). The month with the highest streamflow is generally the result of antecedent conditions including saturation of soil, near maximum ground-water storage, and the accumulation of snow from one month melting and appearing as streamflow the following month. As spring and summer progress, declining streamflow generally is caused by 1) warmer weather accompanied by a higher evaporation rate, 2) more dense land cover and a resulting higher rate of transpiration by plants, and 3) rainfall occurring as storms of short duration, allowing the soils to dry out between events, thus reducing the chance of runoff during subsequent precipitation.

Some of the annual precipitation percolates downward under gravity to the zone of saturation and becomes ground water. Ground water is that subsurface water in the saturated zone—the zone in which all the spaces or interstices in the rocks are filled with water under pressure equal to or greater than atmospheric pressure. Ground water eventually discharges to land surface from springs, flowing wells, or as ground-water discharge to streams.

Precipitation

Annual precipitation data at Warren for the calendar years 1984 through 1987 (table 1) (National Climatic Data Center, 1984-87) indicated above-average precipitation compared to the annual mean of 42.89 in. for the period of 1951-87. A similar analysis of precipitation data for Corry in adjacent Erie County, Pa., for the years 1984-87 also shows above-average precipitation for the 4-year period.

Annual Hydrologic Balance

The annual hydrologic balance or water budget is the quantitative expression of the parts of the hydrologic cycle. The quantity of water entering a ground-water basin is balanced with the quantity of water leaving the basin. An equation expressing this balance can be expressed as follows:

$$P = R_g + R_s + ET + S \,, \qquad (1)$$

where

P is precipitation,
R_g is ground-water discharge to streams,
R_s is surface runoff,
ET is evaporation and transpiration, and
S is change in ground-water storage.

Table 1. Annual precipitation at Warren and Corry, Pennsylvania, 1984-87.

Calendar year	Annual precipitation, in inches[1]	Departure from mean annual precipitation for period of record 1951-80
	Warren	
1984	51.30	+8.41
1985	46.45	+3.56
1986	43.63	+.74
1987	45.03	+2.14
	Corry	
1984	50.66	+4.26
1985	50.77	+4.37
1986	50.31	+3.91
1987	46.40	0

[1] National Climatic Data Center, 1984-87.

Annual hydrologic balances were computed for **water years** 1984-87 for the Brokenstraw Creek Basin. No significant quantities of surface water or ground water are transferred across the basin boundaries of Brokenstraw Creek. Thus, the water-balance equation is used to compute the major components of the water budget. Streamflow was obtained from the USGS **streamflow-gaging station** on Brokenstraw Creek at Youngsville (station number 03015500). The drainage area of Brokenstraw Creek at this site is 321 mi^2. Streamflow at this site is not regulated by releases from reservoirs as is the case with the other streamflow-gaging stations in Warren County. Hydrograph separation into the ground-water and surface-runoff components was accomplished with the computer program HYSEP (Sloto and Crouse, 1996), which uses hydrograph-separation methods developed by Pettyjohn and Henning (1979). During 1984-87, ground-water discharge made up from 47 to 50 percent of total runoff or streamflow (table 2). Comparisons of ground-water discharge to total runoff can be made for areas with different geologic settings. Comparison of ground-water discharges were made in Ohio by Pettyjohn and Henning (1979)

Table 2. Ground-water discharge computed from streamflow hydrograph of Brokenstraw Creek at Youngsville, Pennsylvania.

Water year	Precipitation, in inches[1]	Ground-water discharge		
		Inches	Percentage of total runoff	Percentage of precipitation
1984	52.75	13.94	47	26
1985	44.55	13.38	50	30
1986	51.50	15.80	49	31
1987	47.15	13.99	49	30
4-year average	48.99	14.28	49	29

[1]Mean of the annual precipitation recorded at Corry and Warren for the water year.

for 1) till-covered regions, 2) till and streamside-outwash regions, and 3) outwash-covered regions. For years with normal precipitation, ground-water discharges were highest in outwash-covered regions and lowest in till-covered regions. Tills of low permeability generally result in greater surface runoff than permeable outwash.

Estimates of the annual precipitation for the Brokenstraw Creek Basin were derived from the mean of the precipitation at Corry and Warren. The precipitation data from Corry roughly estimate the precipitation of the western part of the Brokenstraw Creek Basin. The Warren data represent an approximation of the precipitation falling on the eastern half of the basin. Because of insufficient data, S is disregarded and assumed to be zero in the hydrologic balance equation.

Evapotranspiration (ET) is the evaporation of water from land and water surfaces plus transpiration by vegetation. The amount of ET in a water year varies with the length of the growing season, average temperature, amount and timing of precipitation, wind velocity, and humidity. The amount of water lost to ET was determined by computing the difference between precipitation and streamflow ($ET = P - [R_g + R_s]$).

The 4-year average annual hydrologic budget for 1984-87 (table 3) indicates that 40 percent of precipitation is lost to evapotranspiration. Ground-water discharge to streams, commonly defined as **base flow**, accounts for about 29 percent of precipitation, and surface runoff makes up 31 percent.

The Brokenstraw Creek Basin is a till and streamside-outwash region. For this geologic setting in Ohio during normal precipitation years, Pettyjohn and Henning (1979) noted the average ground-water discharge was 51 percent of total streamflow and ranged from 39 to 63 percent. The 4-year average ground-water discharge of 49 percent for the Brokenstraw Creek Basin compares favorably to the data generated in Ohio by Pettyjohn and Henning (1979).

Physiography and Geologic Setting

Warren County is within the Northwestern Glaciated Plateau Section and the High Plateau Section of the Appalachian Plateaus Physiographic Province (fig. 3). The Northwestern Glaciated Plateau was sculpted into broad, rounded hills and wide, drift-filled valleys by several cycles of continental glaciation. These glaciers transported and eventually deposited substantial quantities of unconsolidated sand, silt, and clay, as well as smaller amounts of gravel, cobbles, and boulders, over most of northwestern Warren County. **End moraine** and ice-contact deposits mark the terminus of the most recent ice advance. These deposits are shown on maps of surficial geology (appendix). Outwash, ice-contact, and alluvial deposits commonly are mined for aggregates. Although the High Plateau Section

Table 3. Annual hydrologic budget for the Brokenstraw Creek Basin, Pennsylvania, 1984-87.

Water year	Precipitation (P), in inches[1]	=	Ground-water discharge R_g, in inches	+	Surface runoff R_s, in inches	+	Evapotranspiration ET, in inches
1984	52.75	=	13.94	+	15.53	+	23.28
1985	44.55	=	13.38	+	13.36	+	17.81
1986	51.50	=	15.80	+	16.61	+	19.09
1987	47.15	=	13.99	+	14.39	+	18.77
4-year average	48.99	=	14.28	+	14.97	+	19.74
Percentage of total (4-year average)	100		29		31		40

[1]Mean of the annual precipitation recorded at Corry and Warren for the water year.

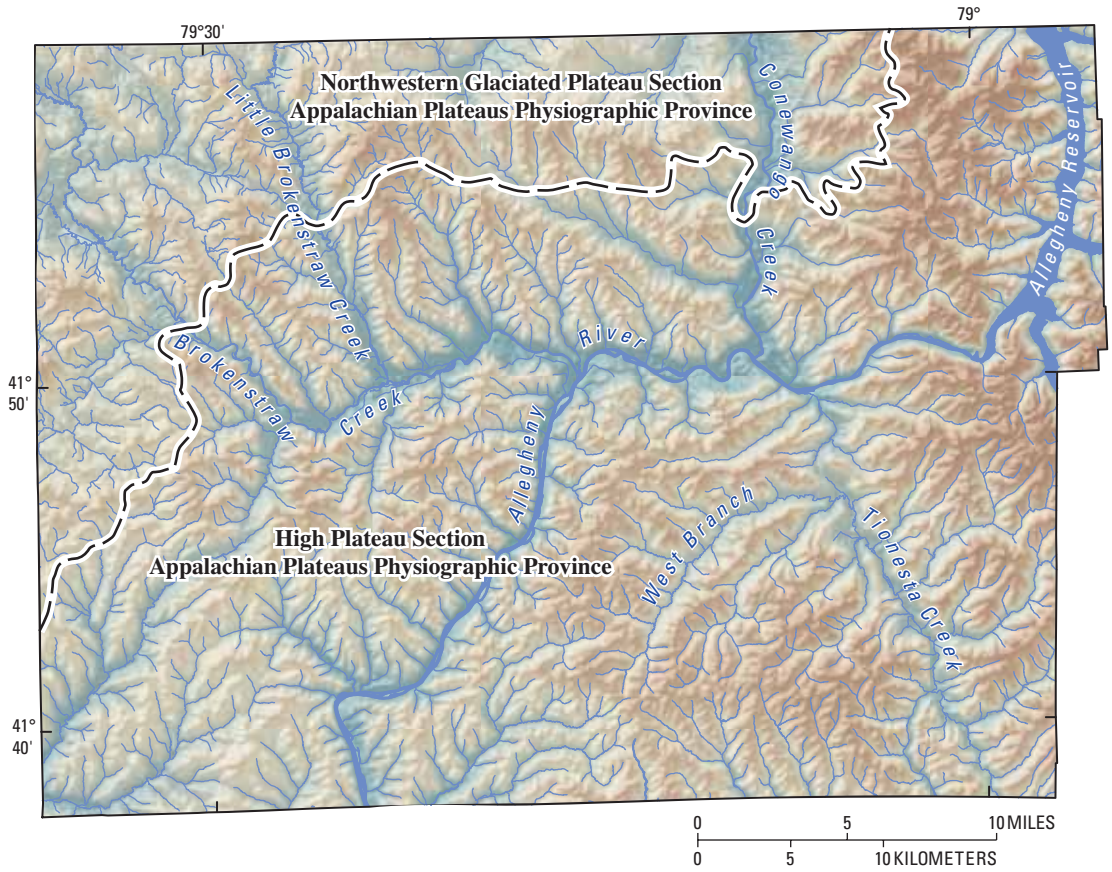


Figure 3. Physiographic provinces and major stream drainages of Warren County, Pennsylvania (modified from Berg and others, 1989).

escaped extensive effects of continental ice sheets, the landscape was altered by environmental impacts from it, including fluvial erosion, periglacial mass wasting, and deposition of glacially transported sediments. Deep angular valleys and rounded to flat hills characterize the topography in this area. Clay deposits make up the glacial lake deposits in the southwestern corner of the county. Repetitive cycles of freezing and thawing fragmented the exposed bedrock and soil. Large blocks of Pottsville sandstone and conglomerate, separated from ridge-capping outcrops and slid by gravity downslope on a bed of finer colluvium, litter the slopes and valleys in the High Plateau Section. Most valleys in the High Plateau Section contain substantial thicknesses of colluvium, commonly covered with a thin blanket of alluvium derived by reworking native and glacially derived material. Stream valleys, which were enlarged during glaciation, now harbor streams that meander on top of thick accumulations of unconsolidated sediments.

Beneath the unconsolidated material are sedimentary rocks of Pennsylvanian, Mississippian, and Upper Devonian age (figs. 4 and 5). The geology and structure of these rocks are shown in a series of page-size quadrangle maps in the appendix of this report. The page-size maps were derived from the bedrock geologic and structure-contour maps of the county by Dodge and Glover (1995). The oldest and most commonly recognized bedrock unit exposed in the county is the Chadakoin **Formation**, which crops out in the valley bottoms in the northern part of the county (appendix). The Chadakoin Formation comprises predominantly fine-grained (siltstone and shale) marine clastics, including a thick purplish-pink sequence reported by oil and gas well drillers as the "pink rock." The Chadakoin Formation is most significant as a stratigraphic marker separating the deeper (older) Bradford group from the overlying Venango Formation and the younger Devonian units. In the eastern part of the county, where the Catskill Formation has been mapped, the bedrock units exhibit the telltale red color and plant debris characteristic of terrestrial origin; whereas, in the western part of the county, fossil bivalves confirm a facies change to the marine origins of the laterally equivalent Venango Formation. This continental to marine transitional environment was ideal for deposition of coarse-grained clastics such as sandstone and conglomerate. These coarse-grained sedimentary units later became the reservoirs for the oil and natural gas that have sustained the economy for much of northwestern Pennsylvania for the past 100 years.

In the southern two-thirds of the county, the Devonian units are overlain by the shale and siltstone of the Mississippian Cuyahoga Formation and above that the sandstone-dominated Shenango Formation. Throughout most of the county, the ridge tops are capped unconformably with the sandstone and conglomerate of the Pennsylvanian Pottsville Group.

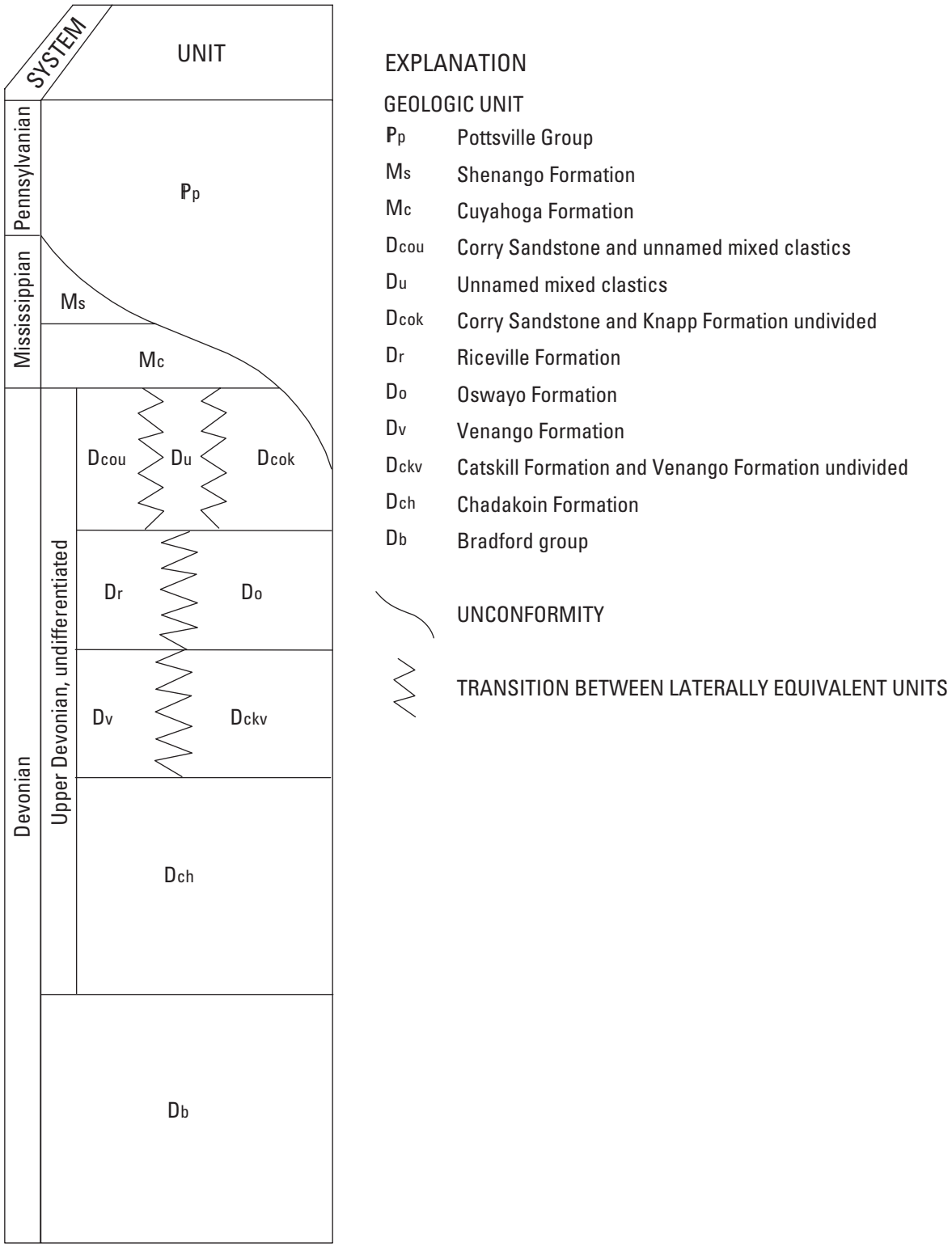
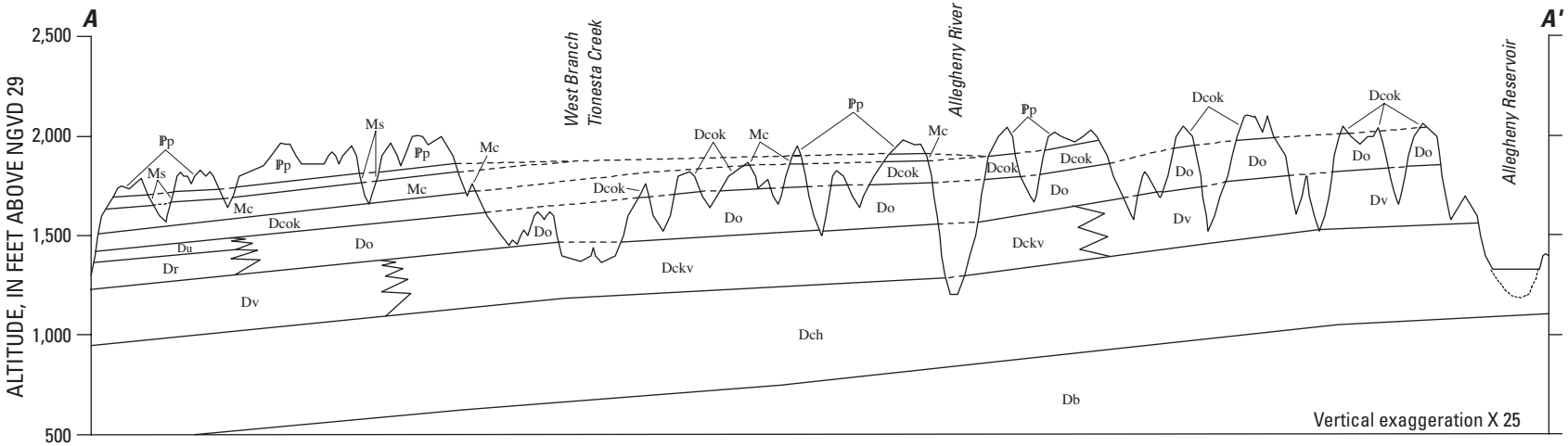


Figure 4. Stratigraphic column for Warren County (modified from Dodge, 1992, fig. 1).



EXPLANATION

GEOLOGIC UNITS

Pp	Pottsville Group
Ms	Shenango Formation
Mc	Cuyahoga Formation
Du	Unnamed mixed clastics
Dcok	Corry Sandstone and Knapp Formation undivided
Dr	Riceville Formation
Do	Oswayo Formation
Dv	Venango Formation
Dckv	Catskill Formation and Venango Formation undivided
Dch	Chadakoin Formation
Db	Bradford Group

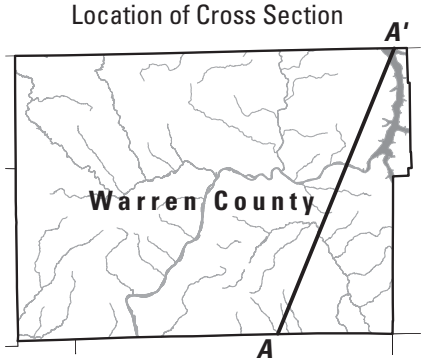


Figure 5. Geologic cross section, Warren County, Pennsylvania. (Geology from Dodge and Glover, 1995)

Geologic Structure

After deposition of the Mississippian units but before the deposition of the overlying Pottsville Group, the bedrock was uplifted, tilted to the south, and then eroded. Today, the Mississippian and older bedrock units strike west-northwest and **dip** to the southwest an average of 22 ft/mi (appendix). The Pottsville Group was deposited unconformably on top of this eroded and deformed landscape. The contact between the Pottsville Group and the underlying older units also dips to the southwest but at slightly less than 22 ft/mi. As a consequence, the Pottsville Group rests on younger sediments in southern Warren County than in the north. These relations are illustrated in figure 5, a roughly north-south trending geologic cross section of the county. In this illustration, the Group truncates the Shenango Formation in the vicinity of the West Branch of Tionesta Creek and has removed the last vestiges of the Cuyahoga Formation near the Allegheny River.

Stratigraphy and Oil and Gas Geology

The distribution of the principal oil or gas producing fields in Warren County are shown in fig. 6. Historically, the Bradford group and Venango Formation have produced the most significant quantities of oil and gas in the county. Since the mid-1970s, gas production from the much deeper (5,000-6,000 ft below land surface) Silurian-aged Medina Group has been most productive (Harper, 1992, p. 49). Petroleum production from the Venango Formation is confined to the southwestern part of the county, where the unit is below local stream levels. Production from the deeper Bradford group is concentrated in a 6-mi wide band trending southeast-northwest through the city of Warren. Although the Bradford group and Medina Group are below the depth of the fresh ground-water system throughout the county, disposal of brine and other wastes associated with well drilling and petroleum production pose a risk to the fresh ground-water system if they are not disposed of in an environmentally sound manner.

Primary and secondary petroleum recovery from the major oil and gas reservoirs is, for the most part, long past (Harper and Cozart, 1988, p. 4). Most of present-day production is from stripper wells, wells that produce only a few barrels of oil per month. Occasionally new fields are discovered. The Elkhorn Run Field, near Chapman State Park, was not discovered until the 1970s. Because production is so small and costs are so high, however, the pumping of stripper wells typically is limited to periods when the price of crude oil is high.

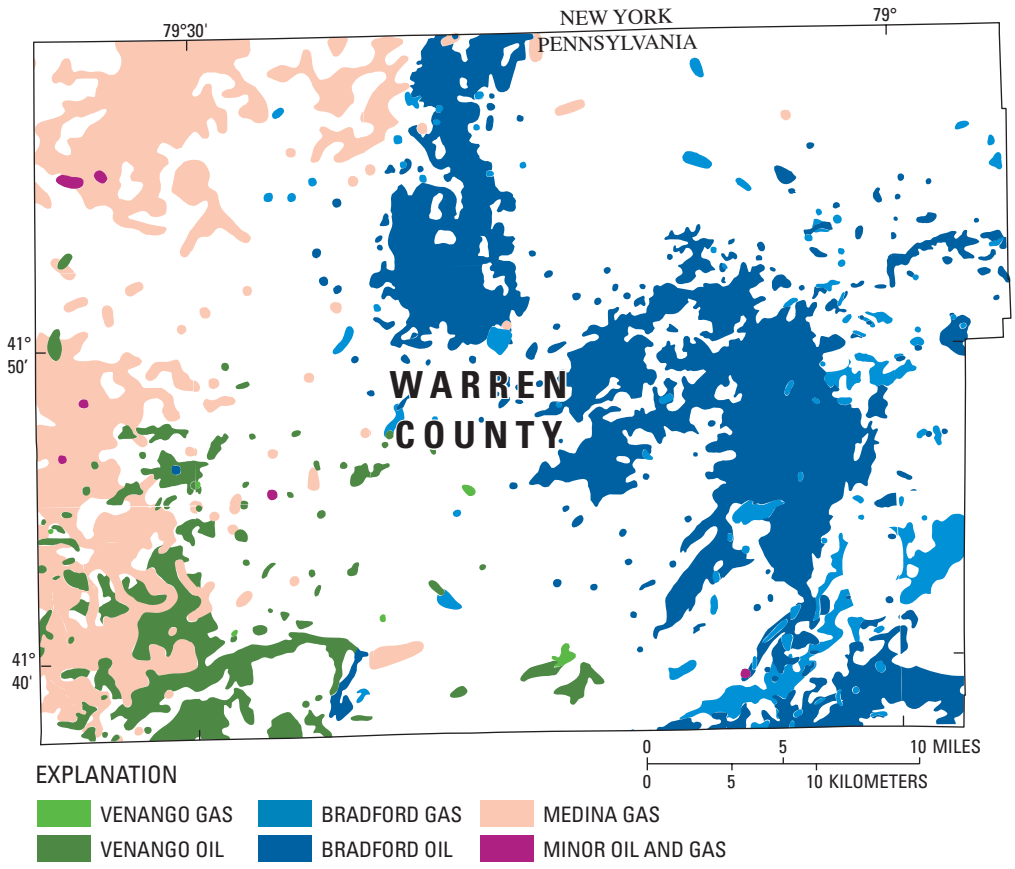


Figure 6. Distribution of principal oil and gas producing fields in Warren County, Pennsylvania (modified from Harper, 1992, p. 48).

Water Use

Total surface-water and ground-water withdrawals in Warren County were greater in 1984 than in 1990 (table 4). The surface-water withdrawals for hydroelectric power decreased substantially from 3,460 Mgal/d in 1984 to 984 Mgal/d in 1990. Data are presented for 1984 and 1990 because these years are the approximate beginning and ending years of data collection for this study.

Ground water includes water from wells and springs. Surface water includes water from streams, lakes, or reservoirs. "Withdrawal" refers to the volume of water pumped from a surface-water or ground-water supply.

"Consumptive use" is the difference between the amount of water delivered and the amount released at a facility. Examples of consumptive loss are incorporation into a product or evaporation. Withdrawals usually are measured and reported to PaDEP; consumptive-use data generally are estimated. For public supply, consumptive use commonly is estimated as 10 percent of the total water withdrawn for public supply (Loper and others, 1989, p. 10).

Wells of public-supply systems provided water for about 20,000 residents in Warren County in 1984. The surface-water withdrawal from George Run (Triumph Township) by the Southwest Warren County Municipal Authority served a population of about 1,000 residents of Tidioute Borough and a part of Limestone Township. In 1984, domestic wells supplied the remainder of the population of Warren County, about 26,700 residents (Loper and others, 1989, p. 13). In 1984, about 98 percent of the total population of Warren County was served by ground water from public supply wells or springs or individual homeowner wells and springs.

Residential water use on a per-capita basis varies extensively. Outdoor consumption varies seasonally, including water used for lawn irrigation, swimming pools, and car washing. Statistics compiled for Pennsylvania on per-capita water use indicated that individuals supplied by municipal systems averaged 110 gal/d; those supplied by individual wells and springs averaged 50 gal/d (Ernst and Young, Inc., 1990, p. 57). The water use of 50 gal/d for individual homeowner wells was estimated by Loper and others (1989, p. 11).

Table 4. Water withdrawals and consumptive use for Warren County, Pennsylvania, 1984 and 1990.

Major water-use category	Withdrawals, in million gallons per day			Consumptive use, in million gallons per day
	Ground water	Surface water	Total	
		[1]1984		
Public supply	4.31	0.12	4.43	0.44
Self-supplied domestic use	1.34	[2]0	1.34	.13
Self-supplied industry	8.85	.03	8.88	2.65
Power—fossil fuel	0	89	89	.21
Power—hydroelectric	0	3,460	3,460	0
Mining	.15	.77	.92	.04
Livestock	.42	.02	.44	.33
Total	15.1	3,550	3,560	3.80
		[3]1990		
Public supply	4.68	.32	5.00	.50
Self-supplied domestic use	1.08	[2]0	1.08	.11
Self-supplied industry	7.70	.04	7.74	1.31
Power—fossil fuel	0	64.3	64.3	.72
Power—hydroelectric	0	984	984	0
Mining	not reported	.73	.73	.05
Livestock	.37	.06	.43	.32
Total	13.80	1,050	1,060	3.01

[1]Loper and others, 1989.

[2]Assumed to be all ground water.

[3]Modified from S. Hoffman, U.S. Geological Survey, written commun., 1993.

Water withdrawals and sources in 1984 for major public supplies are presented in table 5. Slight variations in definitions of public-supply systems account for the small difference in the total average daily withdrawal for public supply systems in table 4 and the total average daily withdrawal for major public water supplies in table 5.

Data on well yields, specific capacities, locations, and construction for public supply and domestic wells inventoried are provided in Moore and Buckwalter (1996).

Table 5. Water withdrawals and sources for major public water supplies in Warren County, Pennsylvania, in 1984.

Public supply	Average daily withdrawals in 1984[1], in gallons per day	Water source(s)[2]	Remarks
Chapman State Park	Annual withdrawals not metered	1 well	Bedrock well taps Venango Formation. See "Chapman State Park Case Study" for additional information.
Clarendon Water Company	150,000	2 wells	Bedrock wells tap Venango Formation.
Grand Valley Water Cooperative	5,500	1 spring	Hydrogeologic unit of spring is Corry Sandstone through Riceville Formation undivided.
Pine Grove Township Water Company	33,800	2 wells	Wells tap outwash sand and gravel next to Conewango Creek.
Sheffield Municipal Water Authority	13,900	3 wells, Reservoir on Deer Lick Run	Authority gradually changing to wells from surface water of Deer Lick Run.
Southwest Warren County Municipal Water Authority	300,000	Reservoir on George Run	Authority provides water to Tidioute Borough and a part of Limestone Township.
Warren State Hospital	200,000	4 wells	Wells tap outwash sand and gravel in the Conewango Creek Valley.
Western Pennsylvania Water Company–Warren District	3,680,000	7 wells	Wells tap outwash sand and gravel next to the Allegheny River. Areas provided with water include Warren Borough and part of Conewango, Glade, Mead, and Pleasant Townships. The water supply for the North Warren Municipal Water Authority is purchased from the Warren District of the Western Pennsylvania Water Company.
Youngsville Municipal Waterworks	399,000	2 wells	Wells tap outwash sand and gravel in Brokenstraw Creek valley.
Total	4,780,000		

[1]Data source from water supply reports filed with Pennsylvania Department of Environmental Resources, Bureau of Resources Programming, Division of Comprehensive Resources.

[2]Well yields, specific capacities, locations, and well-construction data are presented in Moore and Buckwalter (1996).

Hydrogeology

The stratigraphy, hydrologic characteristics, and thickness of the unconsolidated and bedrock hydrogeologic units are described in this section. This information was compiled from literature review, geologic mapping, geophysical logging, well inventory, specific-capacity tests, and ground-water sampling.

The hydrologic properties of a hydrogeologic unit depend on many factors including the **lithology**, thickness, and water-bearing characteristics of the unit. The stratigraphy and the physical and hydraulic characteristics of wells completed in the major hydrogeologic units of Warren County are described sequentially in this section. The well data are summarized in table 6.

Stratigraphy and Hydrologic Characteristics of Unconsolidated Deposits

Alluvium

Alluvium is a thin (<100 ft) stratified unit composed of stream-deposited sand, silt, and clay with minor amounts of gravel. Alluvium is fluvially transported material derived from the weathering and mechanical breakdown of the native bedrock, reworking of glacial deposits, and soil from upland areas.

Relatively few water wells tap only alluvial deposits. The median depth of nine wells was 60 ft. Three wells with specific capacities of 1.9, 4.3, and 27 (gal/min)/ft indicate good availability.

Colluvium

Colluvium is composed of up to 125 ft of unsorted to poorly sorted clay, silt, sand, gravel, and cobbles. Colluvium is derived from the weathering of bedrock hillsides, largely during periods of glaciation. This material was transported downslope by gravity and deposited along the lower flanks of hills and along edges of the valley. Resulting accumulations are thickest in the valley bottoms and thin as you proceed upslope.

Colluvium is a minor hydrogeologic unit in Warren County. Although the sample size is small (six wells with values of specific capacity), one well had an excellent specific capacity of 550 (gal/min)/ft and a yield during the specific-capacity test of 1,370 gal/min. The median yield of the six specific-capacity tests was 17.5 gal/min. This is the second highest median yield of specific-capacity tests of all hydrogeologic units; it is exceeded only by the glacial outwash sand and gravel, which had a median yield of 25 gal/min.

Glacial Drift

Glacial **drift** is a hydrologic unit of undifferentiated glacial deposits that may be made up of till, glaciofluvial, and (or) glacio-lacustrine sediments that were not mapped as distinct units. These deposits are largely confined to the sides and bottom of the valleys. Glacial drift can be both stratified and unsaturated deposits of varying mixtures of clay, silt, sand, gravel, and cobbles. Much of the glacial drift is made up of sediments from source areas north of the county.

Glacial drift is not commonly tapped by wells. The median reported well yield of five wells tapping glacial drift was 6 gal/min, indicating sufficient yield for domestic use; the range of reported well yields was from 5 to 20 gal/min. Four wells have specific-capacity tests; the median specific capacity was 0.23 (gal/min)/ft.

Ice-Contact Stratified Sand and Gravel

Ice-contact stratified sand and gravel deposits form topographically distinctive accumulations on the valley bottoms and low on the hillsides of the glaciated parts of the county. Generally, the deposits are less than 50 ft thick and are composed of sand and gravel with minor quantities of silt.

The median well depth of 21 wells was 75 ft; depths ranged from 40 to 130 ft below land surface. The median specific capacity of 12 wells tapping the ice-contact deposits was 1.8 (gal/min)/ft; the specific capacities ranged from 0.06 to 10 (gal/min)/ft. The median yield of these 12 specific-capacity tests was 10 gal/min; the yields ranged from 2 to 30 gal/min.

Alluvium and Glacial Lacustrine, Undifferentiated

This deposit is associated with a glacial lake that formed because ice dammed the Conewango-Tionesta Basin (fig. 3). Silt and clay were carried into the lake where they were deposited. Drainage into the lake during deglaciation resulted in the breaching of this dam and the covering of the silt and clay with outwash, alluvium, and colluvium. Because the deposits remain buried, very little information about the thickness and extent of the silts and clays is available.

The median well depth for seven wells was only 31 ft. The water levels ranged from 8.52 to 50 ft below land surface for the seven wells, and the median water level was 10 ft below land surface. The median specific capacity of four wells taping this hydrogeologic unit was 0.42 (gal/min)/ft; the specific capacities ranged from 0.28 to 0.62 (gal/min)/ft. The median yield during these specific-capacity tests was 8 gal/min; yields ranged from 6 to 15 gal/min.

Glacial Outwash Sand and Gravel

Glacial outwash is made up of stratified sand and gravel deposited in the relatively flat valley bottoms by meltwater flowing from glacial ice. Particles can range from clay to boulders, but sand and gravel predominate.

The glacial outwash sand and gravel (hereafter referred to as “outwash”) hydrogeologic unit is the most extensively tapped aquifer in Warren County because it can yield large

Table 6. Summary of well data, Warren County, Pennsylvania.

[ft, feet; gal/min, gallons per minute; (gal/min)/ft, gallons per minute per foot; N, number of wells; —, no data]

Hydrogeologic unit	Well depth (ft)					Casing length (ft)				
	N	Median	Minimum	Maximum	Mean	N	Median	Minimum	Maximum	Mean
Unconsolidated hydrogeologic units										
Alluvium	9	60	50	74	62	4	60	50	66	59
Colluvium	11	87	37	128	83	10	64	31	123	68
Glacial drift (undifferentiated)	11	58	21	176	80	9	53	21	175	84
Ice-contact stratified sand and gravel	21	75	40	130	82	21	70	40	130	81
Alluvium and glacial lacustrine, undifferentiated	7	31	28	124	59	6	31	29	105	52
Glacial outwash sand and gravel	164	60	16	180	66	113	49	16	128	53
Bedrock hydrogeologic units										
Pottsville Group	13	100	43	170	103	9	21	9	76	30
Shenango Formation	25	87	47	178	97	23	33	18	55	36
Cuyahoga Formation	41	125	55	260	130	37	39	20	123	43
Knapp Formation	8	155	66	228	152	8	36	20	63	36
Corry Sandstone through Riceville Formation	15	100	50	220	119	14	24	15	110	41
Riceville Formation	18	110	39	292	119	14	28	10	56	30
Oswayo Formation	18	158	72	317	164	16	40	18	76	43
Catskill and Venango Formations	6	120	76	159	121	5	100	56	115	97
Venango Formation	108	80	38	280	101	97	38	8	134	40
Chadakoin Formation	61	80	43	302	98	56	43	17	186	54
Upper Devonian, undifferentiated[1]	7	352	202	904	488	—	—	—	—	—

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 6. Summary of well data, Warren County, Pennsylvania.—Continued

[ft, feet; gal/min, gallons per minute; (gal/min)/ft, gallons per minute per foot; N, number of wells; —, no data]

Hydrogeologic unit	Reported well yield (gal/min)					Static water level (ft below land surface)				
	N	Median	Minimum	Maximum	Mean	N	Median	Minimum	Maximum	Mean
Unconsolidated hydrogeologic units										
Alluvium	—	—	—	—	—	8	19	0.4	38	19
Colluvium	3	35	10	700	—	9	36	0	75	36
Glacial drift (undifferentiated)	5	6	5	20	9	9	20	2.0	96	24
Ice-contact stratified sand and gravel	9	10	6	25	13	16	30	5.7	51	31
Alluvium and glacial lacustrine, undifferentiated	2	—	10	15	—	7	10	8.5	50	17
Glacial outwash sand and gravel	53	15	5	1,000	131	117	24	0	100	26
Bedrock hydrogeologic units										
Pottsville Group	4	7	1	10	6	9	45	7.3	93	47
Shenango Formation	12	5	3	16	9	16	58	21	103	58
Cuyahoga Formation	14	5	2	16	6	38	80	20	140	79
Knapp Formation	3	5	3	6	—	6	50	30	196	88
Corry Sandstone through Riceville Formation	9	7	4	20	11	11	55	22	121	52
Riceville Formation	8	12	5	20	12	16	67	2.2	120	59
Oswayo Formation	12	7	1	15	7	14	76	17	219	84
Catskill and Venango Formations	3	105	10	130	—	2	—	33	47	—
Venango Formation	47	10	1	50	13	89	34	-1.5	168	43
Chadakoin Formation	32	10	3	50	12	45	30	3	120	39
Upper Devonian, undifferentiated[1]	3	80	50	80	—	9	41	0	272	74

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 6. Summary of well data, Warren County, Pennsylvania.—Continued

[ft, feet; gal/min, gallons per minute; (gal/min)/ft, gallons per minute per foot; N, number of wells; —, no data]

Hydrogeologic unit	Specific capacity [(gal/min)/ft]					Yield during specific capacity test (gal/min)				
	N	Median	Minimum	Maximum	Mean	N	Median	Minimum	Maximum	Mean
Unconsolidated hydrogeologic units										
Alluvium	3	4.3	1.9	27	—	3	12	12	30	—
Colluvium	6	2.5	.38	550	94	6	18	10	1,370	243
Glacial drift (undifferentiated)	4	.23	.10	2.0	.64	4	9	2.0	12	8
Ice-contact stratified sand and gravel	12	1.8	.06	10	3.2	12	10	2.0	30	12
Alluvium and glacial lacustrine, undifferentiated	4	.42	.28	.62	.44	4	8	6.0	15	9.3
Glacial outwash sand and gravel	47	6.0	.14	300	970	47	25	2.0	1,600	198
Bedrock hydrogeologic units										
Pottsville Group	5	.50	.03	.68	.40	5	5	2.0	15	7.2
Shenango Formation	10	.44	.06	3.7	1.0	10	9	2.0	16	8.9
Cuyahoga Formation	21	.24	.01	3.0	.50	19	5	1.0	16	7.4
Knapp Formation	5	.45	.16	2.5	.81	5	8	5.0	10	7.8
Corry Sandstone through Riceville Formation	5	.67	.06	20	4.7	5	10	5.0	20	11
Riceville Formation	7	1.5	.20	7.0	2.1	7	12	7.0	30	14
Oswayo Formation	6	.07	.01	.60	.16	6	5	2.0	12	5.7
Catskill and Venango Formations	1	2.5	—	—	—	1	30	—	—	—
Venango Formation	43	1.0	.03	30	3.1	43	10	1.0	39	14
Chadakoin Formation	23	.71	.03	10	1.5	23	15	3.0	50	15
Upper Devonian, undifferentiated[1]	—	—	—	—	—	—	—	—	—	—

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

amounts of ground water and is situated in populated areas. Wells tapping glacial outwash commonly are used for domestic purposes and, in selected locations, have the exceptional sustained yields necessary for large-capacity municipal and industrial use. The median well depth of 164 wells was 60 ft; depths ranged from 16 to 180 ft. The median reported well yield of 53 wells was 15 gal/min; yields ranged from 5 to 1,000 gal/min. The median static water level of 117 wells was 24 ft below land surface. The median specific capacity of 47 wells was 6.0 (gal/min)/ft; specific capacities ranged from 0.14 to 300 (gal/min)/ft. The median yield during these 47 tests was 25 gal/min, and yields ranged from 2 to 1,600 gal/min. Glacial outwash hydrogeologic units supply the ground water to the well fields of Youngsville, Pine Grove Township, Warren State Hospital, and the Western Pennsylvania Water Company servicing Warren and adjacent areas (table 5). Glacial outwash units are also the source of ground water for several high-yielding industrial wells in the county.

Stratigraphy and Hydrologic Characteristics of Bedrock Units

Pottsville Group

Hilltops and ridges throughout much of county are capped with up to 240 ft of the Pottsville Group's conglomerate, conglomeratic sandstone, sandstone, and minor amounts of siltstone and shale and even some impure coal. Most distinctive is the Olean Conglomerate, a thick massively bedded, coarse quartz pebble conglomerate near the base of the formation. The Olean Conglomerate is most visible on the hilltops in the northern part of the county. The Pottsville Group is a terrestrial unit deposited in the floodplains of braided rivers.

Relatively few water wells tap the Pottsville Group. The median depth of 13 wells was 100 ft below land surface. A small sample of five wells indicates generally adequate groundwater availability for domestic wells. The median specific capacity was 0.5 (gal/min)/ft, and the maximum specific capacity was 0.68 (gal/min)/ft. The median well yield during the five specific-capacity tests was 5 gal/min.

Shenango Formation

The Shenango Formation is made up of interbedded sandstone, siltstone, and shale. The lower portion is predominately thin bedded to flaggy sandstone with minor pebbly sandstone to conglomeratic horizons. The Shenango Formation ranges from 80 ft thick in the west to 130 ft in the eastern part of the county.

The median well depth of 25 wells was 87 ft. The median reported well yield of 12 wells was 5 gal/min, and the maximum yield was 16 gal/min. The median specific capacity of the 10 wells was 0.44 (gal/min)/ft. The median yield of 10 specific-capacity tests conducted in wells tapping the Shenango Formation was 9 gal/min; the maximum yield was 16 gal/min.

Cuyahoga Formation

Thinning from 130 ft in the west to 80 ft in the east, the Cuyahoga Formation is dominated by interbedded dark shale and silty shale with only a few thin beds of siltstone and very fine-grained sandstone.

The median reported well depth of 41 wells was 125 ft below land surface; well depths ranged from 55 to 260 ft. The median specific capacity of 21 wells was 0.24 (gal/min)/ft; the maximum specific capacity was 3 (gal/min)/ft. The median reported well yield during specific-capacity tests of 19 water wells tapping the Cuyahoga Formation was 5 gal/min, indicating sufficient yield for domestic use only; the range of reported well yields during these tests was from 1 to 16 gal/min.

Knapp Formation

Interbedded flat quartz-pebble conglomerate, conglomeratic sandstone, and fine- to medium-grained sandstone make up the Knapp Formation. The Knapp Formation becomes increasingly finer grained from east to west until it grades into an unnamed mixed-clastic unit.

The median well depth of eight wells was 155 ft below land surface; well depths ranged from 66 to 228 ft below land surface. The median specific capacity of five wells tapping the Knapp Formation was 0.45 (gal/min)/ft; specific capacities ranged from 0.16 to 2.5 (gal/min)/ft. The median yield of these five specific-capacity tests was 8 gal/min; yields ranged from 5 to 10 gal/min.

Corry Sandstone through Riceville Formation

This unit appears on the 1980 Geologic Map of Berg and others (1980) as consisting, from top to bottom, of the Corry Sandstone, Cussewago Formation, and Riceville Formation. Dodge (1992), however, believes the Cussewago Sandstone has been miss-identified and refers to this sequence of sediments as "unnamed marine mixed clastics" or "unnamed mixed clastics" (Dodge and Glover, 1995). According to Dodge (1992), the unnamed marine mixed clastics is present in western Warren County and is the lateral equivalent of the Knapp Formation. The unnamed unit has a maximum thickness of 60 to 100 ft and consists of interbedded, thin, locally calcareous, mostly very fine grained light-gray sandstone, gray siltstone, and minor dark-gray shale.

The median well depth of 15 wells was 100 ft below land surface; well depths ranged from 50 to 220 ft below land surface. The median static water level was 55 ft below land surface. The median specific capacity of five wells tapping the Corry Sandstone through Riceville Formation was 0.67 (gal/min)/ft; specific capacities ranged from 0.06 to 20 (gal/min)/ft. The median yield of these five specific-capacity tests was 10 gal/min; yields ranged from 5 to 20 gal/min.

Riceville Formation

The Riceville Formation varies from 125 to 170 ft in thickness and is made up of shale with subordinate quantities of siltstone and very-fine-grained sandstone. The sandstones are locally calcareous. The Riceville grades laterally eastward to the Oswayo Formation near Warren.

The median well depth of 18 wells was 110 ft; well depths ranged from 39 to 292 ft. The median reported well yield was 12.5 gal/min; yields in the eight wells ranged from 5 to 20 gal/min. The median static water level of 16 wells was 66.8 ft below land surface. The median specific capacity of seven wells was 1.5 (gal/min)/ft; specific capacities ranged from 0.2 to 7 (gal/min)/ft. The median yield during these seven specific-capacity tests was 12 gal/min; yields ranged from 7 to 30 gal/min.

Oswayo Formation

The Oswayo Formation is confined to the eastern one third of the county, where it is made up of between 150 and 200 ft of interbedded, drab-colored shale and siltstone with subordinate amounts of very-fine-grained drab sandstone. Westward, the Oswayo Formation gives way to the Riceville Formation.

The median well depth of 18 wells was 158 ft below land surface. The median water level was 76 ft; water levels ranged from 17 to 219 ft below land surface for the 14 wells. The median specific capacity of six wells tapping this hydrogeologic unit was 0.07 (gal/min)/ft; specific capacities ranged from 0.01 to 0.60 (gal/min)/ft. The median yield during these specific-capacity tests was 5 gal/min; yields ranged from 2 to 12 gal/min.

Catskill and Venango Formations

Because this unit is transitional between the Venango Formation to the west and the Catskill Formation to the east, it contains intermixed lithologies of both units. It is made up of intertonguing beds of terrestrial, grayish red siltstone and shale of the Catskill Formation and the interbedded, largely gray flat pebble conglomerate, sandstone, siltstone, and shale of the Venango Formation. This transitional sequence varies in thickness but averages about 250 ft.

Estimation of hydrologic properties is difficult because of a general lack of hydrologic data for this hydrogeologic unit. The median well depth of six wells was 120 ft; depths ranged from 76 to 159 ft. Three wells have reported well yields of 10, 105, and 130 gal/min. The specific capacity of one well was 2.5 (gal/min)/ft, and the well yield was 30 gal/min.

Venango Formation

This 280 to 330-ft thick unit contains varying amounts of interbedded flat pebble conglomerate, cross bedded sandstone, and drab colored siltstone and shale. Several of the sandstones achieve regional distribution and, particularly in the southwestern part of the county, have produced significant quantities of oil and gas.

On the basis of the number of wells inventoried during this study, the Venango Formation has the greatest number of wells in use in Warren County. The generally acceptable well yield for domestic water use, large areal extent, and extensive thickness are factors contributing to the widespread usage of the Venango Formation. The median well depth of 108 wells was 80 ft; depths ranged from 38 to 280 ft. The median static water level was 34.5 ft below land surface. The median specific capacity of 43 water wells tapping the Venango Formation was 1.0 (gal/min)/ft; specific capacities ranged from 0.03 to 30 (gal/min)/ft. The median well yield of these specific capacity tests was 10 gal/min; the range was from 1 to 39 gal/min.

Chadakoin Formation

The upper 100 ft or so of the Chadakoin Formation consists of interbedded greenish gray to light gray siltstone, shale, and minor sandstone. The lower 350 ft is made up of the reddish-purple interbedded siltstone and shale that oil and gas well drillers routinely identify as the “pink rock.” Marine fossils are common throughout the Chadakoin Formation.

The Chadakoin Formation is another bedrock unit frequently used as a source of water for homes and farms in Warren County. Well depths ranged from 43 to 302 ft; the median well depth was 80 ft. The median static water level was 30 ft below land surface. The median specific capacity of 23 wells was 0.71 (gal/min)/ft; the range was from 0.03 to 10 (gal/min)/ft. The median well yield of these tests was 15 gal/min; the range of yields was from 3 to 50 gal/min.

Upper Devonian, undifferentiated

The unit’s lithology is unknown but is presumed to consist of one or more rocks of Upper Devonian age. Well depths ranged from 202 to 904 ft; the median well depth was 352 ft. The median yield of three wells is 80 gal/min. The median static water level was 41 ft below land surface. No specific capacity information is available.

Bradford Group

The Bradford group consists of numerous sandstones interbedded with siltstones and shales. Although no water wells were inventoried that penetrate the Bradford group, its upper most unit, the Warren First Sand, serves as an excellent geologic marker bed in the county.

Ground Water

Occurrence and Flow System

Ground water occurs and flows beneath the water table in void spaces contained within hydrogeologic units. In this report, the term hydrogeologic unit refers to any geologic unit that contains water in all or part of its thickness. In hydrogeologic units composed of unconsolidated deposits such as sand and gravel, ground water occurs and flows within the pore space between particles. In bedrock hydrogeologic units, ground water is present primarily in **fractures** formed after the rock was consolidated. Wide fractures and well-interconnected fracture networks greatly improve the ability of bedrock hydrogeologic units to transmit ground water.

Ground water is recharged mainly by the infiltration of local precipitation and moves, in general, within the hydrogeologic units from recharge areas beneath uplands and hillslopes to discharge areas in valleys. Ground-water recharge rates vary with location on the landscape and depend on many factors, such as precipitation, temperature, vegetation, soils, slope, and land use. Ground water discharges mostly to streams, lakes, and springs, but some is captured by wells or is lost through evapotranspiration from riparian vegetation.

The depth of the ground-water flow system depends upon the existence of interconnected fractures and pore space within which the water moves. In the bedrock hydrogeologic units, fractures and joints become closed within a modest depth below land surface because of overburden pressure, impeding the downward movement of infiltrating water. The depth of the ground-water system is difficult to determine accurately, but it is usually estimated in Warren County by the depth to which fresh water is encountered as determined from drilling records. It is probable that the saline water found below the fresh water is slow-moving or stagnant; thus, it is not considered part of the active flow system through which most ground water moves. In Warren County, Butts (1910, p. 11) and Lytle (1965, p. 23) recorded surface-casing depths reported from oil and gas well records and assumed that the casing depth represented a point below which freshwater is no longer present. The study area for the investigations was the Russell, Scandia, Warren, and Clarendon 7½-minute quadrangles. Butts noted that pipe or casing to shut out the water in oil wells is rarely installed to depths greater than 600 ft, and generally less. Lytle stated that the casing depth ranges from 180 to 600 ft below land surface.

A hydrogeologic cross section (fig. 7) was constructed using data from the Warren 7-½-minute quadrangle area to illustrate an example of the estimated thickness of the bedrock hydrogeologic units and thickness of the fresh ground-water system. The locations of the wells used to construct the cross section are shown in figure 8. The Warren 7-½-minute quadrangle was selected because of its central location in the county, the presence of uplands and the major valley of the Allegheny River, and availability of water well and oil and gas well records. The base of the fresh ground-water system was estimated by drawing a dashed line connecting the base of the surface-casing depths of the oil and gas wells; where distances between oil and gas wells were considerable and topography changed significantly, the line was adjusted to reflect topography. This line representing the estimated base of the fresh ground-water system also was raised slightly above most surface-casing bottoms because the casing depth generally is located a short distance below the deepest observed water-bearing zone or to a depth based on the experience of the driller or oil operator in the local area.

In addition to those oil and gas well records examined for the construction of the hydrogeologic section, many records for the remainder of Warren County also were reviewed. Few well records indicated the occurrence of fresh ground water deeper than 600 ft below land surface, probably because of decreasing secondary permeability with depth and the low permeability of the Devonian bedrock (particularly shales). Generally, the first saltwater noted in shallow oil and gas wells was at the horizons of the target oil and gas sands in the Upper Devonian Venango Formation or Bradford group. The general lack of reports of saltwater in the bedrock between the base of the fresh ground water (approximately 200 to 600 ft below land surface) and the oil sands are substantiated by oil operators. Quaker State has drilled many shallow oil wells in Warren County; little or no water is produced during drilling once the top hole water has been eliminated (Barber, 1982). Pennzoil, another oil producer in Warren County, has encountered negligible connate water during drilling (Kardos, 1982).

Glaciated Area

In Warren County, ground water moves within and through two general flow systems—a shallow, local aquifer system with active flow, and a deeper, regional aquifer system at flow rates that are slow relative to the circulation of water in the shallow system (fig. 9). Saturated unconsolidated deposits make up the upper part of the local flow system. About 95 percent of the ground-water circulation occurs in the local aquifer system (Williams and others, 1993). Secondary permeability generally decreases with depth in bedrock as “open” fracture density diminishes due mainly to increasing overburden pressures. The depth of the active local flow system is variable, and the transition to the regional flow system is difficult to delineate accurately because of the paucity of data concerning the occurrence of ground water and the hydraulic characteristics of bedrock below about 200 ft in depth. The variable thickness of saturated unconsolidated deposits overlying bedrock also precludes any conclusive statements about the exact depth of the saturated part of the local flow system. In general, however, the bottom of the local flow system roughly parallels the bedrock surface and is about 150 to 175 ft beneath the bedrock surface.

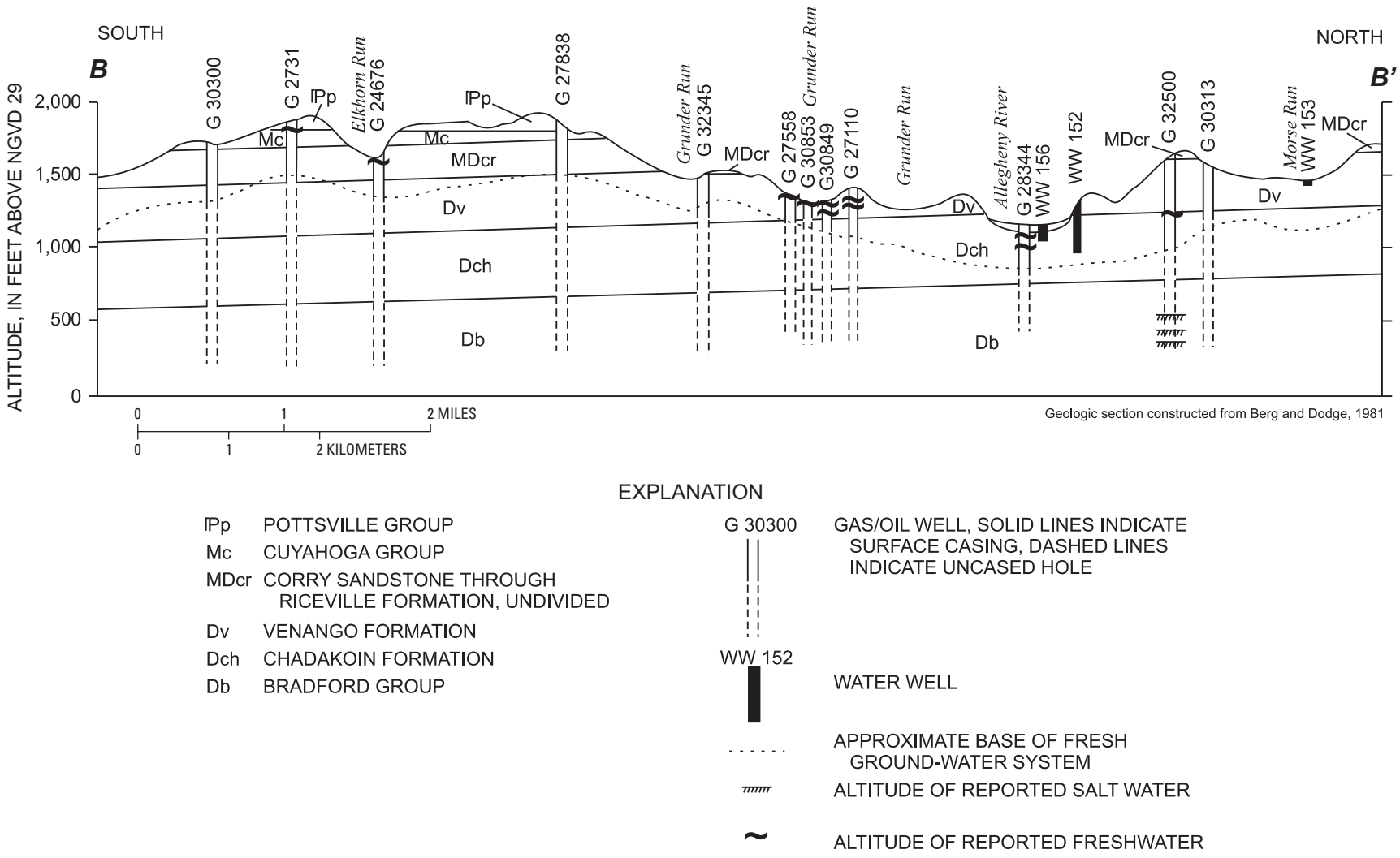


Figure 7. Hydrogeologic cross section B-B' showing approximate base of the fresh ground-water system in Warren 7½-minute quadrangle, Warren County, Pa.
[Trace of this cross section is shown on figure 8.]

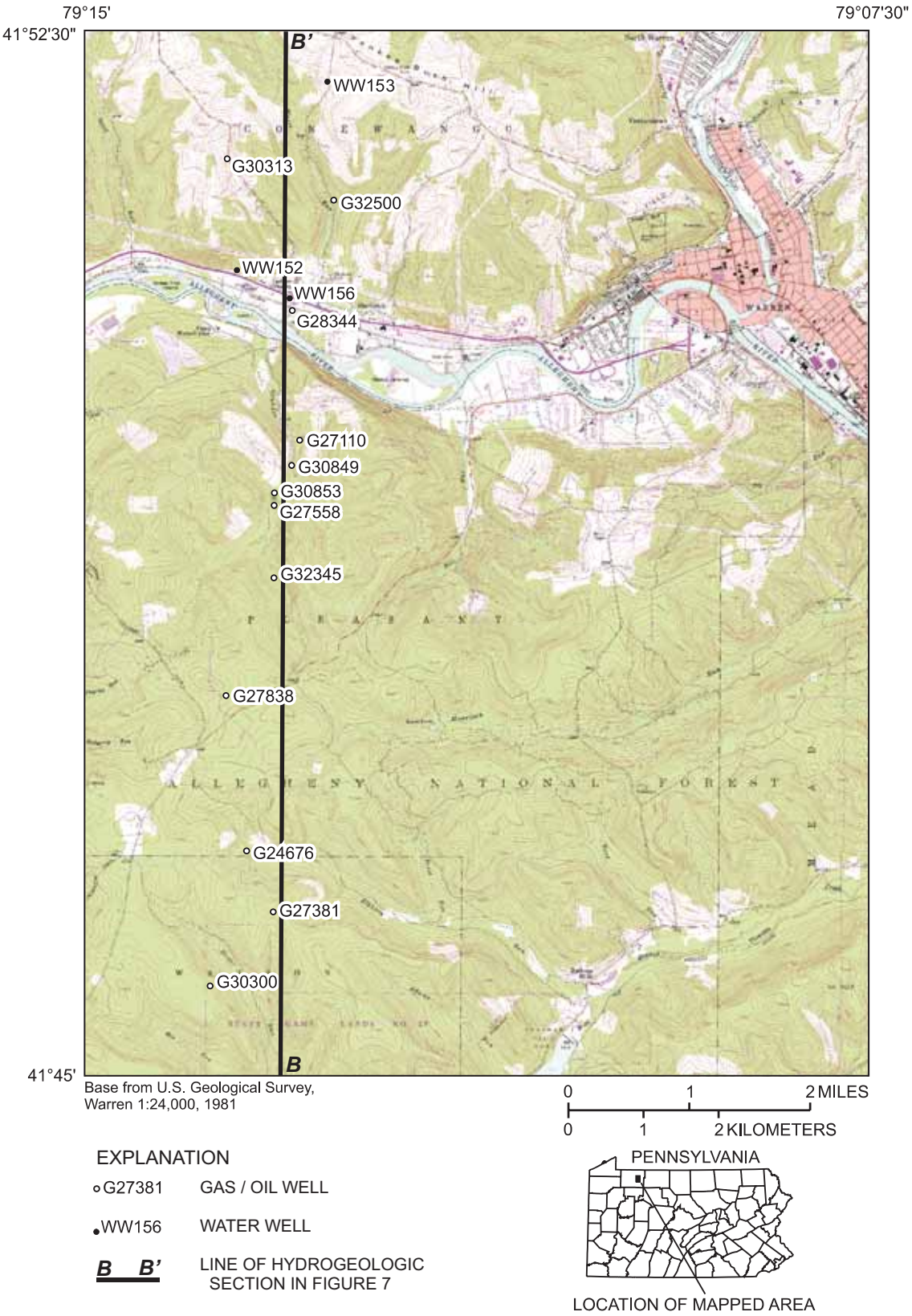


Figure 8. Locations of water and gas/oil wells used in construction of hydrogeologic section B-B', Warren County, Pa.

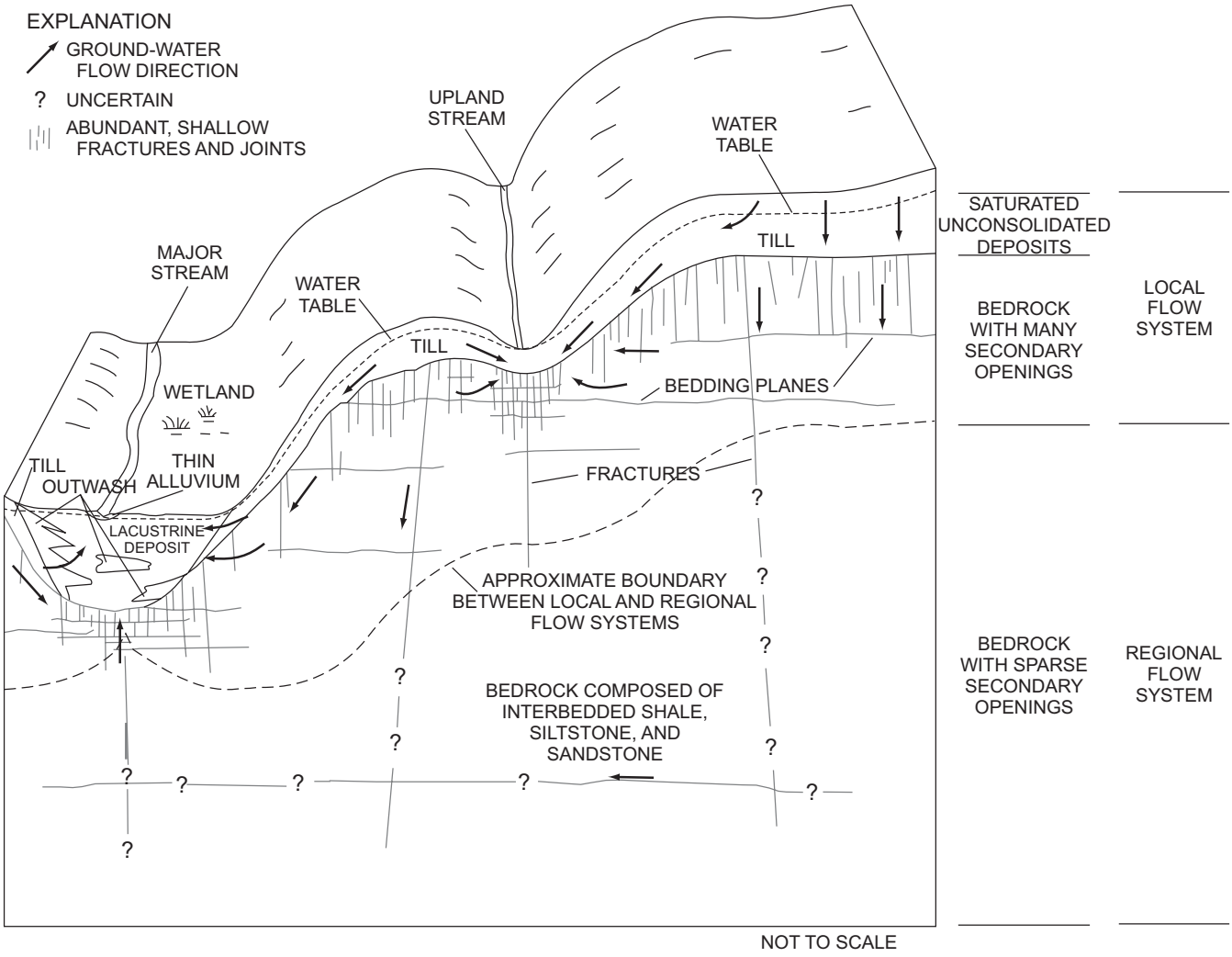


Figure 9. Schematic diagram of ground-water flow in the glaciated section of the Allegheny Plateau in Warren County.

The base of the regional aquifer system in Warren County generally is unknown except in older oil and gas fields, where it can be estimated from the altitudes of bottoms of surface-casing in oil and gas wells, which approximate the base of the fresh ground-water system (fig. 7). Few water wells penetrate the regional system because of prohibitive costs, possibility of finding only salty water unfit for water supply, and lack of success of deep test wells producing adequate quantities of acceptable quality water. In contrast, wells completed in selected sand and gravel aquifers within the local flow system have the largest yields of all wells in Warren County.

Generalized paths of movement of ground water in the glaciated upland plateau are shown in figure 9. Geology, topography, ground-water levels, aquifer hydraulic properties, and literature review were used in the design of this illustration. Actual movement may differ considerably in places than that depicted in the figure because of the complexity and variability of geohydrologic controls and the activities of humans such as large pumping of wells. The direction of shallow ground-water flow is influenced by the composition and structure of the subsurface materials and the location of sources of recharge and discharge areas, but generally it follows topography.

The water table is shown intercepting the upland stream in figure 9. However, water tables can fluctuate and periodically may be below the bottom of upland streams, especially during dry periods. During these periods, ground water moves out of the upland valleys and draws as subsurface flow along the valley floors.

Ground-water flow in the shallow, local bedrock aquifer system is influenced by the density of fractures or **secondary openings** in the bedrock. Many processes affect the degree of fracturing in the shallow bedrock, including stress-relief fracturing, paleoweathering, and differential erosion. Stress relief, the removal of compressional stress on underlying rocks by erosion of overlying rocks, results in predictable fracture patterns of bedrock in valleys in the Appalachian Plateaus Physiographic Province (Wyrick and Borchers, 1981). The bedrock fractures generally are horizontal under valley floors and verti-

cal along valley walls. The horizontal and vertical fractures shown under the upland stream and major stream in figure 9 are the fracture pattern expected by stress-relief fracturing. Stress-relief fracturing of bedrock is expected in Warren County, but data generally are lacking concerning the depth, frequency, and degree of interconnection of fractures in valleys and valley walls. Some documentation of the extent of stress-relief fracturing is reported in adjacent Erie County by Ferguson (1974).

Paleoweathered rock has been weathered prior to or during the Wisconsin glacial stage; this bedrock may be fractured at shallow depth. Differential erosion occurs at irregular or varying rates, and in glaciated areas, the differential erosion of bedrock by glacial ice and meltwater is prevalent. Glacial erosion may partly or completely remove pre-glacial weathered bedrock. Glacial material deposited on the bedrock after removal of the weathered rock zone generally restricts bedrock weathering because the glacial material acts as a protective covering (Kirkaldie, 1991, p. 208). In figure 9, the depth of fractures in the top of the bedrock in the local flow system is shown as nonexistent to very shallow in some areas and deeper in others to reflect the variable nature of paleoweathering and differential erosion of bedrock by meltwater and ice. The amount of bedrock removed by glaciation in Warren County is unknown.

In the Chemung River Basin in north-central Pennsylvania and south-central New York, Taylor (1988) discusses probable modifications to the hydrogeologic system by glaciation. In the Chemung River Basin, as much as 50 to more than 100 ft of rock may have been removed from valleys by glaciation; considerably less material was removed from valley walls and hilltops. According to Taylor (1988), the resulting system consists of low-permeability Devonian sedimentary rock units that are overlain by permeable glacial drift in the valleys. Similar modifications probably took place in Warren County.

Areas of highly weathered and fractured bedrock that remained after glaciation may contribute significantly to secondary permeability. Examination of a series of closely spaced bedrock core borings is one method of identifying areas of highly weathered bedrock. However, descriptions of core borings are not common in the geologic literature for Warren County. One published record in adjacent, glaciated Crawford County indicates the range of depth of highly weathered rock for 17 holes to be from 0.0 ft to greater than 31.5 ft; the average depth was 14.0 ft (Kirkaldie, 1991, p. 207).

Unglaciated Area

Ground-water flow patterns in the unglaciated upland plateau (fig. 10) are similar in many respects to those in the glaciated upland plateau (fig. 9). In the unglaciated plateau, bedrock hillsides and hilltops are mostly covered with colluvium instead of till or other glacial deposits. Infiltration of precipitation through the colluvium recharges bedrock units. Water tables commonly are within the colluvium or alluvium of valleys (fig. 10).

Confining units such as relatively unfractured shales will restrict or reduce downward movement of ground water. Confining units can cause perching of ground water and the flow flow is then directed laterally along bedding planes toward hillsides where the water discharges as springs or seeps. A line of perched contact springs on a hillside generally indicates semi-perched water-table conditions (fig. 10). At greater depths, the hydraulic **head** commonly is great enough to force vertical downward leakage through minor fractures in confining layers into underlying confined water-bearing units.

Ground-water-flow patterns in the unconsolidated deposits and bedrock beneath a major stream, for example, in the valley of Tionesta Creek and the valleys of the West Branch and South Branch of Tionesta Creek, would be expected to follow those depicted in figure 10. Patterns of ground-water flow in upland stream valleys (fig. 10) would be predictable for selected small streams tributary to Tionesta Creek, such as Minister Creek or Messenger Run. Sometimes these upland streams flow on bedrock, such as resistant sandstone beds, with colluvium composing the streambanks. During summer or fall droughts, when many spring discharges decline, flows in small upland streams may decrease to fractions of the flows during winter or spring.

Soils generally are too thin to be represented at the scales of figures 9 and 10. However, low permeability soils and especially impermeable fragipans may affect ground-water occurrence and flow by reducing **ground-water recharge**. Walters and Auchmoody (1989, p. 128) documented the effect of an impermeable fragipan at an unglaciated site in central Warren County in restricting infiltration.

The water level in a well indicates the amount of water stored in the aquifer at an instant in time. Water levels in unconfined unconsolidated deposits, such as sand and gravel, indicate the altitude of the water table. Water levels fluctuate seasonally; the highest water levels generally are in the spring prior to the growing season in response to recharge from precipitation and snowmelt on thawed ground. Although 56 percent of the average rainfall in Warren County occurs during the growing season, April through September, the lowest water levels generally are in late summer and early fall. During this time, discharges from the aquifer exceed recharges to the aquifer. The discharges include pumping wells; ground-water seepage to springs, wetlands, lakes, reservoirs, and streams; losses to evaporation; and consumptive use by vegetation (evapotranspiration). Patterns of water-level fluctuations can vary from average conditions, however, because of prolonged droughts, sustained rainfall, proximity of large pumping wells to streams, or extensive pumping from nearby large capacity wells.

Topographic position affects the water levels in wells. Hilltops are areas of aquifer recharge, valley bottoms are areas of aquifer discharge, and hillside positions are intermediate. Water levels range from above land surface in some valleys (Wr-564, appendix, fig. 10A) to more than 200 ft below land surface in hilltop wells (Wr-612, appendix, fig. 5A). Regionally, the average depth to water is 25-30 ft below land surface in a bedrock valley and about 50 ft below land surface on hilltops (Buckwalter and others, 1981). Depth to water usually

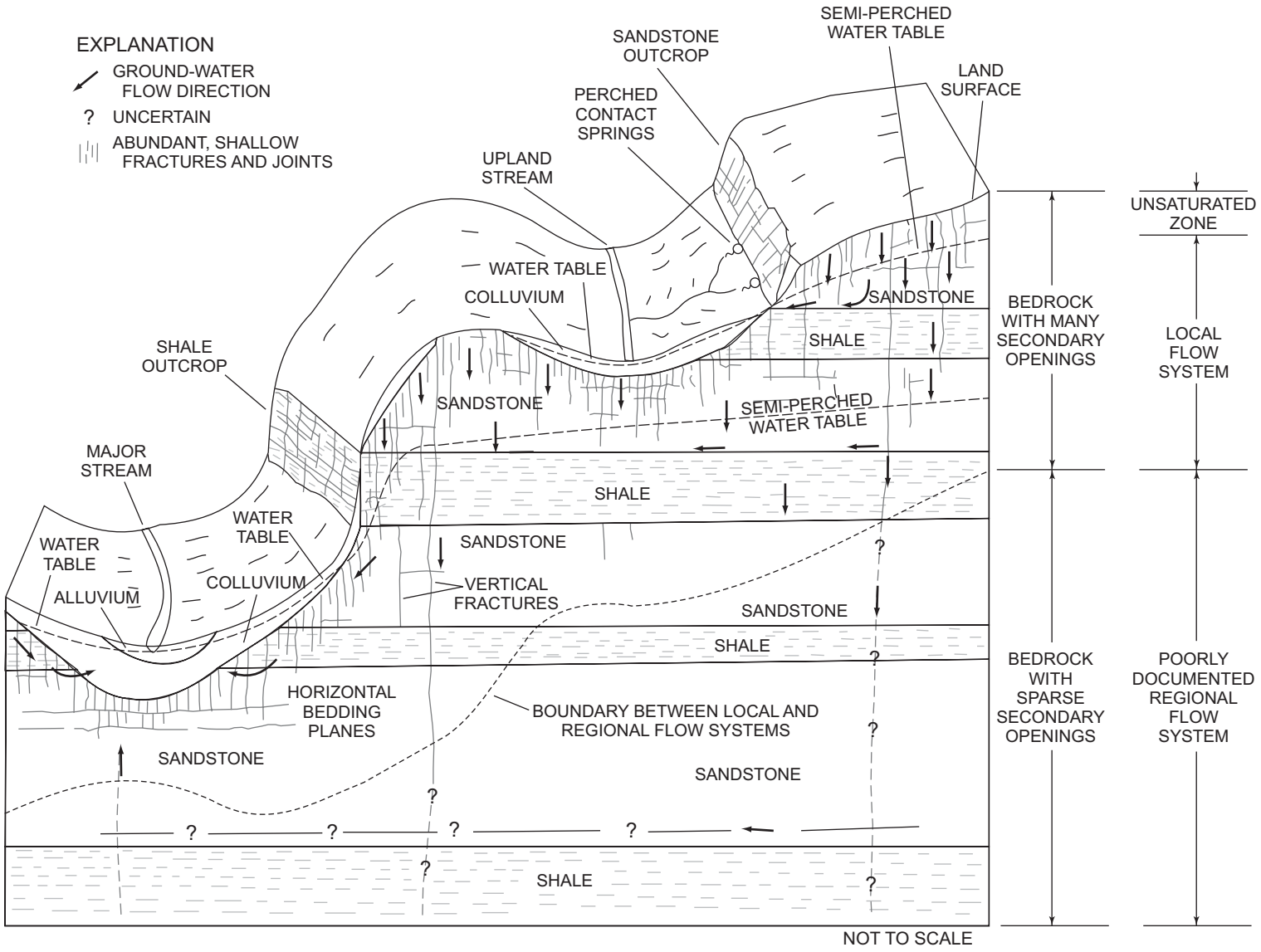


Figure 10. Schematic diagram of ground-water flow in the unglaciated section of the Allegheny Plateau in Warren County.

increases as well depth increases in upland areas. Conversely, depth to water decreases as well depths increase in valley areas.

Ground-water levels were monitored in five wells by the USGS during the study to compare the magnitude of water-level fluctuations at various locations. Two wells (Wr-50 and Wr-283, appendix, fig. 15A) are completed in bedrock hillsides and three wells [Wr-505 (appendix, fig. 3B), Wr-520 (appendix, fig. 14B), and Wr-522 (appendix, fig. 10B)] are completed in unconsolidated deposits in the valley. Hydrographs of wells Wr-50 and Wr-283 and monthly precipitation are presented in figure 11. For wells Wr-50 and Wr-283, well construction has cased out the unconsolidated deposits. The water levels demonstrate semi-confined aquifer conditions, and the hydrographs generally illustrate the seasonal variation of water levels. The damped amplitudes of the hydrographs, the difference between highs and lows, reflect the thick sequence of low-permeability deposits that overlie the bedrock aquifer. The water level in well Wr-50 ranged from 39.49 ft below land surface on August 2, 1987, to 45.42 ft below land surface on November 2, 1983. The water level in Wr-283 ranged from 45.02 ft below land surface on November 29, 1985, to 47.95 ft below land surface on September 18, 1988.

Hydrographs of observation wells Wr-505, Wr-520, and Wr-522 are also shown in figure 11. The water level in well Wr-505 ranged from 6.12 ft below land surface on July 21, 1986, to 10.40 ft below land surface on November 4, 1985. The water level in well Wr-520 ranged from 4.50 ft below land surface on June 17, 1986, to 9.92 ft below land surface on June 20, 1988. The water level in well Wr-522 ranged from 33.26 ft below land surface on April 12, 1987, to 38.96 ft below land surface on November 2, 1985. These wells are completed in alluvial sand and gravel deposits. The rapid rise and fall of the hydrographs indicate the water-table aquifers receive recharge directly from percolation of rainwater or are hydraulically connected with the nearby streams. Observations wells Wr-520 and Wr-522 are close to the Allegheny River. The hydraulic connection between Wr-520 and the Allegheny River is demonstrated in figure 12. The flood stages on the river on April 4 and May 23, 1988, are reflected in the higher water levels on the well hydrographs of the same dates.

Springs

Springs in rural areas commonly are important sources of water supply for local residents. Perched contact type springs that are common in Warren County are shown in figure 10. The reliability of spring discharge throughout the year is dependent on topographic position, the hydraulic properties of the water-bearing formation, and the amounts of precipitation. Springs near the valley floors commonly discharge throughout the year. Springs near hilltops have smaller recharge areas and commonly go dry during periods of little or no precipitation. Sandstone bedrock aquifers have good porosity and permeability and can store and transmit infiltrated precipitation.

Variable spring discharge generally is related to distribution and variation in precipitation events. Warren County experiences fairly uniform monthly precipitation (fig. 11). However, water stored in the snowpack that melts in the late winter months and slightly more precipitation than the late summer months results in large amounts of recharge and maximum spring flows. In the fall and during periods of drought, the recharge to the formations that support springs may be insufficient to keep the springs flowing at a sufficient rate for water-supply purposes.

Springs that become turbid or muddy after rainfall events are closely connected to the land surface and are likely to be unreliable with time and may be contaminated. Spring discharges related to shallow ground water may be contaminated by bacteria and by other pollutants related to upgradient land use. Chemical characteristics of sampled spring discharges are presented in Moore and Buckwalter (1996).

The discharges of 44 springs in Warren County were either measured or estimated, and the data are summarized in table 7 (Moore and Buckwalter, 1996, p. 36). The hydrogeologic unit with the largest spring discharge capability is the Pottsville Group; the average spring discharge was 25.7 gal/min. Most of these discharges were either estimated or measured in June or July.

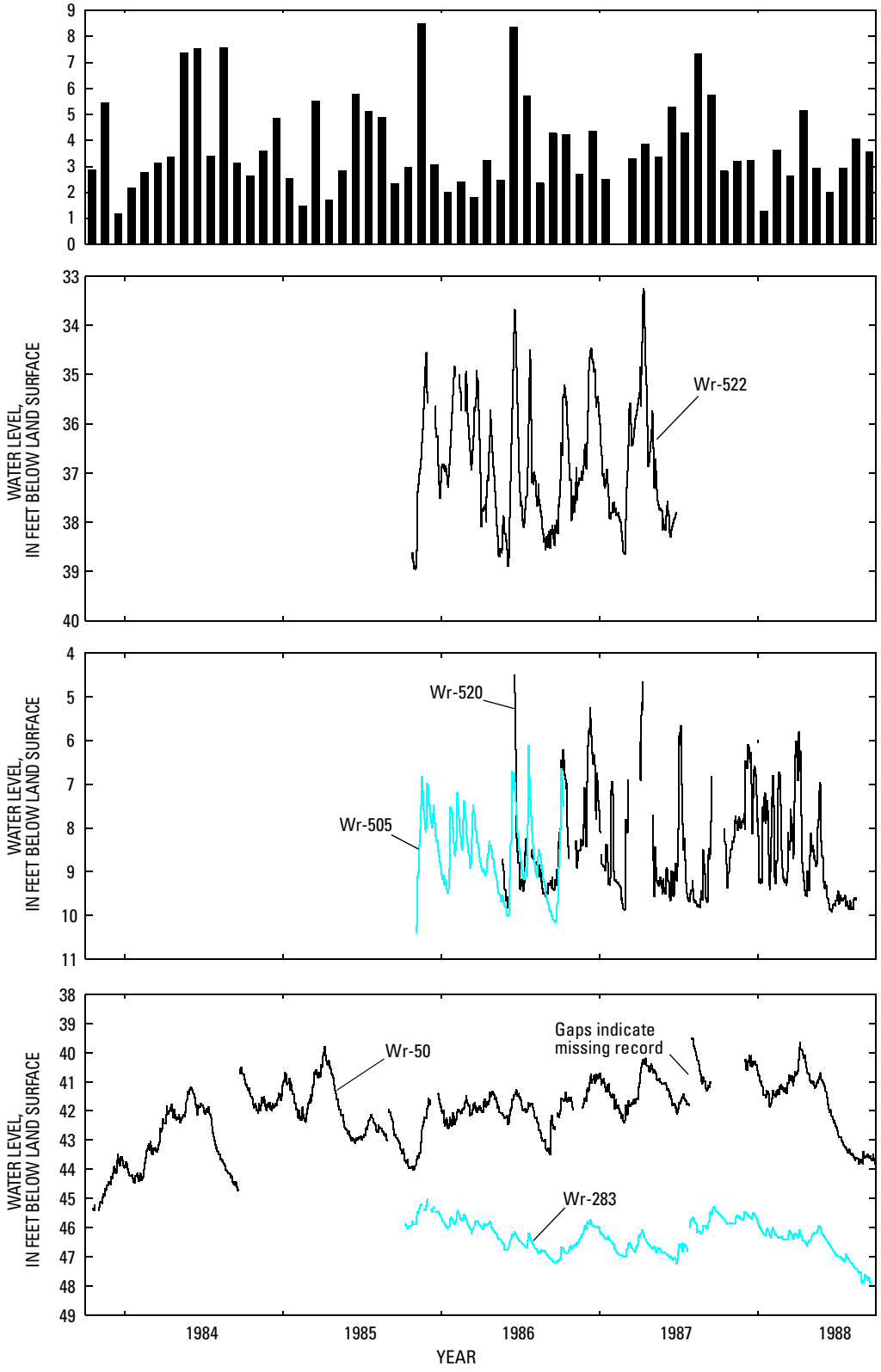


Figure 11. Monthly precipitation and water-level fluctuations in bedrock hillside wells Wr-50 and Wr-283 and valley bottom wells Wr-505, Wr-520, and Wr-522, Warren County, Pa.

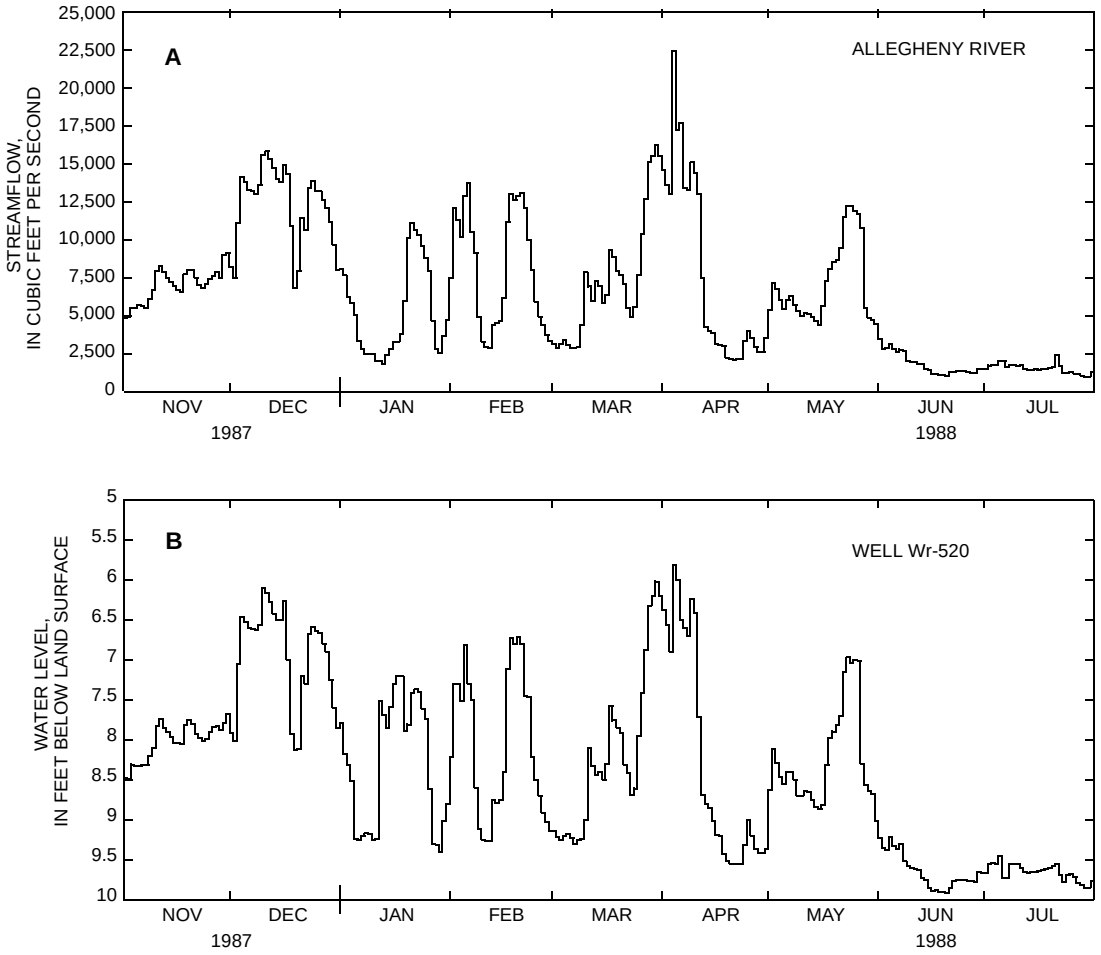


Figure 12. Hydraulic connection between the Allegheny River (A) and well Wr-520 (B), Warren County, Pa.

Table 7. Summary of springs discharges, Warren County, Pennsylvania.

[—, not meaningful]

Aquifer	Number of inventoried spring discharges	Discharge range[1] (gallons per minute)	Average spring discharge (gallons per minute)
Glacial outwash sand and gravel	2	0.01 - 4.4	2
Pottsville Group	16	.7 - 60	25.7
Shenango Formation	2	1.0 - 1.7	1.4
Knapp Formation	8	5 - 40	—
Corry Sandstone through Riceville Formation	1	45	—
Riceville Formation	3	.2 - 40	14
Oswayo Formation	3	5 - 11.1	9
Catskill Formation	3	2.6 - 10	6
Venango Formation	6	2.4 - 25	7

[1]Estimated and measured discharges combined.

Water Quality

The description of ground-water quality of Warren County is separated into the following four sections: 1) major constituents; 2) trace elements; 3) radionuclides; and 4) organics.

Major Constituents

Major constituents and properties used to evaluate the quality of ground water include the following: calcium, magnesium, sodium, potassium, chloride, sulfate, alkalinity, dissolved solids, and pH. Although present generally in trace quantities in ground water, descriptions of orthophosphorus, nitrate, and fluoride also are included in this section because, on occasion, they became significant constituents resulting from anthropogenic sources. Separate subsections of this section are presented for dissolved solids, sodium and chloride, nitrate, and pH because of their importance in the interpretation of groundwater quality. The concentrations of major constituents of water samples from water wells, springs, and abandoned oil and gas wells in Warren County are presented in Moore and Buckwalter (1996, p. 38).

Because of the lack of U.S. Environmental Protection Agency (USEPA) Maximum Contaminant Levels (MCLs) and Secondary Maximum Contaminant Levels (SMCLs) for calcium, magnesium, potassium, alkalinity, and orthophosphorus, only the median concentrations are listed for the most significant unconsolidated hydrogeologic unit (glacial outwash sand and gravel) and the most significant bedrock hydrogeologic unit (Venango Formation). These concentrations are within the range of typical values for natural ground waters (Hem, 1985).

Hydrogeologic unit	Median concentration, in milligrams per liter				
	Calcium	Magnesium	Potassium	Alkalinity	Ortho-phosphorus
Glacial outwash sand and gravel	37	7.5	1.0	116	0.01
Venango Formation	27	9.5	1.9	146	.01

Concentrations of sulfate in samples from wells, springs, and abandoned oil and gas wells were low with respect to the SMCL for sulfate of 250 mg/L. No sample concentration of sulfate exceeded the SMCL. The median concentrations from all hydrogeologic units ranged from <10 mg/L (laboratory detection level) to 25 mg/L. The median sulfate concentration in samples from 70 wells tapping the Venango Formation was 16 mg/L; the maximum concentration was 46 mg/L. The median sulfate concentration in samples from 49 wells tapping the glacial outwash was 20 mg/L.

Most concentrations of fluoride from samples collected from water wells and springs were very low with respect to the MCL of 4.0 mg/L. The median concentration from 45 wells tapping the glacial outwash was 0.05 mg/L; the maximum concentration was 0.62 mg/L. The median concentration was 0.25 mg/L from 70 wells in the Venango Formation. Only one water well tapping the glacial outwash exceeded the MCL for fluoride; the sample concentration was 7.0 mg/L. Concentrations of fluoride in samples from two abandoned oil and gas wells exceeded the MCL. These fluoride concentrations were 62 mg/L in the sample from well Wr-586 and 31 mg/L in the sample from well Wr-587. These samples from the abandoned oil and gas wells were brines with concentrations of dissolved solids of 91,200 mg/L from well Wr-586 and 40,000 mg/L from well Wr-587. High fluoride concentrations in brines are rare although Poth (1962, p. 51) does note a concentration of 21 mg/L from a brine from the Onondaga Limestone of the Middle Devonian.

Dissolved Solids

Samples from water wells, springs, and abandoned oil and gas wells were analyzed in the laboratory for concentrations of total dissolved solids. The total concentration of dissolved material is determined in the laboratory from the weight of the dry residue remaining after evaporation at 105°C of the volatile portion of an aliquot of the water sample. **Specific conductance** measurements also may be used to approximate the dissolved solids content of water. Commonly, the concentration of dissolved solids (in milligrams per liter) is about 65 percent of the specific conductance (in microsiemens per centimeter). Field measurements of specific conductance can be used as a screening tool to indicate high concentrations of dissolved solids.

A standard classification of waters containing various concentrations of dissolved solids (Hem, 1985) is as follows:

Classification	Dissolved solids, in milligrams per liter
Fresh water	less than 1,000
Slightly saline	1,000 to 3,000
Moderately saline	3,001 to 10,000
Very saline	10,001 to 35,000
Briny	More than 35,000

The USEPA has established an SMCL for total dissolved solids of 500 mg/L. The median and range of laboratory measurements of total dissolved solids concentrations are presented in table 8 by hydrogeologic unit. Only 1 of 45 wells sampled in the glacial outwash hydrogeologic unit contained water that exceeded the SMCL. Concentrations of dissolved solids in eight samples from wells in bedrock hydrogeologic units exceeded the SMCL. The two lowest median concentrations for dissolved solids were from wells in the Pottsville Group (66 mg/L) and from wells in the Shenango Group (84 mg/L) (Moore and Buckwalter, 1996, table 7). Because almost all samples for dissolved solids from wells had concentrations less than 1,000 mg/L, this water by definition is freshwater. Only water from wells Wr-256 (tapping the glacial outwash), Wr-593 (tapping the Venango Formation), and Wr-814 (tapping the Venango Formation) (concentrations of 2,140; 1,440; and 1,730 mg/L, respectively) would have a classification of slightly saline.

Table 8. Median and range of concentrations of total dissolved solids for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[SMCL, Secondary maximum contaminant level]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter			Number of samples with concentration exceeding the SMCL	Percentage of samples exceeding the SMCL
		Minimum	Median	Maximum		
Unconsolidated hydrogeologic units						
Alluvium	5	112	174	308	0	0
Colluvium	5	124	202	310	0	0
Glacial drift (undifferentiated)	8	80	232	396	0	0
Ice-contact stratified sand and gravel	12	83	166	302	0	0
Alluvium and glacial lacustrine, undifferentiated	3	108	140	150	0	0
Glacial outwash sand and gravel	45	100	206	2,140	1	2
Bedrock hydrogeologic units						
Pottsville Group	6	40	66	234	0	0
Shenango Formation	7	8	84	152	0	0
Cuyahoga Formation	19	48	126	165	0	0
Knapp Formation	4	94	130	180	0	0
Oswayo Formation	6	46	255	624	1	17
Riceville Formation	7	138	180	376	0	0
Corry Sandstone through Riceville Formation	6	114	133	510	1	17
Catskill and Venango Formations	3	224	308	310	0	0
Venango Formation	69	54	226	1,440	3	4
Chadakoin Formation	37	92	236	464	0	0
Upper Devonian, undifferentiated[1]	15	56	189	1,730	3	20
Total	257				9	3.5

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Sodium and Chloride

Sodium is present in and may be dissolved from almost all rocks and soils. Sodium is a major constituent of brines and generally is present in sewage. Sodium in large concentrations in combination with chloride gives water a salty taste. No USEPA MCL or SMCL is established for sodium. The range and median concentrations of dissolved sodium from water samples from wells in Warren County are presented in table 9 by hydrogeologic unit.

Table 9. Median and range of concentrations of dissolved sodium for water samples from wells in Warren County, Pa., by hydrogeologic unit.

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	5	4.6	5.4	84
Colluvium	5	4.8	7.5	37
Glacial drift (undifferentiated)	8	4.6	12	120
Ice-contact stratified sand and gravel	12	2.3	7.6	220
Alluvium and glacial lacustrine, undifferentiated	3	5.2	10	11
Glacial outwash sand and gravel	49	1.7	8.8	150
Bedrock hydrogeologic units				
Pottsville Group	6	.2	1.4	18
Shenango Formation	7	.6	1.7	3.8
Cuyahoga Formation	20	.4	3.6	34
Knapp Formation	4	1.7	8.3	17
Oswayo Formation	6	.7	13	74
Riceville Formation	7	2.8	3.7	68
Corry Sandstone through Riceville Formation	6	2.0	2.5	40
Catskill and Venango Formations	3	23	54	60
Venango Formation	70	1.0	16	570
Chadakoin Formation	40	2.2	21	160
Upper Devonian, undifferentiated[1]	14	3.1	18	200
Total	265			

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Chloride is dissolved from rocks and soils and is found in large concentrations in brines. Other sources of chloride in ground water include sewage, industrial waste, and road-deicing chemicals. Chloride in large concentrations increases the corrosiveness of water. The USEPA has established a recommended SMCL of 250 mg/L for chloride. Only 1 of 82 wells (Wr-256; on the Tidioute quadrangle) tapping the glacial outwash exceeded the SMCL of 250 mg/L for chloride. Concentrations of chloride in ground-water samples from the 265 water wells throughout Warren County generally were low with respect to the SMCL of 250 mg/L. Evaluation of the median and maximum concentrations of dissolved sodium (table 9) and dissolved chloride (table 10) in 265 wells indicates salty water is rarely a ground-water problem.

Nitrate

Samples from water wells, springs, and abandoned oil and gas wells were routinely analyzed in the laboratory for nitrate. Principal sources of nitrate in ground water are decaying organic matter, sewage, and fertilizers. Drinking water exceeding 10 mg/L of nitrate (reported as nitrogen) may cause methemoglobinemia, a disease commonly fatal in infants. The USEPA MCL for nitrate (as nitrogen) is 10 mg/L. Nitrate concentrations in samples from water wells, springs, and abandoned oil and gas wells rarely exceeded the MCL (table 11). Only samples from 2 of 260 wells exceeded the MCL for nitrate. These two wells were in the Venango Formation, and the exact source(s) of the nitrate is unknown. The nitrate concentrations in samples from 56 springs and 15 abandoned oil and gas wells did not exceed the MCL.

Table 10. Median and range of concentrations of dissolved chloride for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[<, less than]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	5	2.0	4.0	33
Colluvium	5	<1.0	18	27
Glacial drift (undifferentiated)	8	2.0	13	28
Ice-contact stratified sand and gravel	12	2.0	6.0	48
Alluvium and glacial lacustrine, undifferentiated	3	5.0	6.0	13
Glacial outwash sand and gravel	49	1.0	14	253
Bedrock hydrogeologic units				
Pottsville Group	6	1.0	7.5	44
Shenango Formation	7	1.0	5.0	15
Cuyahoga Formation	20	<1.0	4.5	115
Knapp Formation	4	5.0	6.0	33
Oswayo Formation	6	5.0	10	23
Riceville Formation	7	2.0	5.0	88
Corry Sandstone through Riceville Formation	6	1.0	3.0	166
Catskill and Venango Formations	3	13	29	29
Venango Formation	69	<1.0	6.0	474
Chadakoin Formation	40	<1.0	8.5	143
Upper Devonian, undifferentiated[1]	15	4.0	10	53,000
Total	265			

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 11. Median and range of concentrations of total nitrate (as nitrogen) for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[<, less than]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	5	<0.04	<0.04	0.04
Colluvium	5	<.04	<.04	<.04
Glacial drift (undifferentiated)	8	<.04	<.04	6.6
Ice-contact stratified sand and gravel	12	<.04	<.04	1.4
Alluvium and glacial lacustrine, undifferentiated	3	<.04	<.04	.14
Glacial outwash sand and gravel	45	<.04	.54	3.8
Bedrock hydrogeologic units				
Pottsville Group	6	.16	.69	6.1
Shenango Formation	7	<.04	.17	.64
Cuyahoga Formation	20	<.04	.11	4.0
Knapp Formation	4	.12	.81	1.1
Oswayo Formation	6	<.04	<.04	.24
Riceville Formation	7	<.04	.15	1.6
Corry Sandstone through Riceville Formation	6	<.04	.13	1.6
Catskill and Venango Formations	3	<.04	<.04	<.04
Venango Formation	70	<.04	<.04	14.1
Chadakoin Formation	38	<.04	<.04	1.6
Upper Devonian, undifferentiated[1]	15	<.04	<.04	3.6
Total	260			

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

pH

The pH or hydrogen-ion activity is a measure of waters reactive characteristics. Low values of pH, particularly below pH 4, indicate a corrosive water. High values of pH, particularly above 8.5, indicate an alkaline water that will tend to form scale when heated. The pH significantly affects the treatment and use of water. The SMCL for pH is outside the range from 6.5 to 8.5. The median and range of field pH measurements of samples from water wells and abandoned oil and gas wells are presented in table 12 by hydrogeologic unit. Although the sample size is small and inferences may be suspect, water from wells tapping the Pottsville Group generally is more acidic than water from unconsolidated and other bedrock hydrogeologic units. Additional data supporting this finding were demonstrated by pH measurements of springs discharging from the Pottsville Group; the median pH of 18 springs was 5.0; the pH values ranged from 4.1 to 6.8 (Moore and Buckwalter, 1996, table 7).

Table 12. Median and range of field pH for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[SMCL, Secondary maximum contaminant level]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter			Number of wells with pH exceeding the SMCL	Percentage of wells with samples exceeding pH range of the SMCL
		Minimum	Median	Maximum		
Unconsolidated hydrogeologic units						
Alluvium	5	6.5	6.7	7.4	0	0
Colluvium	5	7.0	7.6	7.7	0	0
Glacial drift (undifferentiated)	8	5.7	6.0	8.1	6	75
Ice-contact stratified sand and gravel	12	6.2	6.9	8.2	1	8
Alluvium and glacial lacustrine, undifferentiated	3	6.4	6.6	6.8	1	33
Glacial outwash sand and gravel	40	5.0	6.8	7.6	10	25
Bedrock hydrogeologic units						
Pottsville Group	6	4.2	5.0	6.2	6	100
Shenango Formation	7	6.0	6.2	7.4	5	71
Cuyahoga Formation	17	3.8	6.5	7.4	6	35
Knapp Formation	4	6.4	6.7	7.2	1	25
Oswayo Formation	6	5.3	7.4	7.7	2	33
Riceville Formation	7	6.0	6.6	7.1	2	29
Corry Sandstone through Riceville Formation	6	5.4	6.3	6.8	3	50
Catskill and Venango Formations	3	7.2	7.4	7.4	0	0
Venango Formation	67	5.2	6.7	8.2	24	36
Chadakoin Formation	34	5.3	6.8	7.7	8	24
Upper Devonian, undifferentiated[1]	12	6.2	6.9	8.2	0	0
Total	242				75	31

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Trace Elements

Samples from water wells, springs, and abandoned oil and gas wells were analyzed for the following trace elements: aluminum, arsenic, barium, cadmium, chromium, iron, lead, manganese, nickel, strontium, and zinc. The data are presented in Moore and Buckwalter (1996, p. 73).

Iron and Manganese

Concentrations of iron and manganese in samples from water wells in Warren County commonly were above the SMCLs of 300 and 50 µg/L, respectively. Iron and manganese are dissolved from many rocks and soils. Iron concentrations in samples from water wells also may be partially derived from iron pipes, pumps, and other equipment. The SMCLs for iron and manganese were not established for health reasons but for aesthetic reasons. Concentrations of iron and manganese greater than the SMCLs can cause stains on laundry and plumbing fixtures. In higher concentrations, iron and manganese give water an unpleasant taste.

Concentrations of dissolved iron (table 13) exceeded the SMCL in samples from 95 of the 266 wells sampled (36 percent). The Riceville Formation is the only hydrogeologic unit for which concentrations of iron in samples did not exceed the SMCL. Dissolved manganese concentrations (table 14) exceeded the SMCL in samples from 155 of 260 wells sampled (60 percent). Concentrations of dissolved manganese in samples from at least 40 percent of the wells in each hydrogeologic unit exceeded the SMCL (table 14), indicating a widespread problem.

Table 13. Median and range of concentrations of dissolved iron for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[SMCL, Secondary maximum contaminant level]

Hydrogeologic unit	Number of wells sampled	Concentration, in micrograms per liter			Number of wells with a sample concentration exceeding the SMCL	Percentage of wells with samples exceeding the SMCL
		Minimum	Median	Maximum		
Unconsolidated hydrogeologic units						
Alluvium	5	100	2,020	54,400	4	80
Colluvium	5	5	740	850	4	80
Glacial drift (undifferentiated)	8	5	300	520	4	50
Ice-contact stratified sand and gravel	12	5	135	655	2	17
Alluvium and glacial lacustrine, undifferentiated	3	81	2,350	4,030	2	67
Glacial outwash sand and gravel	49	5	130	25,250	14	29
Bedrock hydrogeologic units						
Pottsville Group	6	5	300	707	3	50
Shenango Formation	7	5	50	534	1	14
Cuyahoga Formation	20	5	108	12,400	6	30
Knapp Formation	4	5	232	680	2	50
Oswayo Formation	6	19	56	2,670	1	17
Riceville Formation	7	5	50	220	0	0
Corry Sandstone through Riceville Formation	6	50	255	22,400	3	50
Catskill and Venango Formations	3	5	1,060	1,193	2	67
Venango Formation	70	5	180	34,100	20	29
Chadakoin Formation	40	5	170	10,400	14	35
Upper Devonian, undifferentiated[1]	15	200	580	72,000	13	87
Total	266				95	36

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 14. Median and range of concentrations of dissolved manganese for ground-water samples from wells in Warren County, Pa., by hydrogeologic unit.

[SMCL, Secondary maximum contaminant level]

Hydrogeologic unit	Number of wells sampled	Concentration, in micrograms per liter			Number of wells with a sample concentration exceeding the SMCL	Percentage of wells with samples exceeding the SMCL
		Minimum	Median	Maximum		
Unconsolidated hydrogeologic units						
Alluvium	5	25	140	190	4	80
Colluvium	5	127	340	3,400	5	100
Glacial drift (undifferentiated)	8	13	155	460	6	75
Ice-contact stratified sand and gravel	12	25	95	310	8	67
Alluvium and glacial lacustrine, undifferentiated	3	5	450	510	2	67
Glacial outwash sand and gravel	45	5	25	2,810	20	44
Bedrock hydrogeologic units						
Pottsville Group	6	5	101	251	3	50
Shenango Formation	7	5	53	407	4	57
Cuyahoga Formation	20	5	25	920	8	40
Knapp Formation	4	5	67	207	2	50
Oswayo Formation	6	25	138	450	4	67
Riceville Formation	7	5	25	393	3	43
Corry Sandstone through Riceville Formation	6	25	260	1,510	4	67
Catskill and Venango Formations	3	5	76	161	2	67
Venango Formation	70	5	70	2,180	44	63
Chadakoin Formation	38	5	85	1,210	22	58
Upper Devonian, undifferentiated[1]	15	25	200	7,000	14	93
Total	260				155	60

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Although the number of springs sampled was small with respect to the number of wells sampled, iron and manganese concentrations generally were lower in springs than in water wells. Concentrations of iron exceeded the SMCL in only 5 of 57 springs sampled or 9 percent. Manganese concentrations exceeded the SMCL in 15 of 57 springs sampled or 26 percent. Although bacteria contamination of roadside springs may be widespread and warnings of contamination mostly ignored, the popularity of roadside springs for drinking water is, in part, because of the low concentrations of iron and manganese. Well owners that prefer not to remove high concentrations of iron and manganese with water-treatment systems sometimes use springs for drinking water and their well water for other water uses. Causes of the low concentrations of iron and manganese in springs probably are related to the shorter ground-water-flow paths, the shorter ground-water residence time of springs, and the oxidation state of the ground water.

A variety of treatment methods is available to remove iron and manganese from domestic and municipal well water (U.S. Environmental Protection Agency, 1991, p. 91-93). Concentrations of iron in ground water near the SMCL of 300 µg/L are fairly easy and economical to remove. Large concentrations of iron pose costly removal problems including expensive treatment equipment, frequent equipment maintenance, and disposal of the large quantities of iron. For example, the prohibitive cost of removing greater than 10,000 µg/L of iron from high-yielding outwash aquifers at Tidioute prevented these aquifers from being developed for municipal supply.

Brines or saline water produced during oil and gas production commonly have large concentrations of iron. The analysis of 35 brine samples from oil and gas formations in western Pennsylvania indicated a range of iron concentrations from 130 to 286,000 µg/L; the median concentration was 52,000 µg/L (Poth, 1962, p. 33). Analyses of production fluids from producing oil formations in Warren County indicated a range of dissolved iron concentrations from 100 to 116,000 µg/L. Improper disposal of production fluids high in iron concentration have the potential to contaminate the upper fresh ground-water system.

The cause and effect relations of this possible ground-water contamination process are difficult to accurately establish and were not investigated for many reasons including the rapid natural change in iron concentrations within an aquifer, the complexity of iron geochemistry, and because high iron concentrations in ground water generally are not of any significant health consequence.

Arsenic and Barium

Arsenic is widely distributed in the environment, and humans are exposed to low levels of this element in the air, water, soil, and food. Inorganic arsenic is a human poison, and large doses can cause death. Lower levels of exposure to inorganic arsenic may injure a number of different body tissues or systems (U.S. Environmental Protection Agency, 1976, p.15). The arsenic found in air and water is mostly inorganic. Organic forms of arsenic are usually less toxic than inorganic forms.

The occurrence of arsenic in ground water of the United States has been an ongoing subject of research by the USGS. In 1988, Welch and others (1988) published a comprehensive literature review of arsenic in ground water of the western United States. Although arsenic is a frequent ground-water topic in the USGS and other scientific literature, many unresolved issues exist concerning the complex geochemistry of arsenic and its occurrence, especially in hydrogeologic settings of the eastern United States. Naturally occurring forms of arsenic include As(III), As(V), arsanilic acid ($C_6H_8AsNO_3$), monomethylarsinic acid, and dimethylarsinic acid.

Arsenic geochemistry, especially speciation, is one of many inputs needed to predict the hydrogeologic environments that produce elevated arsenic concentrations. Knowledge of speciation of arsenic is critical to the delineation of the degree of toxicity of arsenic in drinking water to humans. Differences in toxicity for arsenic species are not considered in the USEPA drinking water limit of 10 µg/L expressed simply as total arsenic (U.S. Environmental Protection Agency, 2002). Total arsenic was the only arsenic species measured in the Warren County study.

Geochemical controls influencing aqueous concentrations of arsenic are poorly understood (Welch and others, 1988). Factors that may limit our ability to define geochemical reactions responsible for arsenic concentrations in ground water include 1) the lack of thoroughly evaluated thermodynamic data for the aqueous complexes and minerals of arsenic, 2) limited analytical data that include speciation, and 3) the adsorption of trace constituents and how they can be affected by a variety of factors, including competition with other anionic solutes for adsorption sites (Welch and others, 1988).

The investigation and geochemical model of Matisoff and others (1982) concerning the occurrence of elevated arsenic concentrations in ground water of a 0.5-mi^2 area in northeastern Ohio near Canal Fulton is relevant to Warren County because the hydrogeologic characteristics of the two areas are similar. Matisoff and others (1982) concluded that there was little evidence for anthropogenic sources of arsenic to the ground water from a 20-mi^2 area surrounding the wells containing arsenic. Concentrations of total dissolved arsenic above 50 µg/L (the USEPA MCL at the time of the study) were detected in only 2 of 88 water wells sampled in a 20-mi^2 area. Matisoff and others (1982) noted no previously reported cases of arsenic contamination of ground water in Ohio. The geochemical model by Matisoff and others (1982) predicts release of adsorbed arsenic when Eh is lowered, perhaps by the introduction of methane into the aquifer from local gas-well drilling and production and (or) leakage from present underground gas-storage operations.

Methane, as the product of bacterial processes in the aquifer or from migration from petroleum reservoirs, also may alter ground-water quality (Grossman and others, 1989) and may play an important role in the transport of gaseous arsenic compounds (Holm and others, 1979). Organo-arsenic species also may contribute significantly to the total arsenic concentration where methane is present (Holm and others, 1979).

For the Warren County study, samples collected from 233 water wells were analyzed for arsenic, and 38 wells contained water that exceeded the USEPA MCL of 10 µg/L for arsenic. Twenty-five of these 38 wells (66 percent) were in the glacial outwash hydrogeologic unit. Twenty-two of the water wells with arsenic concentrations exceeding the MCL were domestic wells in a housing development in Conewango Township.

Water samples were collected from 16 abandoned oil and gas wells; concentrations of dissolved arsenic exceeded the MCL in samples from two of these wells. Concentrations of dissolved arsenic were measured in 17 springs; only 1 sample had a concentration of arsenic equal to the MCL of 10 µg/L.

The geochemical environments sustaining elevated concentrations of arsenic commonly sustain elevated concentrations of barium, a yellowish-white metal that occurs in nature chiefly as the minerals barite (barium sulfate) and witherite (barium carbonate). Because of the toxic effects on the heart and blood vessels, elevated concentrations of barium are considered a health risk in drinking water. Elevated barium concentrations are common in brines and production fluids. In a study of the occurrence of brine in western Pennsylvania, Poth (1962) reported the mean concentration of barium in 35 samples of brine from oil and gas formations in western Pennsylvania was 224,000 µg/L. High concentrations of barium in brines almost always occur along with low sulfate concentrations. Hem (1985, p. 137) states that the sulfate concentrations are probably kept low by sulfate reduction, enabling the dissolved barium concentration to increase, at least up to the point at which the carbonate solubility limit is reached. Analyses of samples of production fluids from oil formations in Warren County indicate a range in concentration of dissolved barium from less than 500 to 355,000 µg/L (table 26). The sample with the highest barium concentration of 355,000 µg/L had a very low sulfate concentration of 7 µg/L, providing probable evidence of sulfate reduction.

In the United States, the occurrence of barium above a concentration of 1,000 µg/L in water sampled from domestic wells is rare. Case histories are documented in New York, Pennsylvania, Kentucky, Illinois, and New Mexico. A USGS ground-

water study in 1982 at the Cattaraugus Indian Reservation of southwestern New York found barium concentrations above 1,000 µg/L (as high as 23,000 mg/L) in bedrock and glacial aquifers used for drinking-water supply (Moore and Staubitz, 1984). At the Reservation, the source of the barium was not attributed to active or abandoned gas wells or to barite drilling muds; rather, they were probably the result of natural dissolution of barite apparently controlled by sulfate-reducing bacteria. The bacteria probably altered the barite equilibrium by removing sulfate ions, which resulted in additional barite dissolving (Moore and Staubitz, 1984, p. 13).

Water samples from three abandoned oil and gas wells exceeded the 2,000 µg/L MCL for barium. Concentrations of dissolved barium exceeded the MCL in two of three samples collected from well Wr-256 tapping outwash deposits; this was the only drinking-water well sampled that exceeded the MCL for barium. Well Wr-256, owned by the Pennsylvania Department of Transportation, was taken out of service because the barium concentrations exceeded the MCL; more information and discussion of the water quality of well Wr-256 is provided in a section entitled "*Tidioute Borough and Local Area*."

Valley Settings

Arsenic contamination in Chapman State Park was documented in the repeated sampling of well Wr-576. This valley well (total depth of 59 ft) is finished in an alluvium hydrogeologic unit. The following data illustrate the persistence and variability in arsenic concentration over time.

Sample date	Arsenic concentration in well Wr-576, in micrograms per liter
6/7/83	67
7/29/83	44
8/8/83	10
9/29/83	100
3/22/84	457
9/12/84	64
11/14/84	107
4/12/85	16
9/24/85	94
2/13/86	181
4/23/86	190
8/5/87	58

The source of the arsenic is unknown. Samples collected from wells surrounding Wr-576 had concentrations of arsenic less than the MCL of 10 µg/L. Extensive information on the ground-water contamination problems at Chapman State Park is presented in a section entitled "*Chapman State Park Case Study*."

Glacial Terrace Settings

Between June 11, 1987, and September 17, 1987, 52 wells in a housing development near North Warren were sampled for arsenic. The arsenic concentration in 15 of the 52 wells exceeded the USEPA MCL of 10 µg/L; the maximum concentration measured was 150 µg/L in 2 wells (Wr-794 and Wr-798) (fig. 13). No samples had barium concentrations above the 2,000 µg/L MCL. On November 17-18, 1987, 18 wells were sampled in the housing development; 11 of those wells sampled were also sampled in the summer, and 7 were not previously sampled. All 18 wells had concentrations of dissolved arsenic greater than 10 µg/L, concentrations of arsenic in the 18 wells ranged from 28 to 150 µg/L (fig. 13). The source of the arsenic probably is natural. None of the 18 samples had barium concentrations greater than or equal to the 2,000 mg/L MCL.

The hydrogeologic setting of the area near the housing development is complex. About 60 wells of various depths pump ground water for domestic supply and discharge the water to on-lot sewage-disposal systems that recharge the ground-water system. The development is on a glacial sand and gravel outwash terrace. Most of the wells tap an outwash aquifer that generally thins to the west and south in the vicinity of the steep slope of the adjacent bedrock hillside. Data generally are lacking concerning the changes in composition with depth of the glacial unit. Oil wells are present on the hillside above the housing development. The problem of elevated arsenic and barium concentrations in the housing development was addressed by extending public-supply water lines to the entire development.

The only water well where ground-water samples exceeded the USEPA MCL of 2,000 µg/L for barium (well Wr-256) was on a glacial outwash terrace in the valley of the Allegheny River near Tidioute. On the basis of samples collected on June 27, 1985; August 6, 1986; and August 12, 1987, the elevated concentrations of barium in the glacial outwash hydrogeologic unit were persistent. These elevated concentrations of barium probably are caused naturally and may reflect some barium-rich ground water that discharges from the Venango Formation to the overlying outwash aquifer. The well is probably finished in sand and gravel that is probably close to the bedrock surface.

Upland Settings

Upland settings generally are defined as hilltops, hillsides, and upland draws and do not include glacial terraces. Most wells in uplands tap bedrock hydrogeologic units. Several wells defined as being in the uplands had arsenic concentrations greater than the USEPA MCL. Hillside wells Wr-574, Wr-422, and Wr-729 had arsenic concentrations of 10, 10, and 11 µg/L,



EXPLANATION

- 100/130 LOCATION OF WELL SAMPLED AND ARSENIC CONCENTRATION IN SUMMER/FALL IN MICROGRAMS PER LITER
- \+ ARSENIC CONCENTRATION LESS THAN 10 MICROGRAMS PER LITER
- N WELL NOT SAMPLED

Figure 13. Dissolved arsenic concentrations in water samples collected from wells in a housing development, Warren County, Pennsylvania.

respectively. Hilltop well Wr-382 had an arsenic concentration of 15 µg/L. Some wells in upland draws have barium concentrations between 900 and 2,000 µg/L. For example, three water wells tapping the Venango Formation (Wr-494, Wr-590, and Wr-589) near Anders Run (Youngsville quadrangle) had concentrations of dissolved barium of 1,600; 970; and 950 µg/L, respectively.

Additional Trace Elements

Detection levels have changed through time for the laboratory analysis of samples of most trace elements. In 1985, laboratory analyses of most trace elements were performed by the Harrisburg PaDEP laboratory using detection levels derived from the use of inductively coupled plasma (ICP) instruments. These detection levels were a problem because the detection level was higher in some cases than the USEPA MCL or SMCL; thus the comparison of sample concentration to the MCL or SMCL was not valid. These high detection levels are reported for the 1985 samples in Moore and Buckwalter (1996). For 1986 samples, laboratory instrumentation changed from ICP to atomic absorption (AA) instruments with lower detection levels that generally were below the USEPA MCL or SMCL. The following data evaluation does not include those analyses of trace elements that have detection levels greater than the MCL or SMCL.

The USEPA MCL for lead during the data collection from 1984 to 1988 was 50 µg/L. Recently, the MCL for lead was lowered to 15 µg/L. When dissolved lead concentrations were analyzed using AA instruments with a detection level of less than 4 µg/L, almost all ground-water sample concentrations were less than 4 µg/L. One sample collected from water well Wr-445 tapping the Venango Formation exceeded the MCL (16 µg/L).

No zinc concentrations in samples collected from water wells, abandoned oil and gas wells, or springs exceeded the USEPA SMCL of 5,000 µg/L. Most concentrations of dissolved zinc were less than 100 µg/L; a few concentrations ranged from 100 to 1,000 µg/L.

The detection level of chromium was 45 µg/L in 1985 and 4 µg/L in 1986-88. The USEPA MCL for chromium is 100 µg/L, and concentrations from two wells in the Pottsville Group exceeded the MCL (160 and 170 µg/L). Results from 90 percent of the samples had chromium concentrations less than the detection level.

The USEPA MCL for cadmium is 5 µg/L. Disregarding those samples collected in 1985 with a detection level of less than 10 µg/L, a total of 181 ground-water samples were analyzed for dissolved cadmium (table 15). Samples from four water wells and one abandoned oil and gas well exceeded the MCL; the maximum concentration was 21.5 µg/L in the oil and gas well (Wr-586).

Organic Constituents

The evaluation of the organic constituents sampled in ground water from wells, springs, and abandoned oil and gas wells is separated into the following four sections: 1) natural gas, 2) oil and grease, 3) volatile organic compounds (VOCs), and 4) total organic carbon.

Natural Gas

Natural gas from petroleum reservoirs in Warren County varies in composition but is made up mostly of methane (fig. 14). Other components may include propane, butane, ethylene, propylene, hydrogen, and helium. Methane is a colorless, odorless, and flammable gas. In the oil and gas fields of Pennsylvania, explosions and fires causing loss of life, personal injury, and property damage have occurred in a few instances when natural gas migrated from petroleum reservoirs to buildings and the "correct" mixture of natural gas and air exploded when exposed to a source of ignition. Natural-gas migration from petroleum reservoirs to land surface and methane production from biogenic processes in the soils, unsaturated zone, or aquifers are potential safety problems because of the flammable properties of these gases. Ingestion of water containing dissolved methane is not a documented health hazard; no USEPA MCLs or SMCLs have been established for methane. Exposure of drinking water containing dissolved or free methane to atmospheric conditions results in a quick volatilization of the methane from the water to the air creating a potentially hazardous environment.

To prevent fires or explosions involving natural gas, most well drillers and residents of Warren County usually vent a buried or capped water well or a pump house to prevent methane accumulation. The flammable properties of methane are specific; an understanding of these properties is critical to evaluate the risk of fire or explosion in a well casing, pump house, or home.

The following is a discussion of the flammable property of methane (Mine Safety Appliances Company, 1980): "When methane is introduced into an area, fresh air is gradually displaced until the area may be completely filled with the gas. During this process, the air/methane mixture passes through three specific regions: lean, explosive, and rich. Mixtures in the lean region, which extends from fresh air to the lower explosive limit (LEL), contain too little gas in relation to the amount of air to burn; that is, propagation of flame does not occur on contact with a source of ignition. A mixture at the LEL, 5 percent by volume, is the lowest concentration of methane in air that will explode or burn when ignited. Mixtures in the explosive or flammable region, which extends from the LEL to the upper explosive limit (UEL), will propagate flame. Large volumes of combustible gases or vapors in these concentrations, if ignited, can cause damage and personal injury. A mixture at the UEL (15 percent) has the highest concentration of combustible gas in air that will burn. Mixtures in the rich region, which extends from the UEL to 100 percent methane, contain too much gas in relation to air to be combustible. However, since the addition of air to these high concentrations of methane creates mixtures in the flammable region, they must be considered equally dangerous."

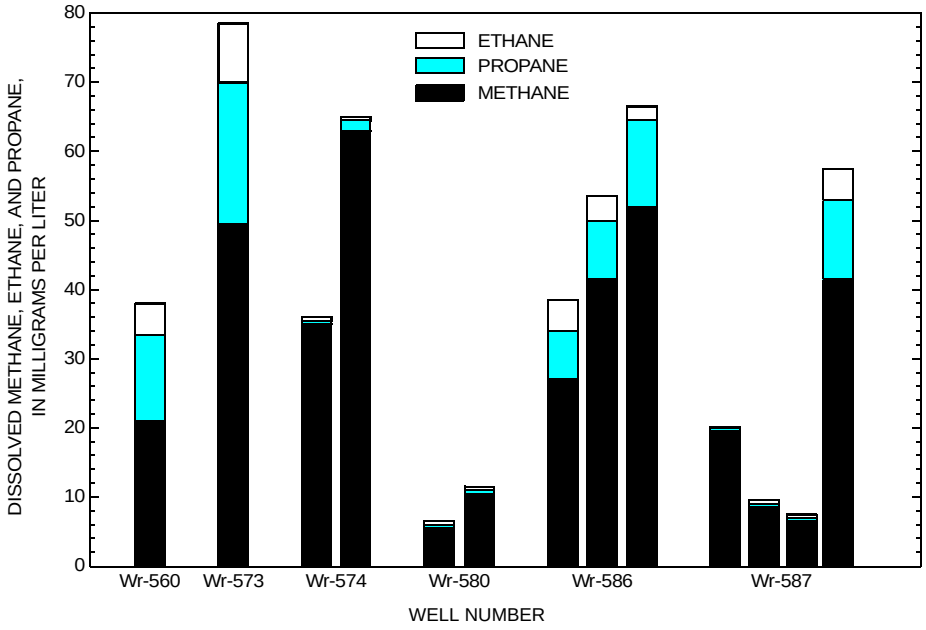


Figure 14. Dissolved concentrations of methane, ethane, and propane in water from abandoned oil wells, Warren County, Pennsylvania.

Table 15. Median and range of concentrations of dissolved cadmium for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[<, less than; —, no samples collected]

Hydrogeologic unit	Number of wells sampled	Concentration, in micrograms per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	5	<0.2	0.33	0.85
Colluvium	4	<.2	.24	.60
Glacial drift (undifferentiated)	6	<.02	.30	1.18
Ice-contact stratified sand and gravel	10	<.02	.18	.98
Alluvium and glacial lacustrine, undifferentiated	—			
Glacial outwash sand and gravel	28	<.02	.25	12.0
Bedrock hydrogeologic units				
Pottsville Group	3	<.02	.52	13.0
Shenango Formation	4	<.02	<.02	2.18
Cuyahoga Formation	7	<.02	.50	1.11
Knapp Formation	2	.43		.47
Oswayo Formation	5	<.02	.66	15.0
Riceville Formation	4	<.02	.23	.24
Corry Sandstone through Riceville Formation	6	<.02	.33	3.75
Catskill and Venango Formations	—			
Venango Formation	55	<.02	.28	18.0
Chadakoin Formation	28	<.02	.28	1.99
Upper Devonian, undifferentiated[1]	14	<.02	.23	21.5
Total	181			

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Sources of methane in soils, unsaturated zones, and aquifers (collectively defined as "near-surface") include 1) biogenic (produced by living organism) processes and 2) migration of natural gas from underlying petroleum reservoirs. The relative proportions of methane and ethane can be examined to determine methane origin. Biogenic gases are characterized by methane to ethane ratios in excess of 1,000 and methane percentages in excess of 99 (Emery and Hogan, 1958; Erdman, 1978).

When dissolved natural gas in ground water is suspected of migrating from a petroleum reservoir, several methods are available to attempt to identify the hydrocarbon source defined as dry gas, gas-condensate, or oil (table 16). The determination of the specific petroleum reservoir responsible for the source of natural gas in ground water or the natural gas observed in a home may be a difficult, complex, costly process. In some cases, the migration of the natural gas may be short, direct, and swift with the gas composition undergoing little or no change in migration from the reservoir to the water well or home. Comprehensive gas analysis of the constituents of the gas in the suspected petroleum reservoir should compare closely with gas analysis of the water well or home. However, if the gas migration is time consuming, long in distance, and through thick intervals of fractured bedrock, the gas composition may be altered substantially. The lighter fractions of natural gas move more readily than the heavier fractions. Hydrogen is a very reactive and mobile constituent of natural gas. Helium is also a mobile constituent of natural gas. In a large petroleum reservoir, the parts of the reservoir overlain by fractured rock may be depleted in hydrogen and helium because of enhanced vertical migration. Propane and butane will migrate slower than methane because of their larger molecular size.

The median and range of concentrations of dissolved methane, ethane, and propane for ground-water samples collected from water wells and abandoned oil and gas wells are presented in tables 17, 18, and 19 by hydrogeologic unit.

Table 16. Geochemical parameters used to identify hydrocarbon sources of near-surface gases.

[modified from Weismann, 1979]

Deep hydrocarbon source	Geochemical parameters of near-surface gases		
	Percent methane	Methane/ethane ratio	Propane/methane ratio multiplied by 1,000
Dry gas	100 - 90	200 - 25	2 - 20
Gas-condensate	90 - 75	25 - 10	20 - 60
Oil	75 - 45	10 - 4	60 - 500

Oil and Grease

The water samples were analyzed in the laboratory for oil and grease by a standard procedure (Partition-Gravimetric Method) that gives a final concentration, but upon interpretation, the results are really more qualitative than quantitative. In the laboratory analysis for oil and grease, oil and grease are defined as any materials recovered as substances soluble in trichlorotrifluoroethane. Unlike some constituents that represent distinct chemical elements, ions, compounds, or groups of compounds, oils and greases are defined by the method used for their determination. No known solvent will selectively dissolve only oil and grease (American Public Health Association, American Water Works Association, and Water Pollution control Federation, 1981, p. 461). Thus, sample complexity may result in either high or low results because of lack of analytical specificity (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1981, p. 460). Oil and grease determinations may include other materials soluble in trichlorotrifluoroethane including sulfur compounds and chlorophyll that results in higher than expected final concentrations. In addition to these limitations on the interpretation of the results of the oil and grease analyses, this standard laboratory method lacks the ability to measure organic fractions that readily volatilize including many of the components of gasoline. Thus, the volatile fractions of crude oil will not be measured by this standard laboratory procedure. A further limitation is that some of the heavier residuals of petroleum may contain a significant portion of materials that are not extractable with trichlorotrifluoroethane (American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1981, p. 461). In part because of the analytical limitations of the procedures used to determine oil and grease, the USEPA has not established a MCL or SMCL for oil and grease.

Additional restrictions on the interpretation of low concentrations of oil and grease were found by the application of quality-assurance techniques. The suspect problem was discovered when high purity distilled water containing no organic compounds at the microgram per liter level was sent to the PaDEP laboratory as a double blind sample. Double blind samples appear to the laboratory as a routine sample but contain water of a specified composition. The laboratory determined an erroneous high concentration of oil and grease of 4.0 mg/L. Thus, low concentrations of oil and grease near the detection levels may be suspect.

Because of the lack of a MCL, critical lack of a SMCL, and all the analytical limitations previously discussed, the interpretive value of the oil and grease data are mostly a rough measure or inaccurate screening tool for detection of "oil and grease." For the ground-water samples collected for this study, low concentrations of oil and grease should not be the sole factor determining organic contamination of samples.

The samples of water and other fluids collected from abandoned oil and gas wells were analyzed for oil and grease as one of several methods to screen for the presence or absence of the

Table 17. Median and range of concentrations of dissolved methane for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[—, no samples collected]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	7	0.0	3.5	28.0
Colluvium	5	.0	.2	40.5
Glacial drift (undifferentiated)	4	.0	.0	.0
Ice-contact stratified sand and gravel	5	.0	.0	.0
Alluvium and glacial lacustrine, undifferentiated	—			
Glacial outwash sand and gravel	20	.0	.0	10.0
Bedrock hydrogeologic units				
Pottsville Group	—			
Shenango Formation	2	.0	.0	.0
Cuyahoga Formation	3	.0	.0	.0
Knapp Formation	2	.0		.0
Oswayo Formation	6	.0	.2	3.0
Riceville Formation	4	.0	.0	.0
Corry Sandstone through Riceville Formation	5	.0	.0	2.5
Catskill and Venango Formations	—			
Venango Formation	59	.0	.0	27.5
Chadakoin Formation	24	.0	.0	16.5
Upper Devonian, undifferentiated[1]	10	.8	7.2	35.0
Total	156			

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 18. Median and range of concentrations of dissolved ethane for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[—, no samples collected]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter			Number of detectable concentrations
		Minimum	Median	Maximum	
Unconsolidated hydrogeologic units					
Alluvium	7	0.0	0.0	14.5	2
Colluvium	4	.0	.0	10.0	1
Glacial drift (undifferentiated)	4	.0	.0	.0	0
Ice-contact stratified sand and gravel	5	.0	.0	.0	0
Alluvium and glacial lacustrine, undifferentiated	—				
Glacial outwash sand and gravel	12	.0	.0	.0	0
Bedrock hydrogeologic units					
Pottsville Group	—				
Shenango Formation	2	.0	.0	.0	0
Cuyahoga Formation	3	.0	.0	.0	0
Knapp Formation	2	.0		.0	0
Oswayo Formation	6	.0	.0	2.0	1
Riceville Formation	4	.0	.0	.0	0
Corry Sandstone through Riceville Formation	5	.0	.0	.0	0
Catskill and Venango Formations	—				
Venango Formation	56	.0	.0	1.3	4
Chadakoin Formation	24	.0	.0	3.5	3
Upper Devonian, undifferentiated[1]	10	.0	.0	12.5	4
Total	144				15

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

Table 19. Median and range of concentrations of dissolved propane for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[—, no samples collected]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter			Number of detectable concentrations
		Minimum	Median	Maximum	
Unconsolidated hydrogeologic units					
Alluvium	7	0.0	0.0	7.0	1
Colluvium	4	.0	.0	4.5	1
Glacial drift (undifferentiated)	4	.0	.0	.0	0
Ice-contact stratified sand and gravel	5	.0	.0	.0	0
Alluvium and glacial lacustrine, undifferentiated	—				
Glacial outwash sand and gravel	12	.0	.0	.0	0
Bedrock hydrogeologic units					
Pottsville Group	—				
Shenango Formation	2	.0	.0	.0	0
Cuyahoga Formation	3	.0	.0	.0	0
Knapp Formation	2	.0		.0	0
Oswayo Formation	6	.0	.0	1.5	1
Riceville Formation	4	.0	.0	.0	0
Corry Sandstone through Riceville Formation	5	.0	.0	.0	0
Catskill and Venango Formations	—				
Venango Formation	56	.0	.0	.2	1
Chadakoin Formation	23	.0	.0	1.0	2
Upper Devonian, undifferentiated[1]	10	.0	.1	4.5	5
Total	143				11

[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

components of crude oil. Results of these oil and grease analyses are presented in Moore and Buckwalter (1996). Concentrations of oil and grease in the samples in excess of 100 mg/L commonly were associated with strong hydrocarbon odors of the samples, colorful sheens routinely associated with petroleum products, and selected observations of droplets of what appeared to be crude oil.

Volatile Organic Compounds (VOCs)

VOCs are a special class of organic compound extensively used in industrial, commercial, and household applications. Benzene, ethylbenzene, toluene, and xylenes are examples of common VOCs. These compounds are components of crude oil, gasoline, fuel oil, and many commonly used household products. Although gasoline and fuel oil float on the surface of the water or the water table, the benzene and toluene components, for example, are soluble and can, therefore, disperse throughout the zone of saturation. Because many VOCs are confirmed or suspected human or animal carcinogens, USEPA MCLs have been established for some of them. For example, the USEPA MCL concentration for benzene is 5 μg/L; for ethylbenzene, 700 μg/L; for toluene, 1,000 μg/L; and for total xylenes, 10,000 μg/L. VOCs may enter the ground-water system from leaking storage tanks and pipelines, spills, and discharge from septic systems. Oil and gas field brines and production fluids may contain VOCs. If not disposed of properly, these VOCs may contaminate ground water. Once in the ground-water system, VOCs are difficult to remove, and treatment generally is expensive. Additional information on the problems of assessment, abatement, and cleanup of organic chemical contamination of aquifers are described in Yaniga (1990).

Improper disposal of solvents that results in ground-water contamination is a serious problem for public and private well owners who depend on ground water as a source of drinking-water supply. The Starbrick area west of Warren Borough is the site of extensive ground-water contamination from organic compounds, especially solvents. One of the major VOCs contaminating the ground water at Starbrick is the solvent trichloroethylene (TCE). The USEPA, PaDEP, and consulting firms under contract to the USEPA investigated this problem (Stone, 1985). The high costs associated with cleaning up the large area of contaminated ground water were considered impractical. Municipal water lines were extended into the Starbrick area to provide an alternative water supply to the residents and the local businesses.

Selected water wells and abandoned oil and gas wells were sampled for analysis of VOCs (table 20). Benzene that was detected at a concentration of 1 mg/L (table 20) in a water sample from well Wr-561 was anticipated because of that well having a prior history of organic chemical contamination. The exact source of the benzene is unknown, but contamination of ground water from oil and gas development are suspected. The abandoned oil and gas wells Wr-586 and Wr-587, within 200 ft of Wr-561, contain elevated concentrations of benzene greater than 650 μg/L (table 20). On one occasion, the abandoned well Wr-586 discharged to land surface an undetermined volume of crude oil that was in sufficient quantity to flow overland toward the nearby stream. More information about the hydrogeology and the fluid contained in the abandoned oil and gas wells of this site is included in a subsequent section entitled "*Abandoned Oil and Gas Wells*."

The water wells sampled for analysis of VOCs (table 20), with the exception of well Wr-561, were selected to screen for unsuspected ground-water contamination by VOCs. Chloroform that was detected in the sample collected from well Wr-568 (1.6 μg/L) was unexpected, and the source is unknown. Wr-568 is an unused municipal well owned by Tidioute Borough.

The laboratory report of the presence of various alkanes and cyclic hydrocarbons in the sample collected from Wr-Sp-124 was anticipated. An oil sheen was observed on the surface of the water pool collecting the spring discharge. Oil sheens were observed at the spring site by a variety of Federal and state officials prior to the collection of the sample on November 7, 1986. Oil containment materials were in place at the downstream end of the pool prior to the date of sample collection. The exact source of the various alkanes and cyclic hydrocarbons in the spring discharge is unknown; a nearby suspected oil pipeline leak may have been a cause of the problem.

Total Organic Carbon

Ground-water samples are routinely analyzed for total organic carbon as a means to estimate organic content of samples. Measurements of total organic carbon provide an inexpensive screening tool to detect samples with high organic content. The range and median concentrations of analyses of total organic carbon are presented in table 21. The highest concentrations of total organic carbon were observed in ground-water samples from abandoned oil and gas wells—Wr-570, 90.0 mg/L; Wr-580, 80.5 mg/L; Wr-586, 151.0 mg/L; and Wr-587, 32.0 mg/L.

Table 20. Results of analysis of volatile organic compounds in water from wells, abandoned oil and gas wells, and one spring, Warren County, Pennsylvania.

[µg/L, micrograms per liter; —, not detected]

Well or spring number	Hydrogeologic unit	Date of sample	Detection limit (µg/L)	Benzene (µg/L)	Chloroform (µg/L)	Ethyl-benzene (µg/L)	Toluene (µg/L)	Xylenes (µg/L)	Other volatile organic compounds detected but not quantified	Remarks
					Water wells					
Wr-50	Venango Formation	7/28/87	1.0	—	—	—	—	—	—	Observation well
Wr-283	Cuyahoga Formation	7/23/87	1.0	—	—	—	—	—	—	Observation well
Wr-389	Venango Formation	7/30/87	1.0	—	—	—	—	—	—	Domestic well
Wr-520	Glacial outwash sand and gravel	7/29/87	1.0	—	—	—	—	—	—	Observation well
Wr-522	Glacial outwash sand and gravel	11/5/85	.5	—	—	—	—	—	—	Observation well
Wr-561	Venango Formation	11/4/86	.5	1.0	—	—	—	—	—	Domestic well
		7/23/87	1.0	—	—	—	—	—	—	Domestic well
Wr-568	Glacial outwash sand and gravel	7/29/87	1.0	—	1.6	—	—	—	—	Observation well
Wr-579	Venango Formation	7/30/87	1.0	—	—	—	—	—	—	Observation well
Wr-594	Venango Formation	7/22/87	1.0	—	—	—	—	—	—	Observation well
Wr-733	Glacial outwash sand and gravel	7/21/87	1.0	—	—	—	—	—	—	Domestic well
Wr-749	Corry Sandstone through Riceville Formation undivided	7/30/87	1.0	—	—	—	—	—	—	Domestic well
					Abandoned oil wells					
Wr-573	Upper Devonian, undifferentiated	7/22/87	100	170	—	—	—	200	Several alkanes and an isomer of cumene	Sampling depth 190 feet
Wr-586	Upper Devonian, undifferentiated	11/5/86	50	1,000	—	1,200	2,000	400	—	Sampling depth 400 feet
		11/5/86	50	1,100	—	2,100	1,600	700	Various alkanes trimethylbenzene, and a few cyclic hydrocarbons	Sampling depth 700 feet
		11/5/86	50	650	—	750	550	280	Various alkanes	Sampling depth 800 feet
		7/23/87	100	1,200	—	—	160	1,100	Isomer of cumene	Sampling depth 880 feet
Wr-587	Upper Devonian, undifferentiated	11/6/86	25	—	—	150	—	50	—	Sampling depth 160 feet
		11/6/86	25	—	—	—	—	—	—	Sampling depth 292 feet
		11/6/86	25	—	—	—	—	—	—	Sampling depth 500 feet
		11/6/86	50	1,650	—	250	—	50	Ethyl sulfide	Sampling depth 860 feet
					Spring					
Wr-Sp 124	Alluvium	11/7/86	1.0	—	—	—	—	—	Various alkanes and cyclic hydrocarbons	Spring not used for water supply

Table 21. Median and range of concentrations of total organic carbon for water samples from wells in Warren County, Pa., by hydrogeologic unit.

[<, less than; —, no median calculated]

Hydrogeologic unit	Number of wells sampled	Concentration, in milligrams per liter		
		Minimum	Median	Maximum
Unconsolidated hydrogeologic units				
Alluvium	5	<0.5	3	22
Colluvium	5	<.5	1	8
Glacial drift (undifferentiated)	6	<.5	1	3
Ice-contact stratified sand and gravel	7	<.5	3	8
Alluvium and glacial lacustrine, undifferentiated	3	1.4	2	2
Glacial outwash sand and gravel	36	<.5	5	18
Bedrock hydrogeologic units				
Pottsville Group	3	<.5	1	2
Shenango Formation	3	<.5	4	7
Cuyahoga Formation	9	1.4	3	5
Knapp Formation	3	<.5	1	1
Oswayo Formation	6	<.5	2	6
Riceville Formation	4	<.5	1	6
Corry Sandstone through Riceville Formation	5	<.5	1	6
Catskill and Venango Formations	2	3.0	—	6
Venango Formation	64	<.5	3	51
Chadakoin Formation	34	<.5	4	12
Upper Devonian, undifferentiated[1]	15	4.0	10	151
Total	210			

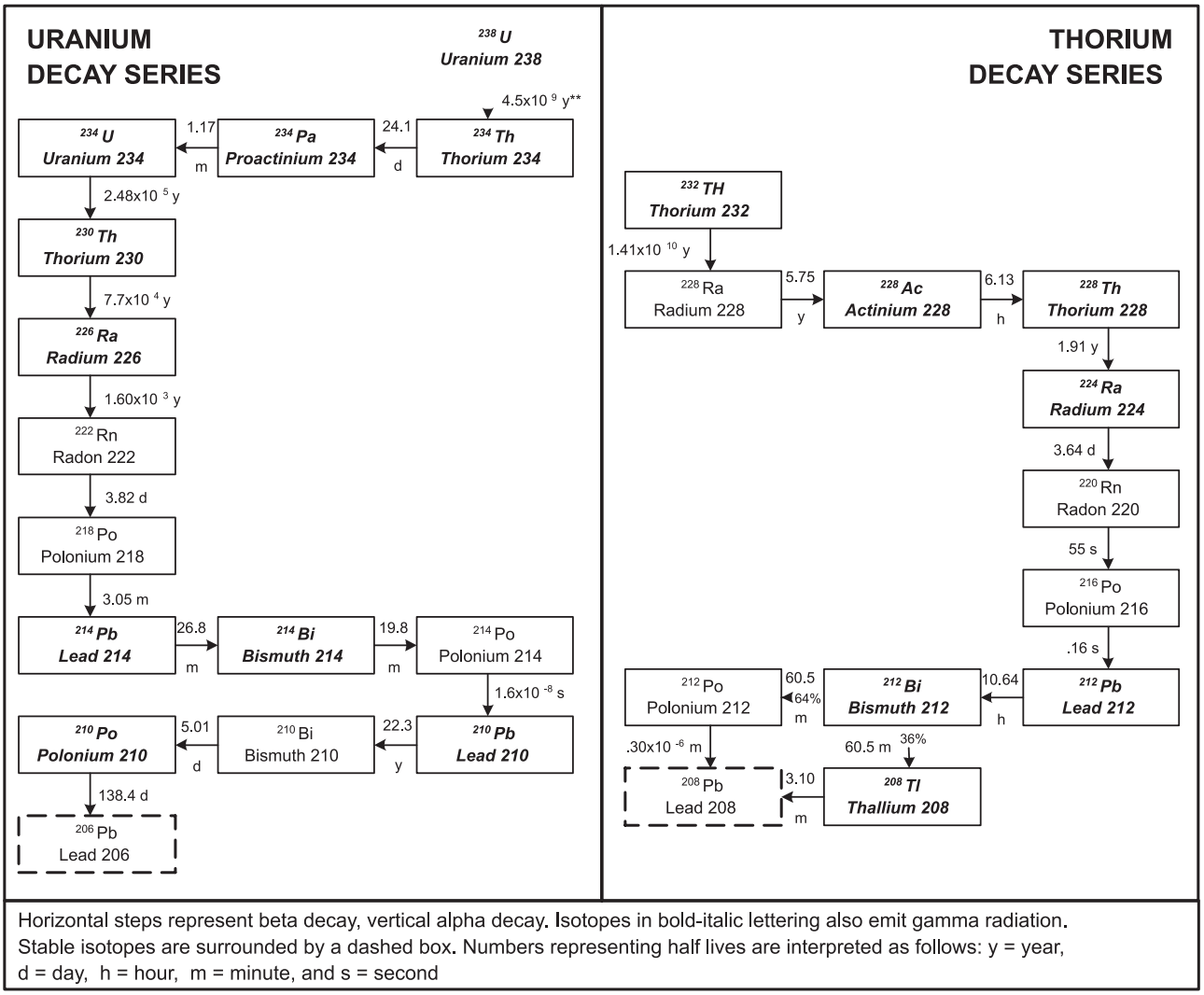
[1]Unknown lithology of abandoned oil and gas well. An assignment used when the water-yielding unit is unknown.

The determination of background concentrations for total organic carbon is difficult for many reasons. Many organic compounds may contribute to the total organic carbon concentration. The majority of organic compounds present in petroleum-contaminated samples may be alkanes, cycloalkanes, ketones, aldehydes, alcohols, and other compounds that cannot be identified completely without segregation of organic-compound classes using expensive clean-up techniques. One USGS study estimated a background concentration of total organic carbon at 6 mg/L or less in ground-water samples collected in Kansas from unconsolidated sand and gravel aquifers of Pleistocene age (Spruill, 1988, p. 80).

Radionuclides

Rising public concern regarding exposure to radioactive elements in the home led to an examination of radioisotopes in the ground water in Warren County. The suite of radionuclides for which the water samples were analyzed is listed in table 22. At the time of the sampling, USEPA had set interim standards for gross alpha and gross beta radiation and total radium. Radium was added to the suite of radioisotopes of interest not only because it had a proposed standard at the time of the study but also because it has chemical properties similar to barium. Water from several wells had barium concentrations that were markedly above background concentrations. Barium concentrations frequently are elevated in production fluids from oil and gas wells, so there was concern that radium might substitute for barium and thereby raise concentrations in ground water.

Two radioactive decay series that include all the radioisotopes tested for in Warren County are shown in figure 15. Radon 222, uranium 238 and 234, and radium 226 are all within the uranium decay series. It was believed that radon was likely to be the most common radioisotope in fresh ground water. Radium 228 is the sole radioisotope tested for in the thorium decay series. Unless an unexpected enrichment mechanism was at work, radium and uranium should have been present in very low (background) concentrations. USEPA established the gross alpha and gross beta testing as a less expensive screening test for the presence of radium. Generally, testing for radium is done when gross alpha results exceed 15 pCi/L. Because in rare circumstances the radium concentration can be unexpectedly high when the gross alpha value is less than 15 pCi/L, all samples were tested for both.



Horizontal steps represent beta decay, vertical alpha decay. Isotopes in bold-italic lettering also emit gamma radiation. Stable isotopes are surrounded by a dashed box. Numbers representing half lives are interpreted as follows: y = year, d = day, h = hour, m = minute, and s = second

Figure 15. Uranium and thorium decay series (World Information Service on Energy Uranium Project, 2005).

Table 22. Radionuclide species analyzed in ground-water samples.

[—, no data available]

Radioisotope	Drinking water standard[1]	Comments
Uranium	30 micrograms per liter (as of 12/8/03)	—
Radium 226	Total of 5 picocuries per liter for Radium 226 and Radium 228 combined	—
Radium 228	See Radium 226	—
Gross alpha	15 picocuries per liter (excluding Radon 222 and Uranium)	Used as a screening test for radon. When greater than 5 picocuries per liter, radon content must be tested.
Gross beta	4 millirems per year for beta particles and photon emitters	—
Radon 222	4,000 picocuries per liter[2]	—

[1]U.S. Environmental Protection Agency, 2002.

[2]Proposed Alternative Maximum Contaminant Level

Sampling Design and Protocol

Representative water wells, springs, and abandoned oil and gas wells were selected from previously sampled sites. Because radium has a chemical behavior similar to barium, a preference was given to wells for which laboratory results had shown elevated barium concentrations. Abandoned oil and gas wells were selected because brines associated with petroleum production typically are high in barium. Finally, six of the larger springs were selected for sampling. The type and distribution of the 25 sampling sites are shown on fig. 16.

A geophysical borehole logger was used to collect discrete interval samples from the abandoned oil and gas wells. Radon analyses were conducted using scintillation vials into which 10 cc's of sample was injected. The sample volume was measured precisely using a glass syringe. Each vial contained a scintillation fluid with a strong affinity for radon. Two vials were collected for each sample point. All radionuclides except radon were analyzed from water collected in a 1 gal collapsible container. A sample for complete inorganic analysis also was collected and submitted at the time of radionuclide sampling. Results from the Warren County radionuclide analyses are presented in table 23.

Results of Radionuclide Analysis

Radon concentrations in samples at 11 of 21 water well and spring sites exceeded 300 pCi/L. The value of 300 pCi/L has been discussed for several years as a possible standard for drinking water. If the results from the sampling done for this project are representative, radon can be expected to become a constituent of major concern in Warren County in the future.

Perhaps more surprising than the radon concentrations in well water are the concentrations in spring water. When finalizing the program for radionuclide sample collection, springs were nearly excluded because it was thought radon concentrations would be too low to measure. It seemed reasonable to assume that the exposure of spring water to the atmosphere would deplete the radon before it reached the discharge point.

Not only does spring water appear to be enriched in radon, but it also seems depleted of uranium, when compared to the samples collected from water-supply wells (fig. 17). The figure shows that radon concentrations in spring water commonly were higher than in well water containing the same concentration of uranium.

One explanation for this anomaly may be that well-water samples can be expected to closely reflect the radon concentrations attributable to the uranium that one would expect to find in the sedimentary bedrock units in Warren County. The higher radon concentrations in spring water would then require exposure to some form of natural uranium enrichment. Because radon has a half life of slightly less than 4 days, the zone of uranium enrichment should be near land surface. Oxidation and precipitation of uranium on fracture and grain surfaces in the near-surface bedrock could explain the creation of a zone of natural uranium enrichment and the relative depletion of uranium in spring water as compared to well water.

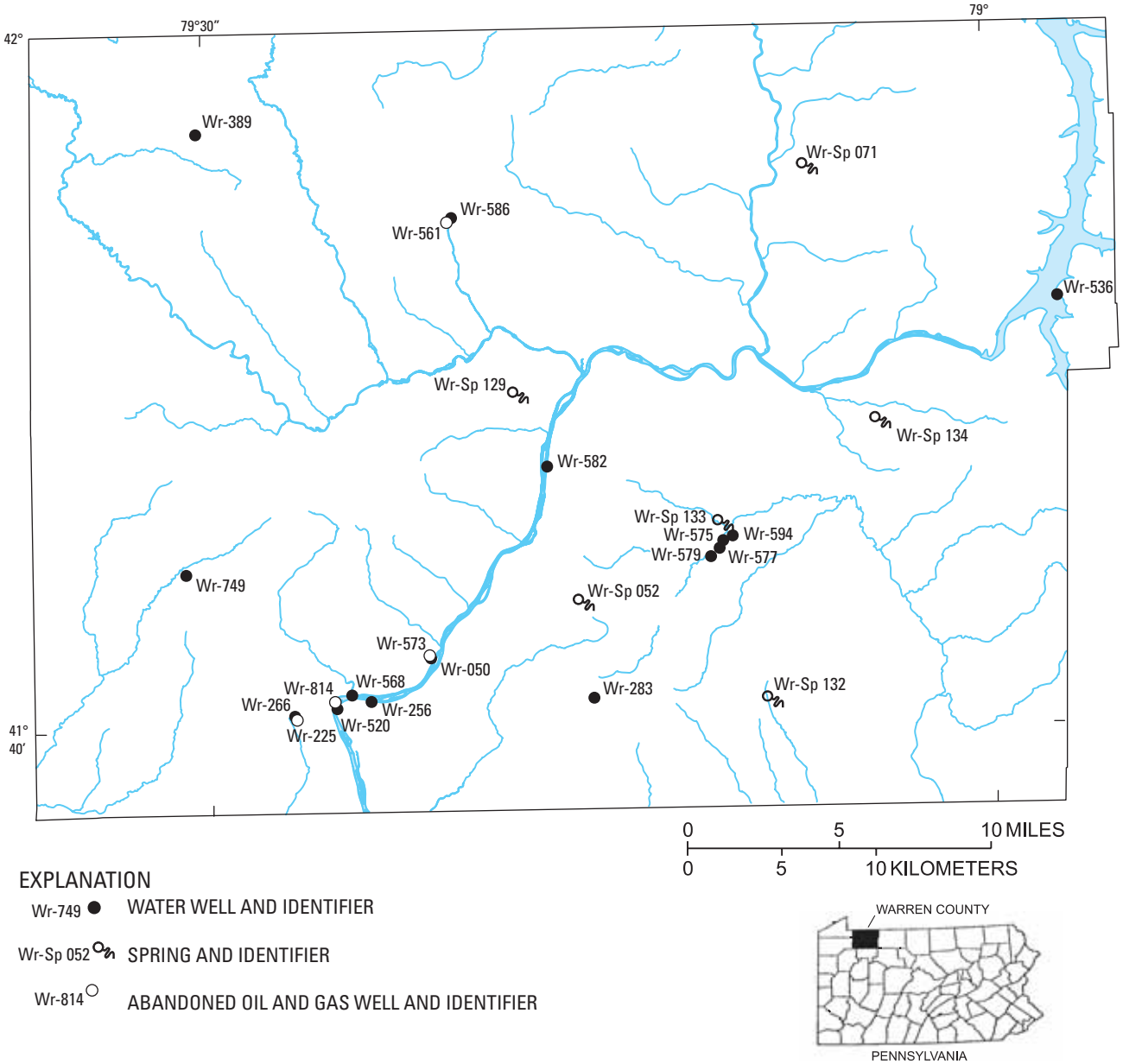


Figure 16. Location of wells sampled for radionuclide analysis, Warren County, Pennsylvania.

Table 23. Radionuclides in ground water in Warren County, Pennsylvania.

[µg/L, micrograms per liter; pCi/L, picocuries per liter; —, below the lowest level of detection; ND, not analyzed for; Bold values exceed the U.S. Environmental Protection Maximum Contaminant Level]

Well	Hydrogeologic unit	Uranium (µg/L)	Radium 226 (pCi/L)	Radium 228 (pCi/L)	Gross alpha (pCi/L)	Gross beta (pCi/L)	Radon (pCi/L)[1]
			Water wells				
Wr-050	Venango Formation	0.38	0.20	—	—	—	172
Wr-225	Cuyahoga Formation	.07	.28	—	—	4.10	—
Wr-256	Glacial outwash sand and gravel	ND	ND	—	—	—	179
Wr-283	Cuyahoga Formation	.56	.11	—	—	—	834
Wr-389	Venango Formation	.35	1.12	1.62	**21.2**	25.9	170
Wr-520	Glacial outwash sand and gravel	.29	.45	—	—	—	406
Wr-536	Chadakoin Formation	.93	.44	—	**5.43**	17.7	1,010
Wr-561	Venango Formation	.32	.16	—	—	—	126
Wr-568	Glacial outwash sand and gravel	.68	.09	—	—	—	504
Wr-575	Alluvium	.40	.15	—	—	—	1,410
Wr-577	Alluvium	.31	.19	—	—	3.38	156
Wr-579	Venango Formation	.26	.44	—	—	—	355
Wr-582	Chadakoin Formation	.27	.67	—	—	7.39	106
Wr-594	Venango Formation	.46	.53	—	—	—	309
Wr-749	Corry Sandstone through Riceville Formation, undivided	.50	1.33	—	—	—	136
			Springs				
Wr-SP 052	Pottsville Group	.24	.22	—	—	—	755
Wr-SP 071	Glacial outwash sand and gravel	.37	.02	—	—	—	1,490
Wr-SP 129	Venango Formation	.11	1.60	—	—	6.03	193
Wr-SP 132	Pottsville Group	.52	.17	—	—	—	1,290
Wr-SP 133	Corry Sandstone through Riceville Formation, undivided	.22	.06	—	—	1.94	1,180
Wr-SP 134	Knapp Formation	.24	.03	—	.854	—	185
			Oil and gas wells				
Wr-266	Upper Devonian, undifferentiated	.44	.13	—	—	4.90	—
Wr-266	Upper Devonian, undifferentiated	.44	.64	—	—	24.1	—
Wr-573	Upper Devonian, undifferentiated	1.02	.21	—	—	—	—
Wr-586	Upper Devonian, undifferentiated	178	**10.1**	**23.4**	—	—	—
Wr-814	Venango Formation	1.00	**11.5**	**15.2**	**20.9**	24.6	—

[1] Radon concentration is the average of the two scintillation vials.

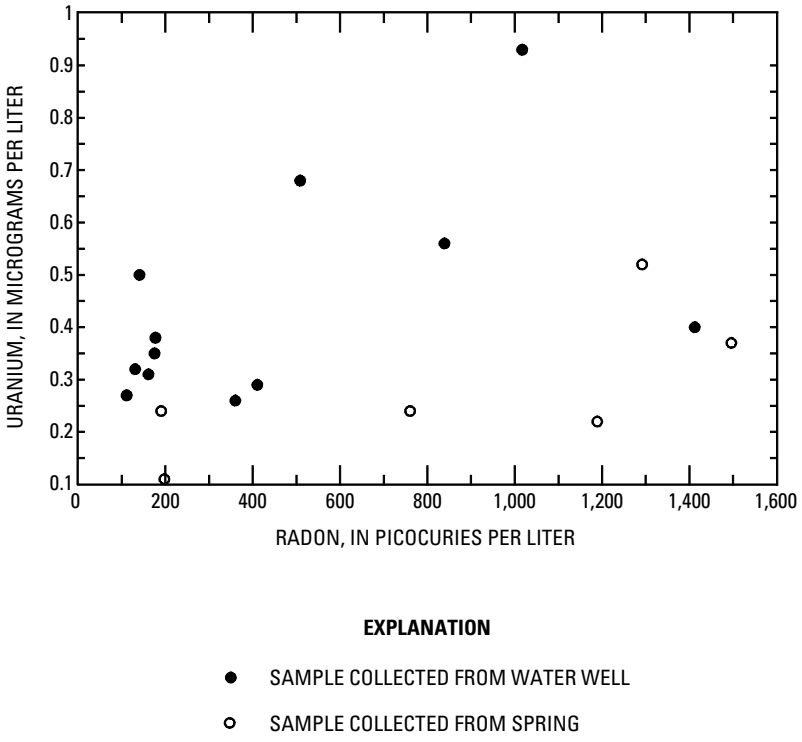


Figure 17. Comparison of radon and uranium concentrations between well water and spring water samples, Warren County, Pennsylvania.

Hydrologic Effects of Petroleum Occurrence and Development

Documentation of the hydrologic effects of crude oil and natural gas occurrence and development is presented mostly by literature review and by hydrologic data collection and interpretation. The lack of historical water-quality data for wells and springs in Warren County prevents the meaningful comparison of water quality before and after oil and gas development. The paucity of water wells to sample in many of the oil and gas fields also makes it difficult to determine the effects of oil and gas operations on ground-water quality.

This section contains four initial subsections that describe specific hydrologic issues related to oil and gas occurrence and development, which are followed by three case histories in which hydrologic data and ground-water contamination are described and evaluated.

Drilling and Well Completion Practices

Faulty drilling and well-completion practices can result in contamination of freshwater aquifers from the migration of crude oil, natural gas, and brines from deep oil and gas reservoirs into the aquifer. The information provided in this section initially describes typical well drilling and well-completion practices. Special emphasis is directed to surface casing installation and depth because of their importance in the protection of aquifers from contamination. Finally, this section notes deficiencies in well-completion practices that have contributed to ground-water contamination in some parts of Warren County.

Lytle (1965) discussed drilling and surface-casing practices of shallow oil and gas wells in the Warren 15-minute quadrangle (composed of the Russell, Scandia, Warren, and Clarendon 7½-minute quadrangles). These well constructions are relevant to many of the shallow oil and gas fields in production during the 1980s because they are composed of many older wells drilled prior to or during the research of Lytle (1965).

Lytle (1965, p. 22-23) describes, as follows, the notable drilling and casing procedures: "The portable spudding machine with wire line is generally used in the quadrangle. A 10-in. hole is spudded to bedrock and a wooden conductor or, if the walls of the hole will not stand, 8-in. **drive pipe** is used. About 20 to 150 ft of drive pipes are used, depending on the location of the well. As much as 250 ft of drive pipe might be needed in a few areas where the glacial cover is that thick. An 8-in. hole is drilled to the casing point, a point below which freshwater is no longer encountered (varying from 180 to 600 ft below the surface), and 6¼-in. casing is installed. A 6¼-in. hole is then drilled to total depth, which generally includes a 10- to 20-ft pocket below the bottom of the sand." In the Bradford Oil

Field (shallow oil) in adjacent McKean County, Fettke (1938, p. 417) also noted that surface casing was installed to seal off ground water.

The cable tool or portable spudding machines used extensively in the past, and still in limited use today, are being phased out for shallow oil and gas well drilling by modern air-rotary-drilling rigs. Detailed discussions of the step-by-step procedures of rotary drilling, casing installation, and **cementing** procedures of **shallow and deep oil and gas wells** are beyond the scope of this report. These procedures are presented in a study prepared for PaDEP by Waite and Blauvelt (1983).

The depth, integrity, and cementing of the surface casing of oil and gas wells are critical to the protection of fresh ground-water resources from contamination from crude oil, natural gas, and brines. Surface-casing placement for typical oil and gas well constructions common to northwestern Pennsylvania are shown in figures 18 and 19 (modified from Waite and Blauvelt, 1983). The range of surface-casing depths on figures 18 and 19 cited from Waite and Blauvelt (1983) agree generally with cursory examination of surface-casing depths reported for shallow oil and gas wells in Warren County in Lytle (1965) and McGlade (1964) and for deep wells in **oil and gas well-completion reports** reviewed in the office of the Subsurface Geology Section of the Pennsylvania Geological Survey.

The USGS, in cooperation with PaDEP, conducted a feasibility study to estimate minimum surface-casing depths to prevent ground-water contamination in the Warren 7½-minute quadrangle and three other quadrangles in western Pennsylvania (Buckwalter and Squillace, 1995). The findings of Buckwalter and Squillace generally indicate most contamination of freshwater aquifers by leakage of oil, gas, and brines in boreholes of oil and gas wells probably would be prevented if the following PaDEP guidelines were followed: (1) The surface casing should extend at least 50 ft below the deepest freshwater-bearing strata; (2) the surface casing should be pressure cemented along its entire length to the surface; and (3) the surface casing should be installed prior to drilling into any strata that contain oil or gas.

Intermediate casing strings, sometimes referred to as **water strings**, are infrequently installed in selected oil and gas wells in Warren County. The purposes of the intermediate strings include protecting the hole from caving, providing attachment for blowout preventers, and preventing entry of unwanted fluids including ground water. The **annular space** of intermediate strings of casing commonly is cemented for strength requirements. Intermediate strings of casing when cemented may act to protect freshwater below the surface casing and prevent upward migration of gas, brine, or **stimulation fluids**. Intermediate casing strings may be initially installed in selected problem areas as a preventative measure or installed at a later time as a remediation technique when adverse hydrologic effects of oil and gas wells have been observed and solutions to those problems are required.

Deficiencies in ground-water protection in shallow oil and gas wells may include insufficient depth of surface casing, lack of cement between the surface casing and borehole, and casing that leaks. The uncemented annular space from the bottom of the surface-casing seal (fig. 18) to the bottom of the hole may enable undesirable fluids, such as salty water, oil, or gas, to rise in the borehole. Movement of these fluids into the freshwater zones in the fractured bedrock is possible if surface casing is not deep enough or is leaky. Freshwater aquifers also may be dewatered if surface casing is too short or poorly installed. Fresh ground water under these circumstances may move down the annular space of the well to deeper permeable strata. Wells in the dewatered aquifer may go temporarily or permanently dry.

As discussed in Waite and Blauvelt (1983, Part 3, p. 38-39), the following is an example of crude oil contamination of three water wells in Glade Township because of apparently faulty surface casing in oil wells: "During the summer of 1978, the PaDEP investigated the occurrence of crude oil in three water wells near an old but still operating oil lease in Glade Township, Warren County. The oil wells were very old (80-90 years) and the surface casing apparently leaked and oil was introduced to the ground-water flow system. The case was settled in court and the lease operator was found guilty. When new casing was installed, the problem appeared to improve but due to the slowness of ground-water flow and the difficulty of recovering contaminants lost to ground water many years may be required before the problem is completely resolved."

The introduction of production fluids including brines into the ground-water system as a result of well completion and production practices is discussed in a subsequent section entitled "*Production Fluids*." Examples of natural-gas contamination of aquifers in Columbus and Pleasant Townships resulting from oil and gas well-completion practices are included in "*Natural-Gas Migrations*."

Natural-Gas Migrations

Major subsurface natural-gas migrations have been studied and documented in at least seven counties of Pennsylvania including Clearfield, Clinton, Crawford, Erie, Lackawanna, Luzerne, and Warren (Walker, 1984). Other states with case histories documenting gas migrations, sometimes referred to as subsurface gas blowouts, include Kentucky, Michigan, Oklahoma, New York, and West Virginia. Natural-gas migrations have resulted from natural-gas explosions, which in turn have caused personal injury and loss of life. Natural gas migrated in the subsurface about 3 mi from a gas well to a water well in Clearfield County, Pa.; an explosion occurred in the water-well pump house, causing injury to a maintenance man. High gas pressures in gas storage fields in combination with faulty well-construction materials, poor well-completion practices, and management problems of the storage fields are some of the contributing causes of some of the gas migrations in Pennsylvania and other states. In some cases, several producing gas wells or a group of producing oil and gas wells of a petroleum field have been implicated as the source of the gas migrating to aquifers and land surface. The contamination of aquifers by overpressur-

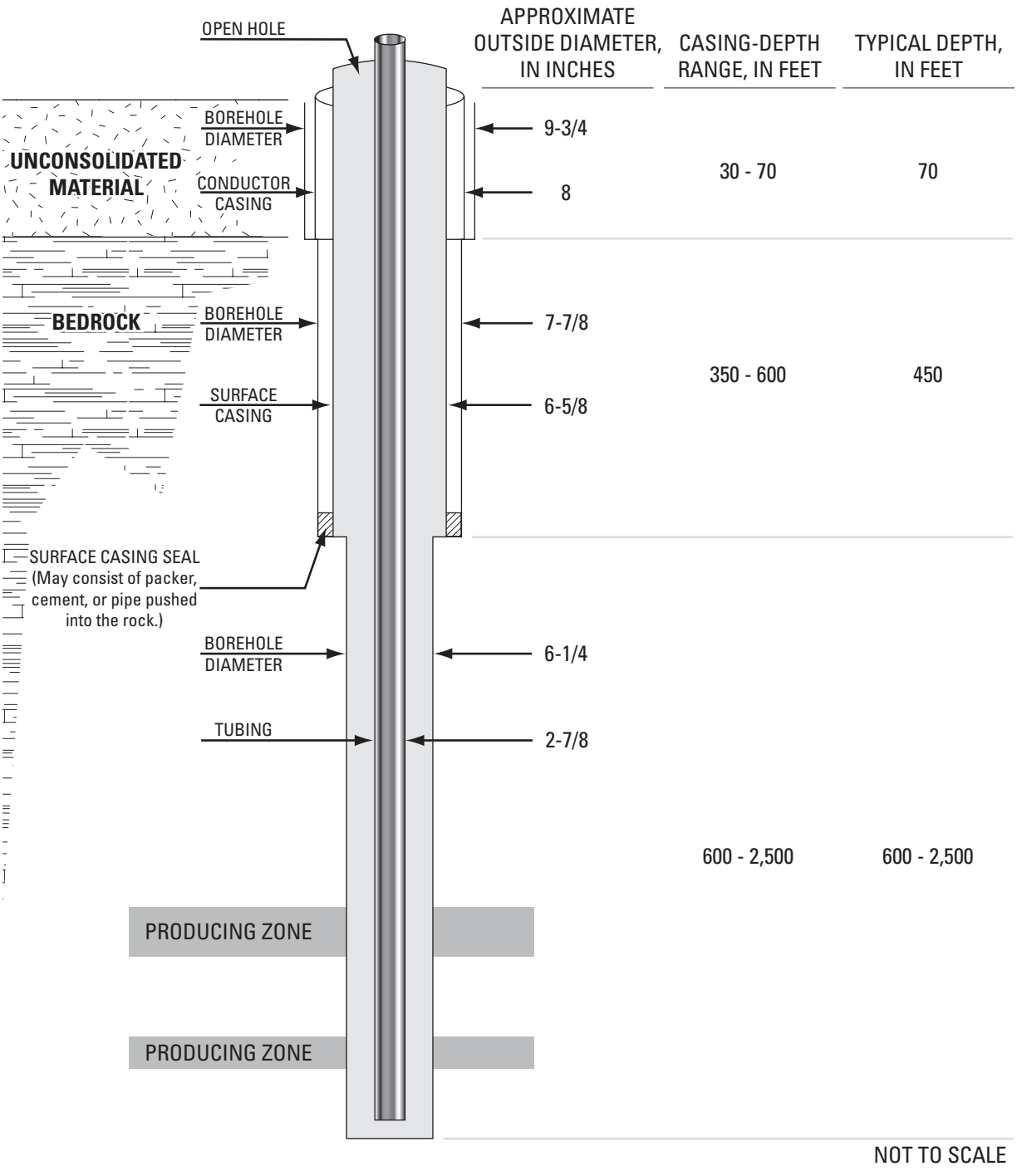


Figure 18. Typical well construction of a shallow oil well in Warren, McKean, or Elk County, Pa. (modified from Waite and Blauvelt, 1983).

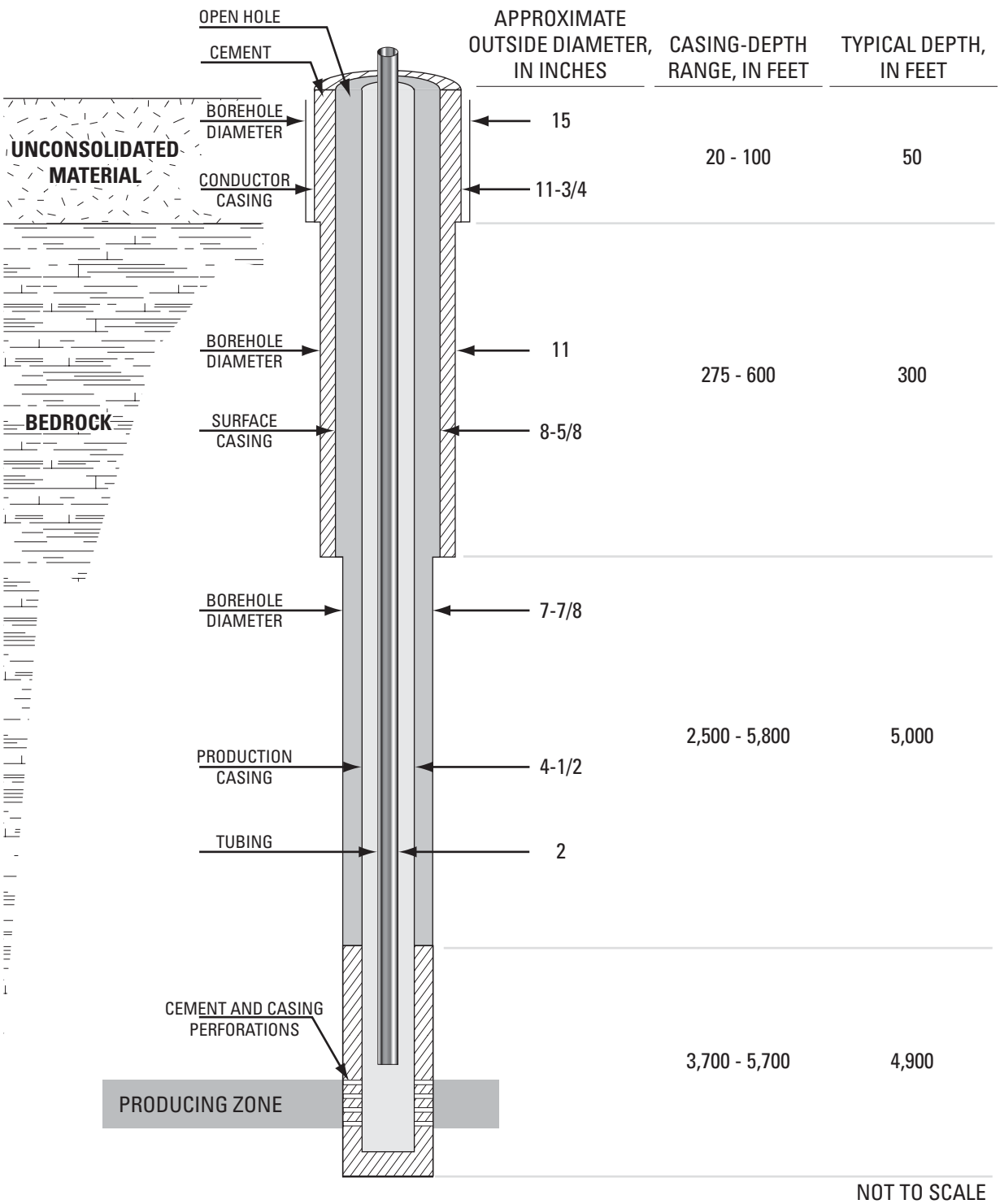


Figure 19. Typical well construction of a deep gas well outside the coal region in Crawford or Warren County, Pa. (modified from Waite and Blauvelt, 1983).

ing the annulus of oil and gas wells has received considerable attention by hydrogeologists (Harrison, 1985) and state regulatory agencies.

In Pleasant Township, Warren County, a major subsurface natural-gas migration at Chapman State Park and vicinity was described by John Walker in a PaDEP report dated September 7, 1984 (Walker, 1984, p. 20-29). In February 1983, high concentrations of natural gas were observed in water wells and a spring. The lake and a tributary stream at Chapman State Park also vented large volumes of natura1 gas. The natural gas was believed to be migrating from improperly completed oil and gas wells in the Elkhorn Run Oil Field, northwest of Chapman State Park. The severity of the natural-gas migration problem decreased over time.

Hydrologic investigations at Chapman State Park were completed as part of this study because of continuing natural-gas presence in aquifers and inorganic constituents were found exceeding the MCLs in several water wells. Concentrations of dissolved methane ranged from 0.1 to 41 mg/L in 12 of the 13 water wells sampled at Chapman State Park and vicinity in 1986-87. The median dissolved methane concentration of the 13 wells sampled was 6.5 mg/L. Concentrations of dissolved ethane in 5 of the 13 wells sampled ranged from 0.2 to 15 mg/L. Dissolved methane concentrations in ground water exhibited variability when wells were sampled over brief time periods and when wells were sampled over long time periods. Monitoring concentrations of dissolved natural gas in the field was performed on the water discharged during pumping tests of water wells. At times, the concentrations of dissolved natural gas fluctuated widely, probably because of the nonuniform distribution of the natural gas in the complex fractured-rock aquifer system and the overlying alluvial aquifer system. More information on the hydrogeology and ground-water quality problems at Chapman State Park and vicinity are provided in a succeeding case history including a discussion of the probable causes of the natural-gas migration.

Migration of natural gas that contaminated ground water was documented by PaDEP during the summer of 1984 in Columbus Township in northwestern Warren County. A natural-gas analyses of a sample collected from a water well at the western edge of the town of Columbus indicated a methane concentration of 45 to 48 mg/L. Analysis of a water sample collected from another nearby water well indicated a methane concentration of 70 mg/L. The methane contamination was attributed to poor well completion methods and production practices of the deep gas wells producing from the Medina Group in the local area. Remedial measures were undertaken by the gas-well operators at the request of PaDEP to abate the problem of natural gas migration to local aquifers. A committee of PaDEP staff and gas industry representatives was formed to make recommendations to prevent future problems for new wells to be drilled in eastern Erie and western Warren County (table 24). The recommendations are believed to have been mostly successful in the prevention of similar natural-gas migration problems from new wells producing from the Medina Group.

Abandoned Oil and Gas Wells

The effects of abandoned oil and gas wells on surface-water and ground-water hydrology have been investigated in several areas in the oil and gas fields of western Pennsylvania. In the nearby Clarion River and Redbank Creek Basins to the southeast of Warren County, Buckwalter and others (1981) collected water samples from 91 flowing abandoned oil and gas wells, mostly in the valleys. An evaluation of the results of the analyses of those samples indicated the waters discharging from the wells were mostly fresh or slightly saline. Brines or crude oil discharges were not observed. The surface casings of the wells were absent or leaking, allowing the ground water to flow to land surface because of the heads in the confined or semiconfined fractured bedrock aquifers beneath the valleys were higher than land surface elevation. In adjacent McKean County, Westlund (1976) investigated abandoned oil and gas wells, their effect on the ground-water flow system, and plugging priority for ground-water protection.

Many abandoned oil and gas wells are in Warren County. The age of many of the wells may be difficult to establish. Abandoned oil and gas wells were observed mostly in the vicinity of the shallow oil and gas fields in central and eastern Warren County. Most of the deep gas wells having production from the Medina Group are modern PaDEP permitted wells.

The conditions of abandoned oil and gas wells were highly variable. Some well casings at land surface leaked natural gas and a few were discharging fresh ground water to land surface. No abandoned oil and gas wells were observed discharging brine or crude oil, although crude oil was observed on the land surface at some abandoned well sites. When abandoned oil and gas wells were discharging ground water, field constituents were measured, and samples for laboratory analysis commonly were collected. When abandoned well bores were unobstructed and vehicle access possible, selected abandoned oil and gas wells were geophysically logged and water samples collected from various depths in the well.

The laboratory analyses of the water samples collected from the 15 abandoned oil and gas wells are presented in Moore and Buckwalter (1996). The exact depths of ground-water entry into abandoned oil and gas wells generally are unknown. Thus, the hydrogeologic unit assigned to these wells is Upper Devonian, undifferentiated. In prior sections of this report, the median and range of concentrations of selected constituents of ground water sampled from abandoned oil and gas wells are listed by the hydrogeologic unit Upper Devonian, undifferentiated.

Table 24. Recommended gas well completion methods to prevent natural-gas contamination of the fresh ground-water system.

[Pennsylvania Department of Environmental Protection, written commun., 1987]

ER-OG-66: 12/87	Commonwealth of Pennsylvania Department of Environmental Protection Bureau of Oil and Gas Management

GAS WELL COMPLETION METHODS
FOR CONCORD AND WAYNE TOWNSHIPS, ERIE COUNTY
COLUMBUS, FREEHOLD, SPRING CREEK AND
SUGAR GROVE TOWNSHIPS, WARREN COUNTY

To help prevent this problem, the following completion practices were developed by a joint DER-Industry Committee for all new wells in the Columbus area. Both DER and the Industry Committee members believe these practices, if followed, will eliminate the problem. However, each operator is responsible for any gas migrating from his well(s) and may wish to take additional precautions.

1. A one and one-half (1½) inch minimum radius annular space should be provided between the surface casing and borehole.
2. Set at least 500 feet of surface casing with a minimum of two (2) centralizers, securely attached to the pipe, and a cement basket at the base of the unconsolidated surface material (top of bedrock) when the depth to bedrock is 50 feet or greater.
3. Pressure cement with the pump and plug method to the surface or with at least 30% excess cement.

5. Before cementing the production string, the well should be killed and cemented by the pump and plug method with sufficient cement to produce a continuous cement column over the Tully Limestone. Centralizers should be used to assure that a proper cement column is achieved.
6. The top of cement must be documented by a cement top log or detailed calculations which include cement loss.
7. The annular space between the surface casing and the production string should remain open. The well should be equipped to be maintained in that condition.
8. In the event that sufficient shale gas is encountered to warrant production, a maximum pressure on the annulus of 100 psi may be approved by the Oil and Gas Inspector on a well by well basis.

Service company cement ticket and copies of any logs run to verify the above should be submitted with the well record.

Production Fluids

Production fluids are defined as naturally occurring formation fluids that are produced along with oil and (or) natural gas after the well is in production. Volumes of production fluid from oil and gas wells vary from formation to formation, from well to well, and over the life of a well. Average volumes of production fluid for deep gas wells range from 2 to 4 barrels per day (Gough and Waite, 1990, p. 387). Average volumes of production fluid for shallow oil wells under primary production range from less than 1 to 2 barrels per day. These generalized statements from Gough and Waite (1990) were obtained from oil and gas operators; Pennsylvania and USEPA regulations do not require quantities of production fluids or brines to be reported. Thus, no reliable estimates are available of the annual quantity of production fluids from the oil and gas wells of Warren County.

Production fluids may be classified as saline waters (greater than 500 mg/L dissolved solids) or as brines (greater than 35,000 mg/L dissolved solids). Production fluids commonly are referred to as brines in the oil and gas fields although the dissolved solids concentrations may, at times, be less than 35,000 mg/L. Production fluids are waste fluids that are disposed in large volumes in Warren County by many methods. Waste fluids produced during oil and gas development are not limited to production fluids but also include drilling fluids and stimulation fluids. Fluids produced during drilling include "top hole" fluids, "bottom hole" fluids, drilling muds, and detergents. Stimulation fluids include a variety of fluids used during processes designed to increase oil or gas production. Examples of stimulation fluids include concentrated acids, water, diesel fuel, crude oil, nitrogen, and carbohydrate polymer gels. The average volume of fluid returned to the surface after stimulation and before production for deep gas wells is 58,000 gal per well (Gough and Waite, 1990, p. 387). Disposal pits or tanks at oil and gas well drilling sites may contain mixtures of drilling fluids, stimulation fluids, and production fluids. Chemical analyses of these waste fluids are presented in Waite and Blauvelt (1983) for deep gas, shallow gas, and shallow oil areas.

Contamination of water resources from disposal of production fluids depends on disposal methods, quantities of production fluids, and composition of the production fluids. A summary of disposal methods for production fluids in Warren County is presented in table 25. Disposal practices vary among oil and gas operators. In some cases, large quantities of production fluids, crude oil, and natural gas from many oil and gas wells on a hillside will be piped to a central location, commonly a flat valley near a stream. Here, the oil, gas, and production fluids are separated. If the large disposal pit(s) for production fluids overflow because of the heavy loading from the many oil and gas wells in production, adjacent water resources probably are affected. Contamination of surface water is possible, especially if adjacent streams are small with little capability to dilute the highly concentrated brines making up the production fluids. In the case of some deep gas fields, however, each well has a separate large tank for storage of production fluids. Trucks haul the production fluids to a PaDEP permitted wastewater treatment plant where various water contaminants are removed. The treated waste water is discharged to the Allegheny River where the river's consistent high discharge rates facilitate dilution.

The composition of production fluids is significant because it may consist of high concentrations of constituents that can contaminate existing or potential sources of water supply. Brines or saline water frequently make up a large fraction of waste production fluids disposed by oil and gas operators during the production phase of oil and gas development. Chemical analyses of production fluids from shallow oil wells in Warren County are presented in table 26. Sodium and chloride are the most common solutes. In one or more of the chemical analyses, concentrations of the following constituents were above their USEPA MCL or SMCL: sulfate, chloride, dissolved solids, barium, iron, and manganese. In some crude oil and production fluid separation procedures used especially in the oil fields, high concentrations of selected organic compounds having MCLs, such as benzene, ethylbenzene, toluene, and xylenes, derived from the crude oil, remain dissolved in the saline water or brine of the production fluids that are disposed.

The USEPA, PaDEP, and Pennsylvania Fish and Boat Commission (PFBC) have investigated a variety of incidents of contamination of surface water from disposal of production fluids in Warren County. The PFBC has documented, for example, the composition of production fluids discharging to Grunder Run in Pleasant Township, including biochemical oxygen demand, oil and grease, benzene, toluene, ethylbenzene, and xylene. The scope of this report does not include a detailed evaluation of these investigations. However, the surface-water contaminants examined in these studies are potential ground-water contaminants if the contaminated stream reach is at the time losing water to the shallow ground-water system.

Effects of disposal of production fluids on the quality of water in wells and springs were not readily observed in the data collected as part of this study. This is mostly because the design of the data collection focused on sampling of water wells and springs in use that are rarely in close proximity to brine-disposal facilities. Ground-water samples from the majority of wells and springs did not exceed the MCLs for the constituents analyzed in this study.

Case Histories

Tidioute Borough and Local Area

The development of ground water for domestic and municipal use in Tidioute Borough (fig. 1) and the adjacent townships has been difficult in some areas because of very shallow petroleum reservoirs in parts of the ground-water system. Drilling wells to shallow depths of about 120 ft, a common depth of water wells in the rest of Warren County, resulted in an oil boom in 1860 in the valley of the Allegheny River at Tidioute. Oil and gas production from these shallow wells was from the Third sand of the Venango Formation. The Third sand in the

Table 25. Summary of disposal methods for production fluids in Warren County, Pennsylvania.

Method of disposal of production fluids	Remarks	General references on specific production fluids disposal methods including aspects of contamination of water resources
Shallow disposal pits sometimes referred to as "blow boxes"	Unlined pits commonly used in Warren County prior to and during the 1980s. Leakage of pit dependent, in part, on permeability of pit walls and loading of pit. Pits overflow at times through overflow pipes. Pits with high-quality synthetic liners maintained correctly, rarely leak.	Waite and Blauvelt, 1983 Pennsylvania Department of Environmental Resources, 1991 Gough and Waite, 1990 Northeast Petroleum-Forest Resources Cooperative and others, 1986 Crain, 1969
Land disposal	"Top-hole" ground water during drilling sometimes blow from air rotary rigs onto land adjacent to drilling pad.	Waite and Blauvelt, 1983 Northeast Petroleum-Forest Resources Cooperative and others, 1986 DeWalle and Galeone, 1990
Road spreading	Pennsylvania Department of Environmental Protection permit required. Dust control on dirt roads in the summer is the major purpose of road spreading.	Waite and Blauvelt, 1983 Northeast Petroleum-Forest Resources Cooperative and others, 1986 Rudd, 1972
Underground injection disposal well	U.S. Environmental Protection Agency permit required. One disposal well in Warren County in Pleasant Township in operation during the 1980s.	Waite and Blauvelt, 1983 Northeast Petroleum-Forest Resources Cooperative and others, 1986 Rudd, 1972
Centralized waste fluids treatment plant with surface-water discharge	One waste treatment plant designed for processing oil and gas well brines began operation in February 1988 in Warren with discharge of treated brine to the Allegheny River. Production fluids at well fields stored in tanks or pits and then transported to plant.	Waite and Blauvelt, 1983 Northeast Petroleum-Forest Resources Cooperative and others, 1986
Surface-water discharge	Discharge to surface water of production fluids requires several Pennsylvania Department of Environmental Protection permits and fluids may require treatment. Overflows of production fluids from disposal pits eventually may discharge to streams depending, in part, on proximity of disposal pits to streams and loading rates.	Waite and Blauvelt, 1983 Northeast Petroleum-Forest Resources Cooperative and others, 1986 Evaldi and Kipp, 1991

Table 26. Results of water-quality analyses of production fluids from oil wells, Warren County, Pennsylvania.

[µS/cm, microsiemens per centimeter; USGS, U.S. Geological Survey; PSU, Pennsylvania State University; deg. C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; —, no data; <, less than]

Site number	Location	Township	Formation	Date	Time	Agency analyzing sample	Specific conductance (µS/cm)	pH (standard units)
	Latitude longitude (degrees, minutes, seconds)							
1	414918 0791103	Pleasant	Glade[1]	8/28/86	1430	USGS	59,800	6.9
2	415029 0791256	Conewango	Glade[1]	8/28/86	0900	USGS	62,000	5.6
3	415610 0791825	Sugar Grove	Glade[1]	9/5/85	0830	USGS	30,100	6.6
4	414130 0793348	Southwest	Venango	1982	—	PSU	75,000	6.5
5	414918 0791211	Pleasant	Glade[1]	1982	—	PSU	134,000	6.9
6	414857 0791239	Pleasant	Glade[1]	1982	—	PSU	112,000	7.1
7	414834 0791232	Pleasant	Glade[1]	1982	—	PSU	138,000	6.8
8	413821 0785741	Sheffield	Cooper[1]	1982	—	PSU	18,000	6.7
9	4138-- 07858--	Sheffield	Cooper[1]	1982	—	PSU	87,900	6.6

[1]Part of the Bradford group.

Site number	Water temperature (deg. C)	Total hardness (mg/L as $CaCO_3$)	Calcium, dissolved (mg/L)	Magnesium, dissolved (mg/L)	Sodium, dissolved (mg/L)	Potassium, dissolved (mg/L)	Alkalinity dissolved (mg/L)	Sulfate, dissolved (mg/L)	Chloride, dissolved (mg/L)	Fluoride, dissolved (mg/L)	Silica, dissolved (mg/L)
1	24.0	13,000	3,900	670	14,000	585	200	320	34,000	<0.10	12
2	14.0	12,000	3,600	630	14,000	51	31	1,900	33,000	<.10	3.6
3	23.0	120	5,800	310	4,400	15	32	210	11,000	<.10	1.4
4	13.0	—	3,930	910	15,200	51	—	7	35,400	<1.0	—
5	11.0	—	11,800	2,050	30,000	85	—	390	63,200	<1.0	—
6	13.0	—	8,680	1,510	24,000	64	—	350	55,800	<1.0	—
7	15.0	—	12,600	2,180	31,000	83	—	850	67,800	<1.0	—
8	—	—	920	100	3,000	49	—	4	5,760	<1.0	—
9	19.0	—	6,110	1,040	17,400	73	—	310	41,200	<1.0	—

Site number	Solids, residue at 180 deg. C dissolved (mg/L)	Solids, calculated sum dissolved (mg/L)	Aluminum, dissolved (µg/L)	Arsenic, dissolved (µg/L)	Barium, dissolved (µg/L)	Bromide, dissolved (µg/L)	Cadmium, dissolved (µg/L)	Chromium, dissolved (µg/L)	Cobalt, dissolved (µg/L)
1	53,000	53,000	<100	3	3,100	—	<1	<1	<1
2	55,500	53,000	<100	17	600	—	<1	<1	<1
3	19,200	17,800	<10	3	1,200	—	2	<1	10
4	—	57,000	—	—	355,000	365,000	—	—	—
5	128,000	109,000	—	—	2,800	792,000	—	—	—
6	100,000	91,000	—	—	<500	609,000	—	—	—
7	129,000	116,000	—	—	<500	835,000	—	—	—
8	—	10,000	—	—	6,800	99,000	—	—	—
9	68,000	67,000	—	—	<500	437,000	—	—	—

Table 26. Results of water-quality analyses of production fluids from oil wells, Warren County, Pennsylvania.—Continued

[µS/cm, microsiemens per centimeter; USGS, U.S. Geological Survey; PSU, Pennsylvania State University; deg. C, degrees Celsius; mg/L, milligrams per liter; µg/L, micrograms per liter; —, no data; <, less than]

Site number	Copper, dissolved (µg/L)	Iron, total recoverable (µg/L)	Iron, dissolved (µg/L)	Lead, dissolved (µg/L)	Manganese, total recoverable (µg/L)	Manganese, dissolved (µg/L)	Mercury, dissolved (µg/L)	Selenium, dissolved (µg/L)	Strontium, dissolved (µg/L)	Zinc, dissolved (µg/L)
1	<1	1,300	800	<5	5,500	5,500	—	<1	54,000	100
2	3	110,000	10,000	<5	5,100	5,100	—	<1	27,000	180
3	4	650	100	2	7,000	6,300	0.6	<1	17,000	10
4	<1	—	116,000	<5	—	4,100	—	—	124,000	40
5	10	—	75,000	<5	—	11,700	—	—	152,000	60
6	10	—	18,000	10	—	7,500	—	—	141,000	70
7	20	—	20,000	10	—	11,100	—	—	151,000	40
8	<1	—	41,000	<5	—	2,200	—	—	5,000	20
9	20	—	98,000	<5	—	4,500	—	—	39,000	40

Tidioute area was described by Cathcart and others (1938, p. 9) as less than 15 ft thick and separated by 70 to 80 ft of shale fromthe Salt sand above and by 20 to 30 ft of shale from the Fourth sand below. Salt water also was produced from the Third sand and from the overlying Salt sand. In August 1860, one of the oil wells drilled to a depth of 124 ft directly across the Allegheny River from Tidioute produced an estimated 100 to 300 barrels of oil a day (Miller, 1983, p. 16). Reservoir pressures during initial pumping resulted in a heavy flow of crude oil shooting 20 ft into the air. Many oil wells were drilled on the shoreline and on islands of the Allegheny River. In the fall of 1860, about 50 rafts on the Allegheny River were actively drilling for oil although they were mostly destroyed or damaged in a large flood late that year (Miller, 1983, p. 10). The relevance of these shallow petroleum reservoirs and their pressures to the ground-water system is that unplugged, abandoned oil and gas wells or improperly cased wells may have acted as conduits for migration of petroleum and other contaminates from the reservoirs to the bedrock and unconsolidated aquifers.

The Southwest Warren County Municipal Water Authority uses a 1-acre reservoir on George Run, a tributary to Tidioute Creek about 3.5 mi northwest of Tidioute Borough, as a source of water supply to businesses and about 1,000 residents of Tidioute Borough and part of Limestone Township. After normal precipitation events, major problems with the water supply include excessive turbidity not only in the raw water but also in the finished (treated) water, requiring frequent boil-water advisories. Low streamflows during droughts in spring, summer, and fall necessitate using most of the streamflow for water supply, but these low flows often are insufficient to meet demands. In 1984, Tidioute Borough and water-authority officials hired a consulting firm and used project staff to assess the feasibility of developing ground water as a secondary or, if possible, primary water supply.

Test drilling was conducted by Tidioute Borough to locate high-yielding aquifers with acceptable water quality meeting USEPA MCLs and SMCLs. Candidate aquifers were rejected if treatment to remove ground-water contaminants was expensive. An outwash glacial aquifer was identified as having the greatest potential for ground-water development because several other communities along the Allegheny River were already successfully using well fields in this aquifer for water supply. The Borough drilled and completed three test wells (Wr-270, Wr-520, and Wr-543) in the outwash deposits in the valley of the Allegheny River (fig. 20). The only productive water-bearing zones encountered in test wells Wr-270 and Wr-520 were in the 3 to 5-ft thick intervals where mostly gravel rested on the top of the bedrock. The highest yielding water-bearing zone in Wr-543 was a sand and gravel interval from about 35 to 39 ft below land surface.

Analyses of water samples collected from the three wells after several pumping periods indicated poor water quality that would require costly treatment. A sample collected from Wr-270 on July 17, 1985, contained dissolved methane at a concentration of 10 mg/L, and the dissolved iron concentration was exceptionally high—25,300 µg/L. Dissolved manganese was also found in high concentration (740 µg/L). Water samples collected from Wr-543 had excessive iron concentrations on May 21, 1986 (4,600 µg/L), and again on August 18, 1986 (7,200 µg/L).

Concentrations of selected constituents of special concern in water samples collected from Wr-520 during several pumping tests are presented in table 27. Although the well yielded about 200 gal/min, these generally high concentrations (table 27) in excess of respective MCLs and SMCLs collectively negated the permanent use of Wr-520 for water supply. The low concentrations of dissolved methane in the samples

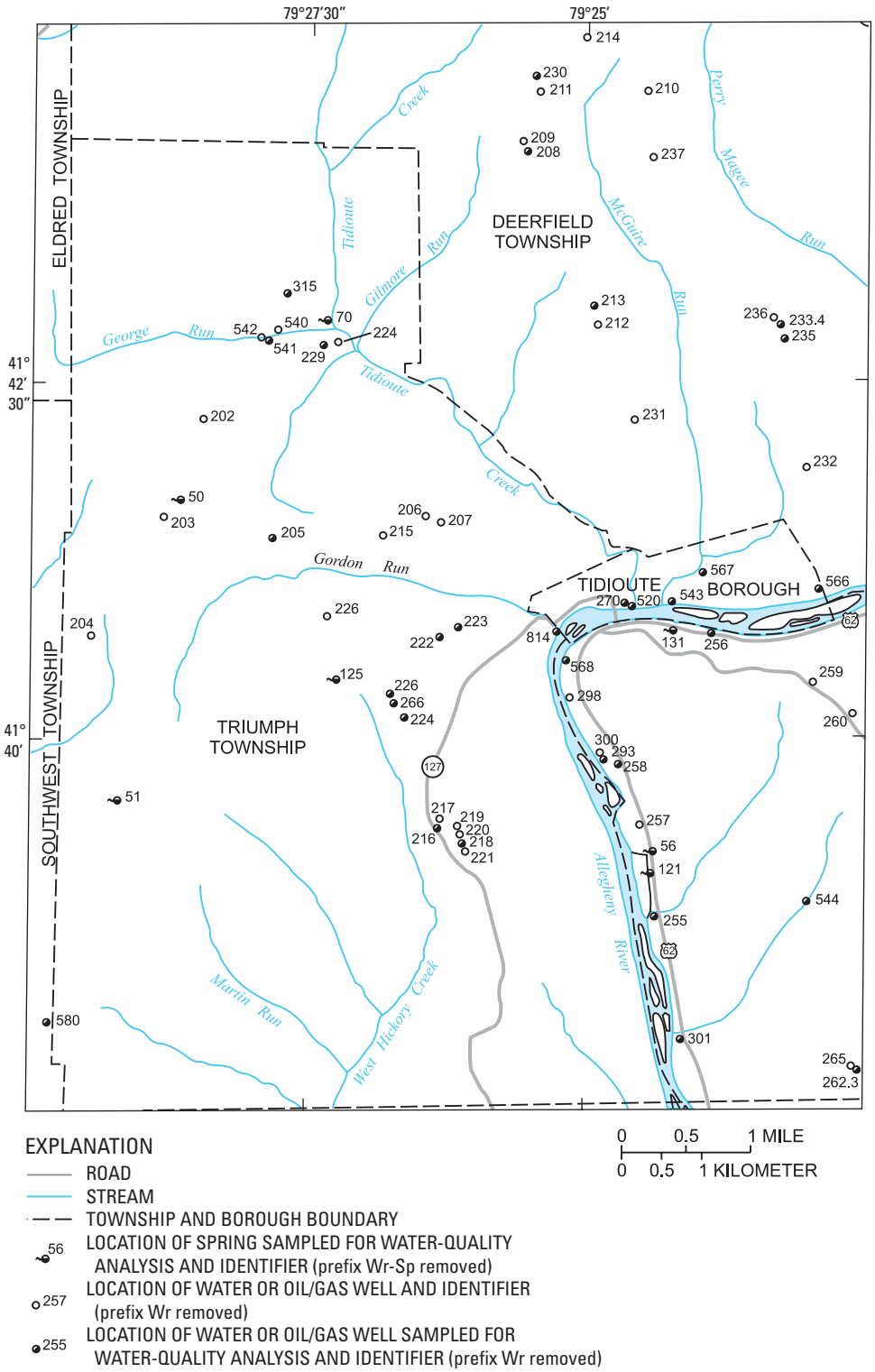


Figure 20. Location of wells and springs on the Tidioute 7½ minute quadrangle, Warren County, Pennsylvania.

Table 27. Selected chemical analyses of water samples from well Wr-520, Warren County, Pennsylvania.

[gal/min, gallons per minute; µg/L, micrograms per liter; mg/L, milligrams per liter; <, less than; —, no data]

Date	Pumping rate (gal/min)	Pumping period (hours)	Aluminum, dissolved (µg/L as Al)	Barium, dissolved (µg/L as Ba)	Iron, dissolved (µg/L as Fe)	Manganese, dissolved (µg/L as Mn)	Methane, dissolved (mg/L)
10/9/85	200	1	600	1,400	15,800	2,400	0.3
10/9/85 (duplicate sample)	200	1	500	1,300	15,100	2,300	.3
7/29/87	12	2	1,000	980	10,600	2,200	.3
8/25/88	180	144	<150	1,100	16,400	2,000	—

from well Wr-520 were unexpected because high concentrations of methane were detected in samples collected from well Wr-270 (only 205 ft away) in 1985.

The duration of the pumping test of Wr-520 on Oct. 9, 1985, was 8.5 hours. During the test, the discharge was monitored for dissolved methane, methane in the head space air of the well casing, pH, water temperature, and specific conductance. These constituents remained nearly constant during the length of the test. Field measurements for methane were negative with a detection limit of about 0.5 mg/L. The laboratory analysis from PaDEP for dissolved methane confirmed low concentrations of about 0.3 mg/L. Because well Wr-520 yielded a selectively high sustained amount of water (200 to 300 gal/min), several water-quality assurance techniques were initiated to test the accuracy and precision of the laboratory analysis. After 1 hour of pumping, duplicate water samples were collected and sent to the PaDEP laboratory. The results of the duplicate samples including those presented in table 27 generally were acceptable. Also, for two constituents of special interest, iron and dissolved methane, water samples were collected by Tidioute Borough and sent to a private laboratory for analysis. The iron concentration of 15,140 µg/L and low dissolved methane concentration of 0.025 mg/L compared favorably with the PaDEP laboratory results.

In addition to the test drilling of wells Wr-27, Wr-520, and Wr-543, some geophysical logs and water samples were collected in the effort to locate high-yielding aquifers for Tidioute Borough public supply. In oil well Wr-814, at the west end of Tidioute Borough (fig. 20), geophysical logging was conducted, and samples were collected to provide data on hydrogeology and water quality in the Third sand of the Venango Formation. The well located in the mostly abandoned eastern part of the Triumph Streak Oil Pool is about 0.7 mi from the sites of Wr-270 and Wr-520 (fig. 20). The saline water sampled with the geophysical logger from a depth of 125 ft indicated elevated concentrations of barium (17,800 µg/L), iron (34,100 µg/L), manganese (2,200 µg/L), strontium (2,000 µg/L), sodium (570 mg/L), chloride (880 mg/L), oil and grease (170 mg/L), methane (14.0 mg/L), and dissolved solids (1,730 mg/L).

Several water wells tapping outwash deposits in Limestone Township were sampled to provide additional hydrologic data for outwash deposits to the south of Tidioute Borough. The water well (Wr-256) servicing the roadside rest area of the Pennsylvania Department of Transportation (PennDOT) was sampled on June 27, 1985. The well was immediately taken out of service by PennDOT officials when analysis indicated a barium concentration of 1,900 µg/L. Analysis of subsequent samples from Wr-256—on August 6, 1986, and on August 12, 1987—indicated concentrations of dissolved barium of 2,300 and 2,400 µg/L, respectively, and also elevated concentrations of dissolved methane of 26.0 and 33.5 mg/L, respectively. An abandoned water well (Wr-568) owned by Tidioute Borough also was sampled on August 20, 1986, and July 29, 1987, indicating dissolved methane below detection levels of 0.5 mg/L and trace constituents below their respective USEPA MCLs and SMCLs. However, analysis of VOCs from water samples collected on July 29, 1987, indicated a concentration of 1.6 µg/L of chloroform of unknown origin.

In December 1987, PaDEP confirmed the presence of giardia lamblia, an organism causing severe intestinal illness, in George Run, which was used for the water supply for the Southwest Warren County Municipal Authority. The PaDEP issued a permanent boil-water advisory, to be lifted only if alternative water supplies were developed or specialized filtration was installed. Because of the many problems caused by the discovery of giardia lamblia, additional efforts were directed in 1988, 1989, and 1990 to find alternative water supplies. The low streamflows in George Run during the summer drought of 1988 caused a severe water shortage for the water authority. Because of the unreliable surface-water supply, several bedrock wells were drilled by the Borough; well yields were in the range of about 10 to 20 gal/min. Although several of these wells were sited away from known oil fields and other nearby domestic water wells in the area were oil free, crude oil was observed during the drilling of several of the test wells. In summary, the bedrock aquifers were deemed unsuitable for water-supply development because well yields were considered too low.

Water-quality problems were successfully resolved when Pennsylvania grant funds were used to design and build a new filtration plant. The plant was put into operation in October 1989, removing stream sediment and giardia from the finished water. In the summer of 1991, a test well located by fracture-trace technology was drilled and converted to a production well after the bottom section of the well that was contaminated with crude oil was successfully sealed with cement. The 40 gal/min discharge of the well is pumped continuously to the treatment

plant to augment the low streamflows in George Run during droughts.

In summary, extensive erosional processes have lowered the Allegheny River valley so that its floor at Tidioute is only 120 ft above the shallow underlying petroleum reservoirs in the Venango Formation. Overlying and underlying the predominantly sandstone petroleum reservoirs is mostly shale with sufficiently low permeability to trap the petroleum. At depths of as little as 120 ft normally occupied by the fresh ground-water system, the tight shales prevent extensive flushing of the natural gas, brines, and crude oil into adjacent rocks or to land surface.

Allegheny Reservoir

The valley and hillsides that contain the Allegheny Reservoir in northeastern Warren County are an area of past and present oil and gas development. Approximately 97 active and abandoned oil and gas wells were plugged prior to the completion of the Allegheny Reservoir and Dam project from 1966 to 1968 (Gough and Waite, 1990, p. 396). However, numerous unidentified, abandoned oil and gas wells still remain. In 1980, the U.S. Forest Service plugged three abandoned wells on the shoreline of the reservoir. One of the wells was leaking natural gas and was considered a safety hazard. Two of the wells were leaking crude oil to land surface; the crude oil leaked directly into the reservoir during high reservoir levels. Additional abandoned oil and gas wells have been plugged by the U.S. Forest Service and USEPA since 1980 in an attempt to eliminate the discharge of contaminants from the abandoned wells to the surface-water and ground-water resources.

Water wells at campgrounds along the shoreline of the Allegheny Reservoir were inventoried and sampled to evaluate the water quality of the hydrogeologic units tapped by the wells. The data and locations of the wells are reported in Moore and Buckwalter (1996). The quality of the ground water of the wells was similar to other wells tapping the same hydrogeologic units in other areas of Warren County. For the constituents analyzed, concentrations in the ground-water samples collected from these wells did not exceed the MCLs.

Selected abandoned oil and gas wells on the hillsides of the Allegheny Reservoir were visited. Many of the wells were obstructed, thereby preventing accessibility to ground-water sampling. Most of the wells also were inaccessible with a geophysical logging truck. These abandoned oil and gas wells were not observed discharging crude oil, fresh or saline ground water, or brine.

Chapman State Park

Attention was drawn to the Chapman State Park area because of the previously mentioned natural-gas-migration problem. Although the gas-migration problem was first reported in January 1983, lingering effects were investigated in 1986 and 1987 as part of this study. In addition, the park superintendent was interested in what interpretations could be made of elevated concentrations of arsenic and barium that had been detected in water samples collected from several supply and non-supply wells subsequent to the gas-migration problem. These samples were collected from wells scattered throughout the park, mostly in the picnic and camping areas. Because of concern for public health, these wells were abandoned. These wells, plus several water-supply test wells in the campground (Wr-577 and Wr-578), provided ready access to the ground-water system in the park. Chapman State Park is now served by a single water-supply well (Wr-584) that was placed into service in about 1979.

Manifestations of Natural Gas Migration

In January 1983, Chapman Lake was covered with a thick layer of ice, but late in the month, mysterious “holes” in the ice were reported in the vicinity where Adams Run enters the southwest side of the lake (fig. 21). Investigation revealed these holes were caused by gas bubbles rising from the lake bottom. It also was noted that gas was bubbling up in the streambed of Adams Run. Reportedly, the gas continued to bubble unabated until mid-April 1983, when a nearby resident noticed gas bubbling into his water-supply well and reported it to the Meadville office of the PaDEP. Over the next several months, the incident was investigated and water samples were collected from the wells that were affected.

Investigations into possible sources of the gas eventually led to three oil companies with wells in the Elkhorn Run Oil Field, just west of the park (fig. 21). At the time, none of the three companies were producing gas from their wells. Because the wells were “shut in,” oil-field pressures were high. Two companies reduced pressures in the wells almost immediately. The third company did not do so as quickly. Although the bubbling of free gas into Chapman Lake began to subside late in the summer of 1983, gas bubbles continued in well-water supplies adjacent to the park into 1987. Data gathered in the vicinity of the park during the county-wide ground-water study also indicated that the source of the gas was probably a gas or oil production well (or wells) in the Elkhorn Run Oil Field, and the avenue of migration was fracture systems coincident with the stream valleys of Adams Run and probably Elkhorn Run.

Lingering Effects of Natural-Gas Migration

In 1986, reports of an explosion in a water-supply well refocused attention on the area just north of Chapman State Park. The ground-water sites inventoried in and around the park are shown in fig. 21. This inventory revealed wells Wr-571 and Wr-572 continued to experience severe natural-gas contamination.

A spark from the pump in the well pit at Wr-571 initiated an explosion that destroyed the pump and the well-pit cover. Free gas continued to be released throughout 1986 and 1987. Gas could be heard bubbling in the well while standing 20 ft away. In the case of well Wr-572, turning on the pump initiated a chain of events that led ultimately to a spectacular discharge of water and gas through a vent pipe in the well cap (fig. 22).

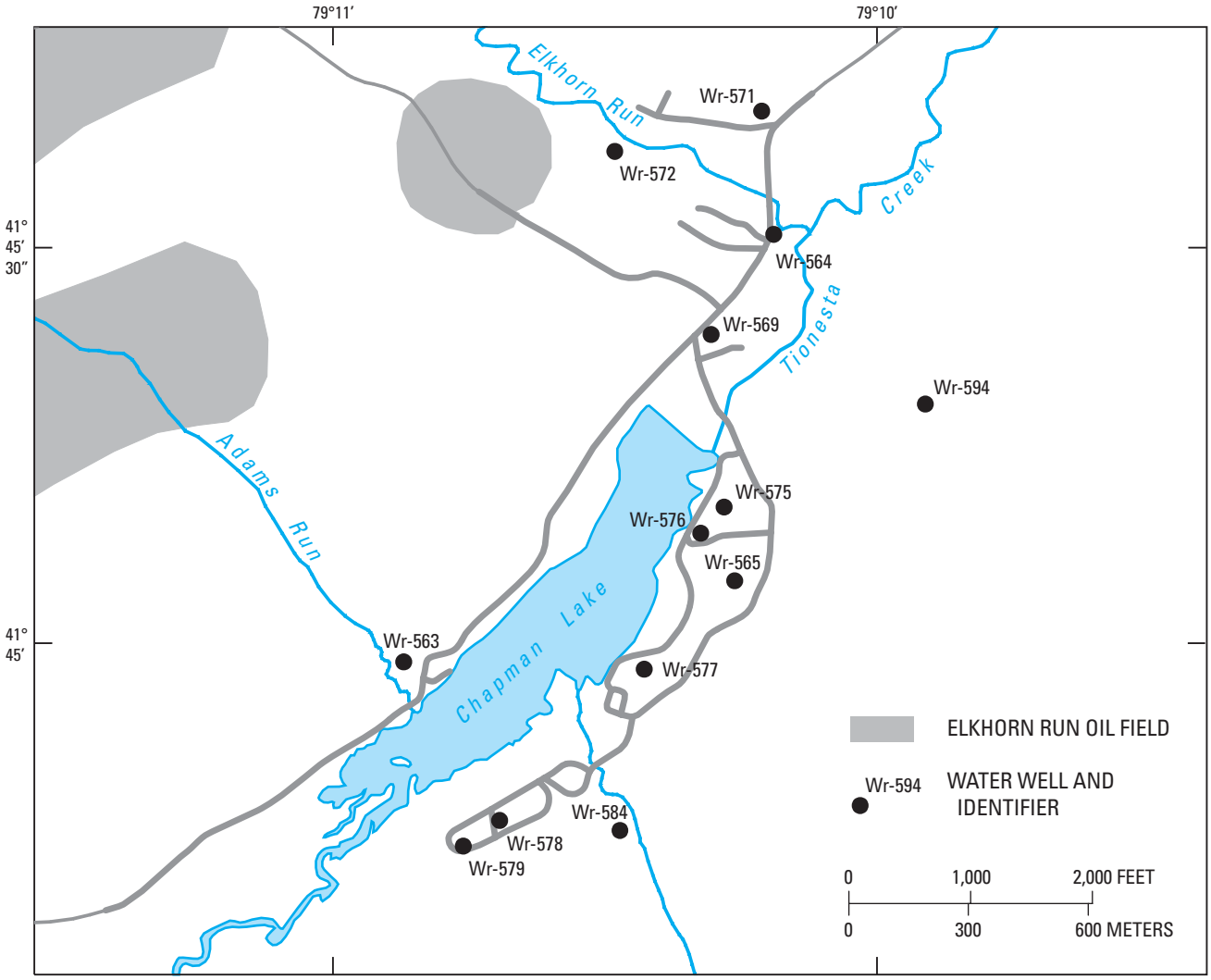


Figure 21. Wells in Chapman State Park and vicinity, Warren County, Pennsylvania.



Figure 22. Natural gas-induced discharge from vent pipe in Wr-572 (Chapman State Park) following pumping.

Apparently the water in wells Wr-571 and Wr-572 was saturated with dissolved natural gas. Pumping either well depressed the water level in the well enough that the change in pressure caused the nearly instantaneous release of large quantities of natural gas from solution.

Although water samples were collected and analyzed periodically from wells throughout Chapman State Park prior to the gas-migration problems, the analysis suite was limited to common inorganic and bacteriologic constituents. After the gas-migration incident, arsenic and barium were added to the list of analytes. The first water samples analyzed for this extended list of constituents were collected in June 1983. Sixty-eight samples from seven wells in Chapman State Park were analyzed for arsenic. The median concentration of arsenic in those samples was 6 µg/L. Thirty-two of the 68 samples (47 percent) equalled or exceeded the USEPA MCL of 10 µg/L (table 28).

Barium concentrations in water from wells in Chapman State Park ranged from 40 to 1,660 µg/L from June 1983 to August 1986, below the USEPA MCL of 2,000 µg/L. The maximum concentration was in a sample from well Wr-569, north of Chapman Lake. During this period, concentrations of barium in all samples collected from this well exceeded the median concentration of 290 µg/L.

Because arsenic and barium data are not available prior to June 1983, it is not known if the elevated concentrations were the result of the gas migration. Generally, the concentrations discussed above are higher than those reported for samples collected from other wells in the county that draw water from the same hydrogeologic unit.

Table 28. Selected trace constituents in water sampled from wells in or near Chapman State Park, Warren County, Pennsylvania.

[All values are in micrograms per liter. <, less than; —, no data available]

County well or spring identification number	Date of sample	Source of sample	Arsenic (As)	Barium (Ba)	Iron (Fe)	Manganese (Mn)
Wr-563	6/7/1983	Bureau of Community Environmental Control	<10	330	420	1,020
	3/22/1984	Chapman State Park	<4	180	590	750
	5/23/1984	Chapman State Park	5	60	1,400	900
	9/12/1984	Chapman State Park	5	60	—	—
	11/14/1984	Chapman State Park	4	40	—	—
	4/17/1985	Chapman State Park	10	100	—	—
	9/24/1985	Chapman State Park	20	140	650	1,620
	2/14/1986	Chapman State Park	9	500	2,710	1,090
	4/24/1986	Chapman State Park	27	200	—	—
	8/14/1986	U.S. Geological Survey	31	<500	560	1,510
Wr-564	3/22/1984	Chapman State Park	21	200	110	50
	5/23/1984	Chapman State Park	26	190	100	50
	9/12/1984	Chapman State Park	<4	170	—	—
	11/14/1984	Chapman State Park	24	130	—	—
	4/17/1985	Chapman State Park	25	160	—	—
	9/24/1985	Chapman State Park	32	300	250	280
	2/13/1986	Chapman State Park	38	<500	200	190
	4/23/1986	Chapman State Park	29	280	—	—
	8/14/1986	U.S. Geological Survey	31	<500	370	60
Wr-565	6/7/1984	Bureau of Community Environmental Control	<10	390	730	—
	3/22/1984	Chapman State Park	<4	60	1,420	—
	5/23/1984	Chapman State Park	<4	280	3,100	—
	9/12/1984	Chapman State Park	<4	140	—	—
	11/14/1984	Chapman State Park	<4	230	—	—
	4/17/1985	Chapman State Park	<4	200	—	—
	2/14/1986	Chapman State Park	<4	<500	4,130	270
	8/14/1986	U.S. Geological Survey	<4	<500	760	150
Wr-569	6/7/1983	Bureau of Community Environmental Control	<10	1,560	2,090	80
	7/20/1983	Bureau of Community Environmental Control		1,210	—	—
	9/29/1983	Bureau of Community Environmental Control	<10	1,370	—	—
	8/8/1983	Bureau of Community Environmental Control		1,660	—	—
	3/22/1984	Chapman State Park	<4	640	1,620	90
	5/23/1984	Chapman State Park	<4	1,000	300	50
	9/12/1984	Chapman State Park	14	1,100	—	—
	11/14/1984	Chapman State Park	<4	1,040	—	—
	4/17/1985	Chapman State Park	5	1,160	—	—
	9/24/1985	Chapman State Park	4	1,080	2,220	250
	2/14/1986	Chapman State Park	6	1,270	1,970	100
	4/24/1986	Chapman State Park	10	1,190	—	—
	8/14/1986	U.S. Geological Survey	6	1,200	2,020	90

Table 28. Selected trace constituents in water sampled from wells in or near Chapman State Park, Warren County, Pennsylvania.—Continued

County well or spring identification number	Date of sample	Source of sample	Arsenic (As)	Barium (Ba)	Iron (Fe)	Manganese (Mn)
Wr-575	6/7/1983	Bureau of Community Environmental Control	25	290	15,100	80
	3/22/1984	Chapman State Park	<4	140	5,960	80
	5/23/1984	Chapman State Park	11	90	6,200	50
	11/14/1984	Chapman State Park	28	60	—	—
	4/17/1985	Chapman State Park	12	40	—	—
	9/24/1985	Chapman State Park	10	100	—	—
	4/24/1986	Chapman State Park	10	200	—	—
	8/18/1987	U.S. Geological Survey	32	<500	13,900	140
Wr-576	6/7/1983	Bureau of Community Environmental Control	67	670	2,900	60
	7/29/1983	Bureau of Community Environmental Control	44	—	—	—
	8/8/1983	Bureau of Community Environmental Control	<10	1,010	—	—
	9/29/1983	Bureau of Community Environmental Control	100	1,480	—	—
	3/22/1984	Chapman State Park	457	740	20,200	110
	9/12/1984	Chapman State Park	64	400	—	—
	11/14/1984	Chapman State Park	107	550	—	—
	4/17/1985	Chapman State Park	16	120	—	—
	9/24/1985	Chapman State Park	94	270	5,030	230
	2/13/1986	Chapman State Park	181	<500	14,200	140
	4/23/1986	Chapman State Park	190	620	—	—
	8/5/1987	U.S. Geological Survey	68	<500	3,000	70
Wr-577	6/7/1983	Bureau of Community Environmental Control	<10	960	1,230	130
	9/29/1983	Bureau of Community Environmental Control	<10	1,030	—	—
	3/22/1984	Chapman State Park	<4	640	5,750	160
	5/23/1984	Chapman State Park	<4	560	220	200
	9/12/1984	Chapman State Park	<4	610	—	—
	11/14/1984	Chapman State Park	<4	840	—	—
	4/17/1985	Chapman State Park	<4	570	—	—
	2/14/1986	Chapman State Park	<4	780	2,080	180
	4/24/1986	Chapman State Park	<10	710	—	—
	8/27/1987	U.S. Geological Survey	<4	720	130	170

Anomalies in Ground-Water Levels

In order to understand the ground-water problems at Chapman State Park, several wells, including Wr-565, Wr-577, and Wr-578, were instrumented with continuous water-level recorders from June 1987 through August 1988. Well Wr-565 is 67 ft deep and well Wr-577 is 50 ft deep; both are completed in alluvium. Well Wr-578 is 156 ft deep, tapping fractured bedrock of the Venango Formation. Anomalies showed up in the water-level hydrographs for all three wells. From mid November 1987 through March 1988, four events produced short-term, nearly instantaneous oscillations of the water level in well Wr-577 (fig. 23). The largest magnitude events were on November 30, 1987, and March 6 and March 16, 1988, and also were recorded at wells Wr-565 and Wr-578. Because the water-level fluctuations were of such short but intense duration and the wells were shallow, a local source, such as hydrofracturing of an oil or gas well or the use of explosives, was suspected. When these anomalies could not be correlated to local activities, more regional sources, including earthquakes, were investigated (fig. 23).

Most of these short-term water-level oscillations have been correlated with earthquakes in the Gulf of Alaska. One event correlates with a moderate quake in southern California. Although water-level records were collected until August 1988, no further anomalies were recorded. It is noteworthy that this time period also was devoid of significant earthquakes in California and Alaska. Although not all wells will exhibit a hydrologic response to distant earthquakes, the phenomenon has been well documented (Vorhis, 1967)

Wells Wr-576 and Wr-577 frequently had water levels above land surface during spring, even though they draw water from the **unconfined** colluvium **aquifer**. Both wells are 4 in. in diameter and are cased through their entire length, effectively making them piezometers. Figure 24 illustrates how the water level in a piezometer monitoring an unconfined aquifer could rise above land surface. Generally, this is most likely to occur where the ground-water-flow gradient (roughly equivalent to the slope of the water table) is steep and upward. Pre-pumping ground-water contours in figure 25 confirm a steep water-table gradient near Chapman Lake.

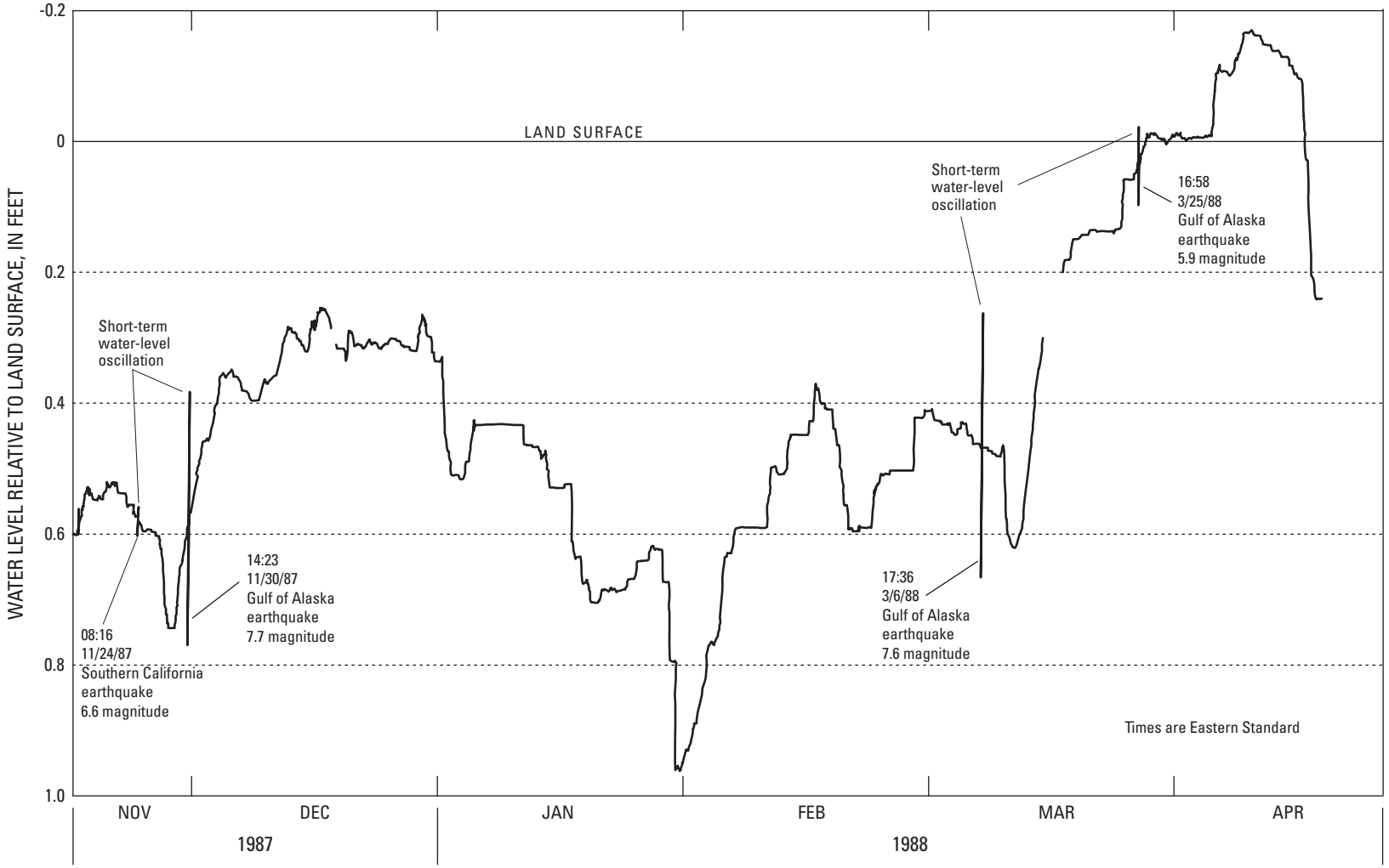


Figure 23. Four short-term water-level oscillations in well Wr-577 possibly caused by earthquakes in western United States, Warren County, Pennsylvania.

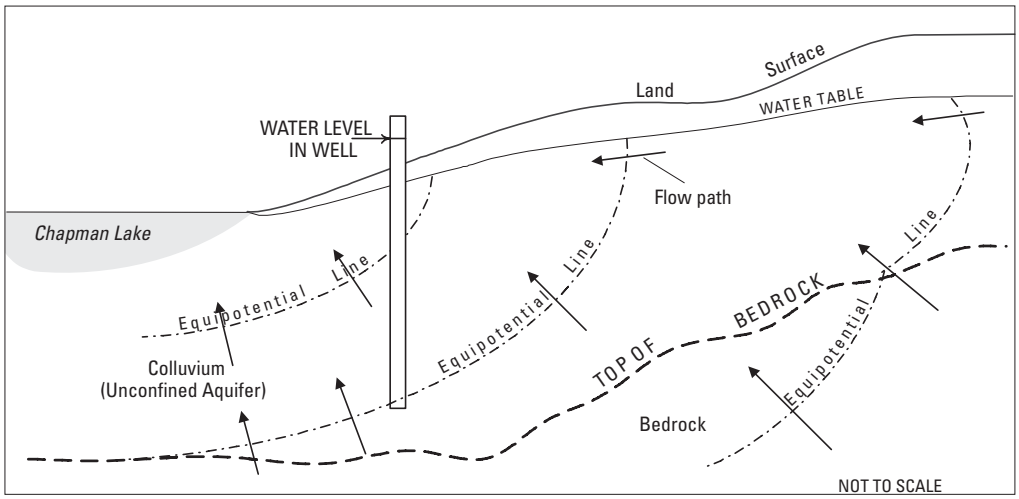


Figure 24. Conceptual ground-water-flow model in vicinity of Chapman Lake, showing water levels above land surface in a well completed in the unconfined aquifer.

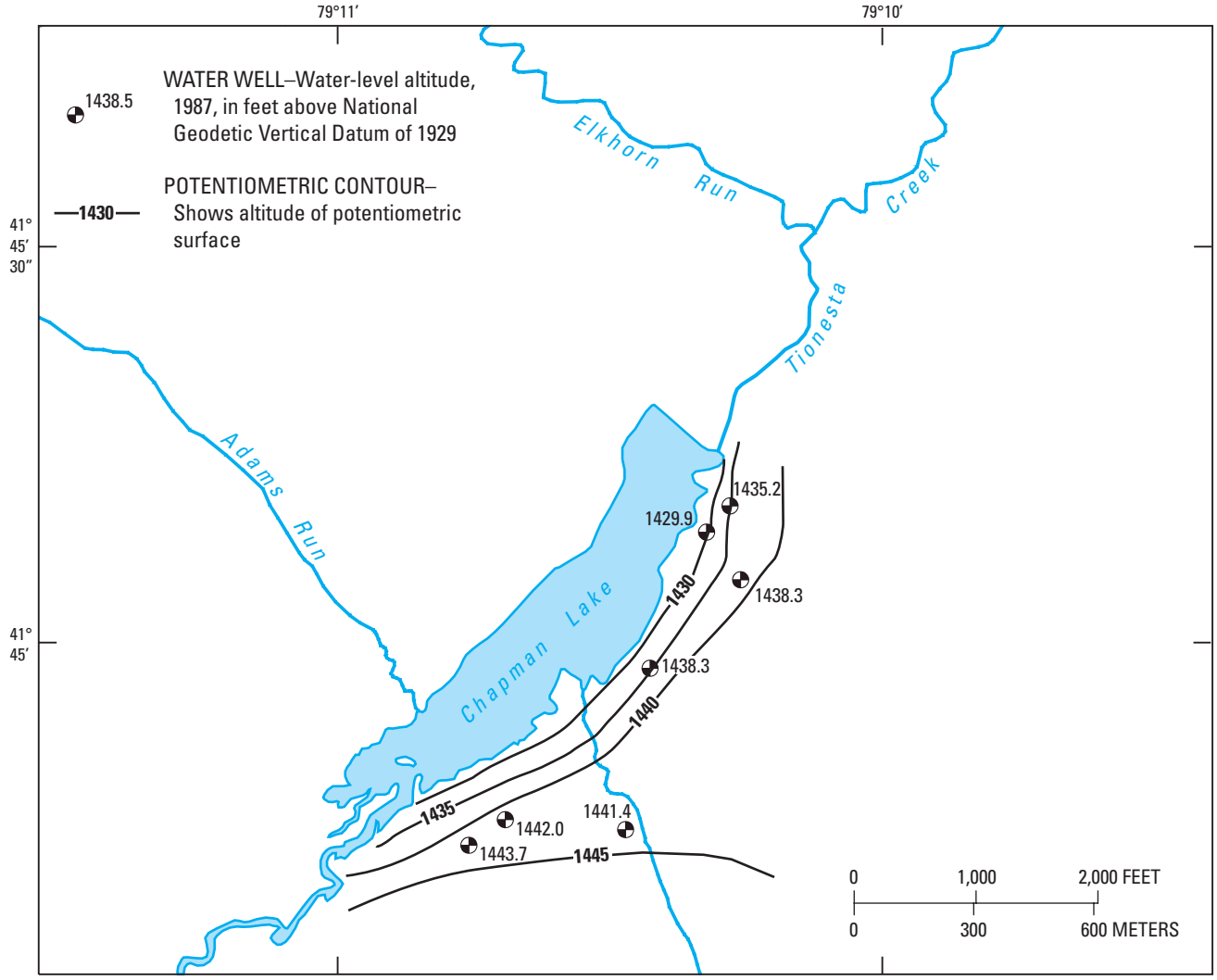


Figure 25. Potentiometric contours in the vicinity of Chapman State Park, Warren County, Pennsylvania.

48-Hour Aquifer Test

To better understand the flow system at Chapman State Park, a 48-hour aquifer test was conducted in October 1987. The park water supply well, Wr-584, was pumped for 48 hours and 10 minutes at a constant rate of 37.5 gal/min. Pumped well Wr-584 is 141 ft deep, cased to 64 ft below land surface, and open to bedrock of the Venango Formation. Water levels in wells Wr-565, Wr-577, Wr-578, Wr-579 and Wr-584 were monitored throughout pumping. Approximately 8 days of recovery data were collected in wells Wr-578 and Wr-579 following pumping (fig. 26).

Successful interpretation of aquifer test data starts with a conceptual model of the hydrogeologic framework under which the test is being conducted. In this case, the setting is similar to that shown in figure 7, with Chapman Lake on a colluvium valley and the pumping well just slightly upslope of the lake. Several lines of evidence support this model.

An interpretation of the geophysical logs collected from Wr-578 are shown in figure 27. These geophysical logs and the resulting interpretation support the conceptual model used to analyze the results of this multiple-well aquifer test. The geophysical logs confirm the presence of approximately 90 ft of colluvium, most of which is saturated. Beneath the colluvium is fractured bedrock composed of interbedded siltstone, sandstone, and shale.

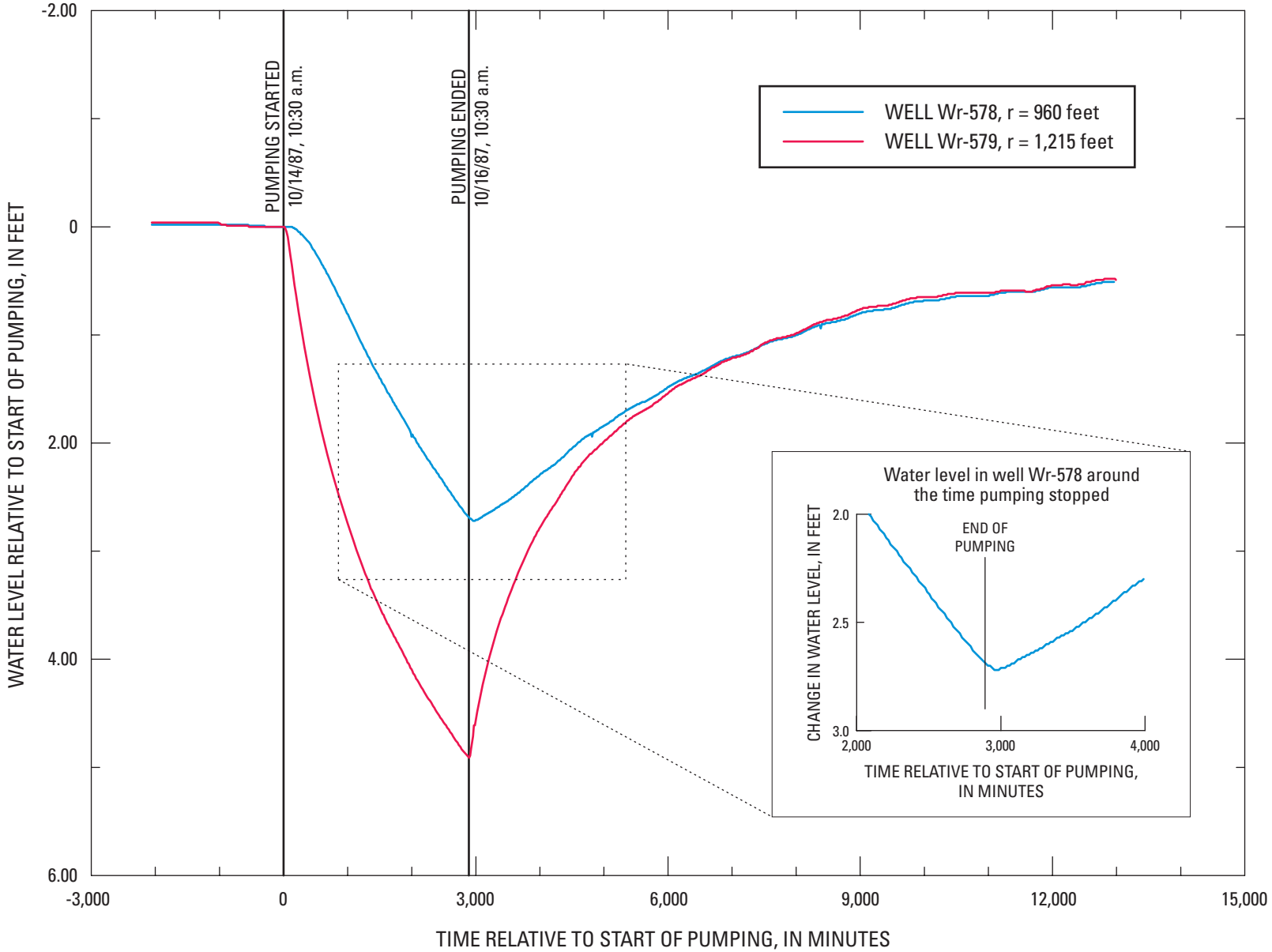


Figure 26. Water-level response in wells Wr-578 and Wr-579 to pumping in well Wr-584, Warren County, Pennsylvania. [A leaky-confined analytical model developed by Hantush (1960) was used to interpret the water-level data.]

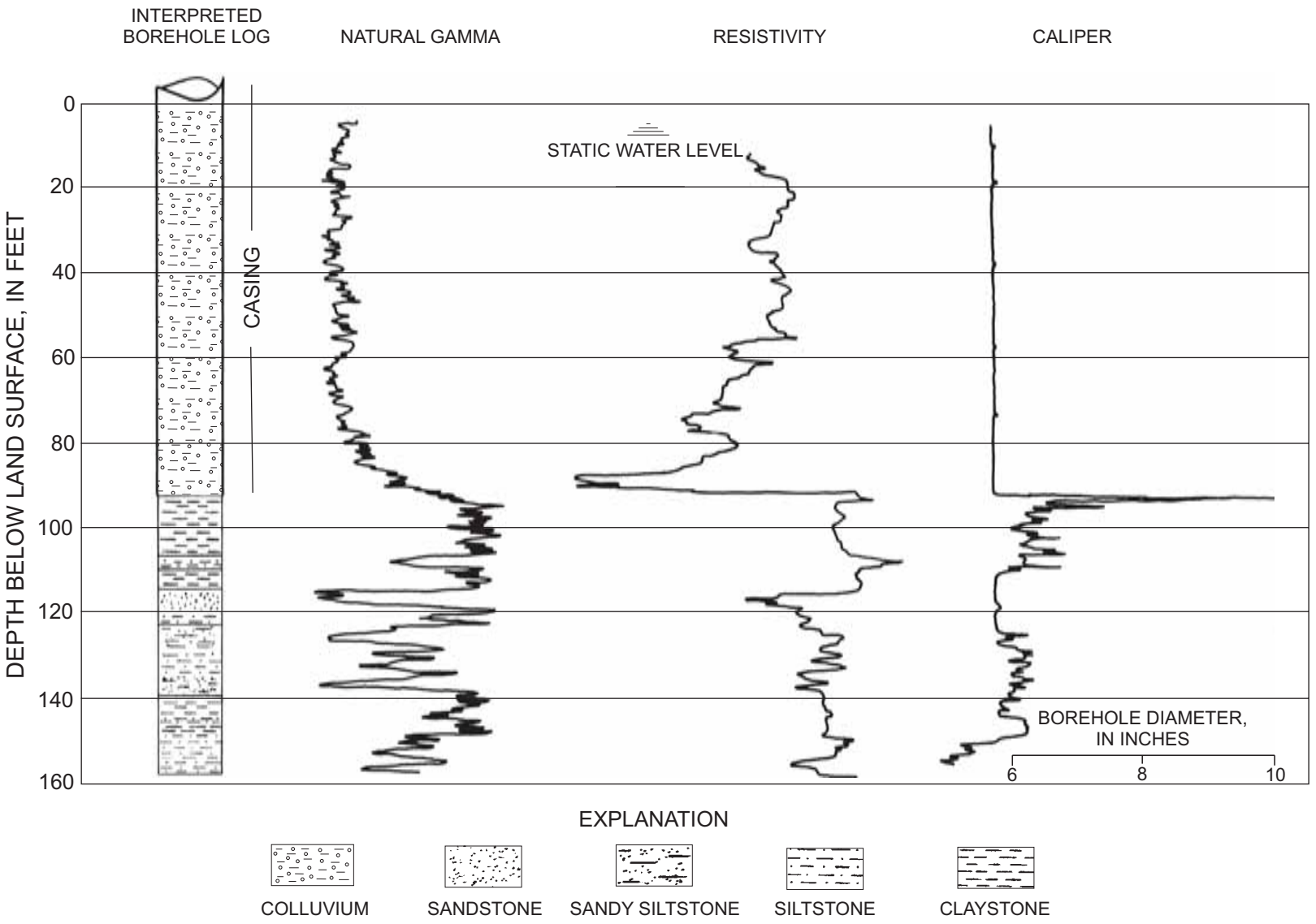


Figure 27. Borehole geophysical logs collected in well Wr-578, Warren County, Pennsylvania.

The saturated colluvium is thickest in the valley bottom under Chapman Lake and thins toward the valley wells. A driller's log for well Wr-584 (the pumping well) indicates 49 ft of colluvium is present. Seismic-refraction data collected along two lines in the park further confirmed the thickness of unconsolidated material overlying the bedrock.

During pumping of the bedrock aquifer, the overlying saturated colluvium may provide recharge to the bedrock as the hydraulic head in the bedrock is lowered. This recharge should manifest itself as less than expected **drawdown** in the bedrock aquifer. Failure to account for this recharge in the analysis of the aquifer-test data would result in an overestimation of the **transmissivity** of the bedrock unit. This in turn would lead to overestimating the quantity of water available to the well.

Water levels (relative to the start of pumping) in wells Wr-578 and Wr-579 are shown in figure 26. The time represented in the graph spans a period beginning approximately 34 hours before the pumping test and 216 hours (9 days) after pumping was stopped. The drawdown in well Wr-579 is nearly twice that of Wr-578 even though it is 255 ft farther than Wr-578 from the pumping well. Although there is no definitive reason for this anomaly, it is most likely because the well is cased from 0 to 90 ft and is open to only the upper 5 ft of bedrock (90-95 ft). Wr-579 is a piezometer monitoring the water level at the interface between bedrock and the colluvium. On the other hand, well Wr-578 is open to a 66-ft interval in the upper part of the bedrock.

A time drawdown plot for pumping well Wr-584 and observation wells Wr-578 and Wr-579 is shown in figure 28. Matching the response of the observation wells to the β=2 type curve of the Hantush (1960) method for leaky confining beds, the transmissivity of well Wr-578 is calculated at 30 ft^2/d while that of Wr-579 is 60 ft^2/d.

As is the case with analyzing the results of aquifer-test data in the fractured-bedrock environment, factors such as aquifer anisotropy, partial well penetration, or differences in well construction have an indeterminable influence on the drawdown in each well. Even in aquifer tests such as this one, where attempts were made to control as many factors as possible, ambiguities exist in the calculation of aquifer properties.

Guidelines for Developing Ground-Water Supplies

The individual homeowner generally has little choice in the selection of a well site. Usually, the well location is restricted to the proximity of the house and a power supply and prevention of possible contamination from a septic system. Siting of a ground-water supply for stock, commercial, or public use may not be as restricted. For both situations, an understanding of the geologic and hydrologic information given in this report, combined with proper well construction, usually can make the difference between a successful or unsuccessful well or spring. The following facts and procedures, listed in order of importance, may be helpful when considering a ground-water supply.

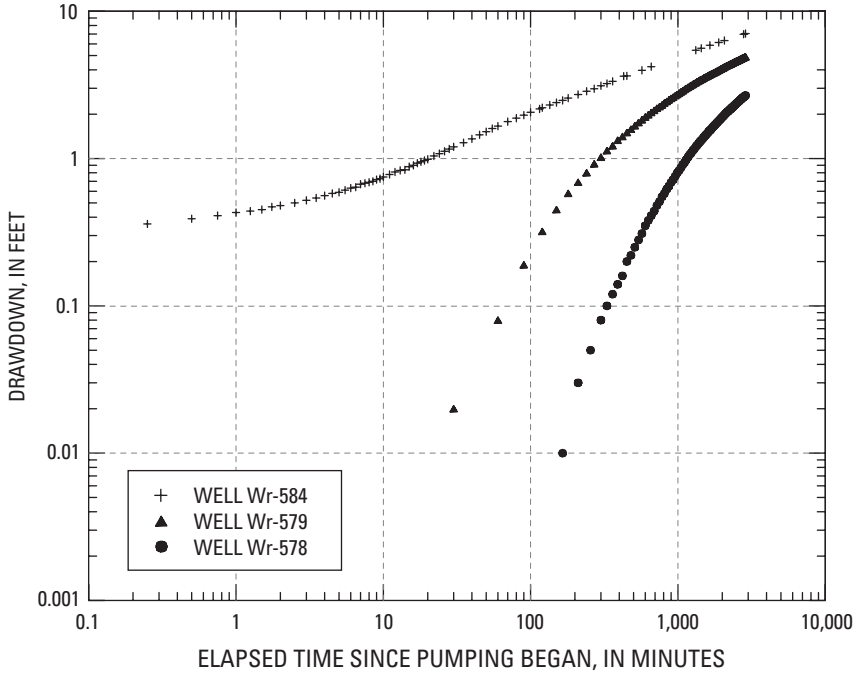


Figure 28. The relation between drawdown and time for pumping well Wr-584 and observation wells Wr-578 and Wr-579, Warren County, Pennsylvania.

- The yields and quality of water of nearby wells and springs commonly indicate what can be expected at a site. The depth of existing wells and the altitude of springs identify the location of aquifers and water-bearing units in a specific area.
- Wells installed and tested during dry periods, when water levels are lowest, permit the optimum setting of pumps. Also, the adequacy of the well is best when tested at that time, and the quality of water is commonly at its worst. The relative permanence of a proposed spring is also best established during this period.
- In Warren County, in areas where thin (less than about 25 ft thick) surficial deposits overlie bedrock, most wells are completed in the underlying fractured bedrock. Data from water well records indicate almost all bedrock wells have water-bearing zones less than 200 ft in depth. Generally, drilling a well beyond 200 ft does not increase well yield, and water quality commonly becomes worse. Furthermore, the depth to water usually increases with greater well depth, which in turn increases the pumping cost. Only in valley settings, where well depth does not significantly affect the depth to water in the well, would drilling to depths greater than 200 ft be practical.
- Where wells yield meager amounts of water, as much storage capacity as possible is desirable. Storage tanks or reservoirs may be used to provide necessary storage. Consideration also may be given to drilling wells with a larger than usual diameter to provide as much storage capacity as possible in the well itself. For example, each foot of water in a 6-in.-diameter well contains about 1.5 gal. Each foot of water in an 8-in.-diameter well contains about 2.5 gal. Thus, wells that contain 50 ft of water have 75 gal in storage in a 6-in.-diameter well and 125 gal in an 8-in.-diameter well. The cost of drilling a well that is more than 8 in. in diameter may become prohibitive below a certain depth. The cost of well storage needs to be compared to that of ground-level storage.

Site Selection Restricted

Characteristics of ground-water system in various topographic settings that may aid in developing a successful water supply.

1. Hilltops: Wells commonly are drilled only to the depth of sufficient yield. Increasing the well depth for added yield or storage commonly results in water-level decline and sometimes complete loss of well yield. Also, an uncased deep well commonly can reduce the yield of a nearby shallow well.
2. Hillsides: In addition to procedures for the hilltop setting, wells need to be sited at some distance from potential contamination points such as septic tanks, trash dumps, or stock pens located upgradient. At many hillside locations, springs are a suitable alternative to wells as a potable water supply. However, care must be exercised to eliminate contamination when using springs for domestic supply. For stock-water supply, the spring box and storage tank construction used by the U.S. Department of Agriculture, Soil Conservation Service (1985) has proven to be successful. In some places, several springs can be developed and the combined discharge piped to the desired location. Where conservation is critical, multiple storage tanks may be used.
3. Valley: Large-yielding shallow wells are possible in the unconsolidated deposits of major valleys, but ground water is susceptible to contamination by surface activities. Some deep wells in large valleys tap confined aquifers that may be under artesian flowing conditions.

Site Selection Unrestricted

On any given hillslope, springs developed in low parts of hills are most likely to produce the significant sustained yields during drought periods.

Of all the topographic settings, wells in valleys have the greatest chance of success of producing large well yields. These large yields commonly are because of a high density of fractures beneath the valley bottom. These fractures typically diminish laterally beneath adjacent hills, thereby limiting the areal extent and yield of such aquifers. Therefore, an aquifer test of more than 48-hours duration needs to be done on valley wells proposed for public or commercial use. Such a test also can be used to document the possible interference of nearby pumping wells. The drawdown area of a high-capacity valley well is expected to extend for long distance along the axis of the valley.

Because many wells are completed in bedrock where water primarily moves through secondary fractures, the locations of fracture traces can help in choosing sites of optimum yield. The most conspicuous linear features can be identified and plotted on aerial photographs. These aerial photographs can then be taken into the field to help locate possible fracture traces. The best site for a well is reported to be at the intersection of two or more traces. Parizek and others (1971) determined that the width of fracture zones ranged from 10 to 60 ft and averaged 39 ft in the siltstones and shales of western Pennsylvania. A trained professional hydrogeologist could be consulted to accurately locate such narrow zones by this method.

General information on the development of small well-supply systems may be obtained from a manual prepared by the USEPA (1991). The manual includes sections on drilled and dug well construction, spring development for domestic use, and sanitary protection of water supplies.

Suggestions for Future Study

Laboratory analyses for total arsenic of samples in ground water from municipal water wells are routinely performed as required by regulations of the Pennsylvania Department of Environmental Protection. Although evaluation with respect to this study has not been comprehensive, reports of arsenic above the 10 μg/L USEPA MCL from water in municipal water wells are unknown for northern Pennsylvania. A large part of the population of northern Pennsylvania, however, relies on privately owned wells for their household water supply, and these wells commonly are not tested for arsenic. Arsenic at concentrations above the 10 μg/L USEPA MCL has been documented in ground water in northern Pennsylvania. It is probable that privately owned wells exist in hydrogeologic settings similar to the identified sites in northern Pennsylvania with arsenic concentrations greater than the USEPA MCL for drinking water. The sources of arsenic at these sites are probably natural. Additional data are needed to refine the arsenic geochemical model and additional descriptive information on the hydrogeologic settings of the arsenic sites are needed prior to any predictions of other areas in northern Pennsylvania that may be prone to the occurrence of elevated arsenic concentrations in ground water. Objectives of a future study of arsenic occurrence in northern Pennsylvania are proposed as follows:

1. Define the geochemical model that accounts for sources, sinks, and mobility of arsenic in the ground-water-flow system.
2. Define where elevated arsenic concentrations have been found.
3. Predict the areas in northern Pennsylvania may be prone to elevated concentrations of arsenic in ground water, using the geochemical and hydrogeologic criteria.
4. Evaluate the success of predicting areas of elevated arsenic concentration in ground water.

Summary

With the exception of electric power generating facilities, ground-water is the predominant source of water supply for domestic homes, municipalities, and industrial facilities in Warren County, northwestern Pennsylvania. This report describes and evaluates the hydrogeology and ground-water resources of Warren County. Data and interpretation in part of this report are devoted to increasing the understanding of ground-water quality as affected by the occurrence and development of oil and gas resources in the county. Information in this report should assist in the development and management of the ground-water resources in Warren County. Ground-water data were collected from 1984 through 1987 by the U.S. Geological Survey, in cooperation with the Pennsylvania Department of Environmental Resources, Bureau of Topographic and Geologic Survey, and the Warren County Commissioners. The scope of the hydrogeologic investigation included well and spring inventory, ground-water sampling, geologic mapping, literature review, geophysical logging, and aquifer testing.

Annual precipitation at Warren for the years 1984-87 was above the long-term mean. The 4-year average of the annual hydrologic budget for 1984-87 indicates 40 percent of precipitation is lost to evapotranspiration, 29 percent recharges the ground-water system, and 31 percent is surface runoff. During 1984-87, ground-water discharge made up from 47 to 50 percent of total streamflow. Total water withdrawals in Warren county decreased from 3,560 Mgal/d in 1984 to 1,060 Mgal/d in 1990, mostly because of a substantial decrease in surface-water withdrawals for hydroelectric power. In 1990, 98.6 percent of all water withdrawals were surface water used for power generation. Total ground-water withdrawals in 1990 were 13.8 Mgal/d.

Most of the northern half of Warren County is in the Northwestern Glaciated Plateau Section of the Appalachian Plateaus Physiographic Province. The remainder of Warren County is in the High Plateau Section.

The glacial outwash hydrogeologic unit is the most extensively tapped unconsolidated unit in Warren County because it is capable of yielding large amounts of water to wells and it is situated in the populated valleys. Most wells tapping this unit are used for domestic purposes and, in selected areas, have the sustained yields necessary for large-capacity municipal and industrial use. The median specific capacity in 47 wells was 6.0 (gal/min)/ft, and the median yield for 47 specific-capacity tests was 25 gal/min. Yields ranged from 2 to 1,600 gal/min.

A comparison of the median specific capacities for unconsolidated and bedrock hydrogeologic units indicates that wells tapping the glacial outwash had the highest median specific capacity of 6.0 (gal/min)/ft and ranged from 0.14 to 300 (gal/min)/ft. The bedrock hydrogeologic units and their respective median specific capacities are as follows: Pottsville Group, 0.5 (gal/min)/ft; Shenango Formation, 0.44 (gal/min)/ft; Cuyahoga Formation, 0.24 (gal/min)/ft; Knapp Formation, 0.45 (gal/min)/ft; Oswayo Formation, 0.07 (gal/min)/ft; Riceville Formation, 1.5 (gal/min)/ft; Corry Sandstone through Riceville Formation, 0.67 (gal/min)/ft; Venango Formation, 1.0 (gal/min)/ft; and Chadakoin Formation, 0.71 (gal/min)/ft.

Major controls on the ground-water-flow system include topography and secondary permeability. The absence of major fractures limit infiltration of freshwater to deeper horizons. In Warren County, ground water moves within and through two general flow systems—a shallow, local aquifer system with active flow, and a deeper, regional system with flow that is almost stagnant. Unconsolidated deposits make up the upper part of the local flow system. About 95 percent of the ground-water circulation takes place in the local flow system. The bottom of the local flow system roughly parallels the bedrock surface, about 200 ft below land surface. The depth of the base of the fresh ground-water system varies from about 200 to about 600 ft below land surface. Few reports of fresh water below 600 ft from land surface were found probably because of

decreasing secondary permeability with depth and the low permeability of the Devonian bedrock (particularly shales).

An observation well network of five wells monitored seasonal changes in water-level fluctuations and the data indicated annual high water levels in the winter or spring. Water levels generally declined during the summer through early fall as a result of the rate of evapotranspiration and ground-water discharge exceeding the rate of recharge during this period.

Most major constituents in samples were within the range of typical values for natural ground waters. Concentrations of sulfate in samples from wells, springs, and abandoned oil and gas wells were low with respect to the USEPA SMCL of 250 mg/L. Only one well tapping the unconsolidated hydrogeologic units exceeded the USEPA SMCL of 250 mg/L for chloride. Two samples of the 260 collected exceeded the USEPA MCL for nitrate. The exact source of the nitrate was unknown. Concentrations of iron and manganese in samples from water wells commonly were above the USEPA SMCLs of 300 and 50 µg/L, respectively. Although the number of springs sampled was small with respect to the number of wells sampled, iron and manganese concentrations generally were lower in springs than in water wells.

Samples collected from 233 water wells were analyzed for arsenic. Of these wells, the arsenic concentration in water from 38 wells exceeded the USEPA MCL of 10 µg/L. Sixty-six percent of these 38 wells were in the glacial outwash hydrogeologic unit.

The development of ground water in Warren County for domestic and municipal use has been difficult because of very shallow petroleum reservoirs in parts of the ground-water system. Analysis of water samples from wells in the Tidioute area indicated poor water quality that would require costly treatment prior to use. Excessive concentrations of iron, manganese, aluminum, chloride, dissolved solids, and methane negated the use of these wells for public supply.

In Pleasant Township, a major subsurface natural gas migration in 1983 resulted in high concentrations of natural gas observed in water wells, a spring, lake, and tributary stream of Chapman State Park. Although natural gas concentrations in ground-water diminished over time in ground water, several wells continued to experience severe natural-gas contamination in 1986. A well containing water that was saturated with natural gas was reported to have exploded, and another well suddenly discharged water from a vent pipe after pumping. Samples from wells in this area had elevated levels of arsenic and barium. Thirty-two of 68 samples collected in this area equalled or exceeded the USEPA MCL of 10 µg/L for arsenic. Barium concentrations ranged from 40 to 1,660 µg/L but were below the USEPA MCL of 2,000 µg/L. It is not know if these elevated concentrations were the result of gas migrations, but the concentrations were higher than those reported for samples collected from other wells in the county that draw water from the same hydrogeologic units.

Acknowledgments

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Glossary

A

alkalinity The capacity of a water for neutralizing an acid solution. Alkalinity in natural water is caused primarily by the presence of carbonate and bicarbonate.

alluvium A general term for clay, silt, sand, gravel, or other similar material deposited in a streambed, on a flood plain, delta, or at the base of a mountain during comparatively recent geologic time.

annular space The open space surrounding a cylindrical object within a cylinder. The open space around a pipe suspended in a wellbore is often termed the annulus, and its outer wall may be either the wall of the borehole or the casing.

aquifer A geologic formation, group of formations, or part of a formation that contains sufficient saturated permeable material to yield usable quantities of water to wells and springs.

aquifer test A test or controlled field experiment involving either the withdrawal of measured quantities of water from, or addition of water to, a well (or wells) and the measurement of resulting changes in head in the aquifer both during and after the period of discharge or addition.

B

base flow Discharge entering stream channels as effluent from the ground-water reservoir; the dry-weather flow of streams.

bedrock A general term for the rock, generally solid, that underlies soil or other unconsolidated or semiconsolidated surficial material.

C

casing Steel pipe placed in a well as drilling progresses. The function of casing is to prevent the wall of the hole from caving during drilling, to provide a means of extracting the oil if the well is productive, and to exclude fluids from the bore hole.

cementing The application of a liquid slurry of cement and water to various points in an oil or gas well, inside or outside the casing. Primary cementing refers to the cementing operation that takes place immediately after the casing has been run into the hole, and that provides a protective sheath around the casing, segregates the producing formation, and prevents the migration of undesirable fluids. After the primary cementing operation has been completed, any subsequent cementing operation is generally referred to as secondary cementing. Among the most useful of secondary cementing methods is that of squeeze cementing, in which the slurry is squeezed out through perforations in the casing by the application of great pressure. Squeeze cementing is used to isolate a producing formation, to seal off water, or to repair casing leaks. Other secondary cementing methods include a plug back job, in which a plug of cement is positioned at the desired point and allowed to set. Wells are plugged back to shut off bottom water or to reduce the depth of the well.

conductor casing A short string of casing of large diameter that is used on offshore and marshy locations and under certain other conditions. Its principal function is to keep the top of the well bore open and to provide means of conveying the upflowing drilling fluid from the well bore to the slush pit. Conductor casing or conductor pipe is also commonly called drive pipe.

confining unit A body of impermeable or distinctly less permeable material stratigraphically adjacent to one or more aquifers.

D

dip The angle that a structural surface, such as a bedding or autoplane, makes with the horizontal, measured perpendicular to the strike of the structure and in the vertical plane.

dissolved Refers to that material in a representative water sample that passes through a 0. 45 micrometer membrane filter. This is a convenient operational definition used by Federal agencies that collect water data. Determinations of “dissolved” constituents are made on subsamples of the filtrate.

dissolved solids The dissolved mineral constituents in water; they form the residue after evaporation and drying at a temperature of 105 degrees Celsius; they also may be calculated by adding concentrations of anions and cations.

drawdown The lowering of the water table or potentiometric surface caused by pumping (or artesian flow) of a well.

drift Any rock material deposited by an ice sheet or by meltwaters of that ice sheet.

drive pipe See conductor casing.

E

end moraine A moraine that is being produced at the front of an actively flowing glacier at any given time; a moraine that has been deposited at the lower or outer end of a glacier.

evapotranspiration The evaporation from water bodies, wetted surfaces, and moist soil by direct evaporation and vapor that escapes from living plants by the process of transpiration.

F

formation The fundamental unit in rock-stratigraphic classification. It is a body of internal homogeneous rock; it is prevailingly but not necessarily tabular and is mappable at the earth's surface or traceable in the subsurface.

fracture A break in the rock.

G

ground water That part of the subsurface water in the zone of saturation.

ground-water discharge Release of water in springs, seeps, or wells from the ground-water reservoir.

ground-water recharge Addition of water to the ground-water reservoir by infiltrating precipitation or seepage from a streambed.

group A stratigraphic unit consisting of two or more formations.

H

hardness A physical-chemical characteristic that commonly is recognized by the increased quantity of soap required to produce lather. It is attributable to the presence of alkaline earths (principally calcium and magnesium) and is expressed as equivalent calcium carbonate ($CaCO_3$).

head (static) The height above a standard datum of the surface of A column of water (or other liquid) that can be supported by the static pressure at a given point. In this report, head is synonymous to water level.

I

intermediate casing string The string of casing set in a well after the surface casing; sometimes called protection casing or water string. Purposes include keeping the hole from caving, affording a strong string of pipe for attachment of blowout preventers, or casing off fresh or salt-water bearing zones.

J

K

L

lacustrine Having to do with lakes or their deposits.

lithology The physical characteristics of a rock, generally as determined by examination with the naked eye or with the aid of a low-power magnifier.

M

micrograms per liter (µg/L) A unit expressing the concentration of chemical constituents in solution as mass (micrograms) of solute per unit volume (liter) of water. One thousand micrograms per liter is equivalent to one milligram per liter.

milligrams per liter (mg/L) A unit for expressing the concentration of chemical constituents in solution. Milligrams per liter represent the mass of solute per unit volume (liter) of water.

moraine A mound, ridge, or other distinct accumulation of unsorted, unstratified glacial drift, predominantly till, deposited chiefly by direct action of glacier ice, in a variety of topographic landforms that are independent of control by the surface on which the drift lies.

N

O

oil or gas well-completion report A form filed with the Pennsylvania Department of Environmental Resources by the well operator which includes well construction, production, formations, location, elevation, and frequently depths to fresh or salt water-bearing zones.

outwash Stratified drift deposited by meltwater streams.

P

pH A measure of the acidity or alkalinity of water. Mathematically, the pH is the negative logarithm of the hydrogen ion activity; pH = $-\log_{10}$ [H+], where [H+] is the hydrogen-ion concentration in moles per liter. A pH of 7.0 indicates a neutral condition. An acid solution has a pH less then 7.0 and a basic or alkaline solution has a pH more than 7.0.

permeability The capacity of a porous rock, sediment, or soil to transmit a fluid under a hydraulic head; it is a measure of the relative ease with which a porous medium can transmit a liquid under a potential gradient.

Q

R

runoff That part of the precipitation that appears in streams. It is the same as streamflow unaffected by diversions, storage, or other works of man in or on the stream channels.

S

secondary openings Voids produced in rocks subsequent to their formation by solution, weathering, or breaks in the rocks.

secondary permeability The increase or decrease in permeability in the soil or rock caused by fracturing, solution or cementation.

shallow and deep oil and gas wells This report uses the Pennsylvania Geological Survey definition of shallow and deep oil or gas well: oil and gas wells are classified as shallow or deep, not depending on depth, but on whether or not the Upper-Middle Devonian boundary was penetrated in the well. Wells that penetrate the boundary (normally the top of the Middle Devonian Tully Limestone, but may be an equivalent shale) are considered deep. Wells that do not penetrate the boundary are considered shallow, regardless of depth. Because of the wedge-shaped character of the sedimentary package deposited in the Appalachian basin, absolute drilling depth is not instrumental. A well in the Lower Silurian Medina Group in Erie County along the lake shore may be only 2,500 ft deep, and a well in the Upper Devonian Bradford group in Clearfield County may be as much as 4,000 ft deep. Yet, the well in the Medina is considered deep and the well, in the Bradford is considered shallow on the basis of geologic age. Shallow wells, which account for the greatest number of wells drilled in Pennsylvania, may produce oil or gas; deep wells most commonly produce gas, but there are some wells in Erie and Crawford Counties that produce small amounts of oil as well (Harper, 1984).

specific capacity The well yield divided by the drawdown (pumping water level minus static water level) necessary to produce this yield. It is usually expressed as gallons per minute per foot [(gal/min)/ft].

specific conductance Is a measure of the ability of a water to conduct an electrical current. It is expressed in microsiemens per centimeter at 25 degrees Celsius. Specific conductance is related to the type and concentration of ions in the solution and can be used for approximating the dissolved-solids content of the water. Commonly, the concentration of dissolved solids (in milligrams per liter) is about 65 percent of the specific conductance (in microsiemens). This relation is not constant from stream to stream, and it may vary in the same source with changes in the composition of the water.

stimulation fluids A variety of fluids used during processes designed to increase oil or gas production. Examples of stimulation fluids include concentrated acids, water, diesel fuel, crude oil, nitrogen, and carbohydrate polymer gels.

streamflow Is the discharge that occurs in a natural channel. Although the term "discharge" can be applied to the flow of a canal, the word "streamflow" uniquely describes the discharge in a surface stream course. The term "streamflow" is more general than "runoff" as streamflow may be applied to discharge whether or not it is affected by diversion or regulation.

streamflow-gaging station A particular site on a stream, canal, lake, or reservoir where systematic observations of hydrologic data are obtained.

surface casing The first string of casing to be set in a well. The length will vary in different areas from a few hundred feet to 3,000 or 4,000 ft on some wells, it is necessary to set a temporary conductor pipe that should not be confused with surface casing as described here.

T

till Dominantly unsorted and unstratified drift, generally unconsolidated, deposited directly by and underneath a glacier without subsequent reworking by meltwater, and consisting of a heterogeneous mixture of clay, silt, sand, gravel, and boulders ranging widely in size and shape.

transmissivity Transmissivity, T, is the rate at which water is transmitted through a unit width of an aquifer under a unit hydraulic gradient. It may be expressed in cubic feet per day per foot or, feet squared per day (ft^2/d).

U

unconfined aquifer An aquifer which contains the water table.

V

W

water-bearing zone A discrete interval in bedrock or unconsolidated materials producing measurable amounts of ground water. Water-well drillers commonly report water-bearing zones on water well-completion reports. Water-bearing zones in bedrock wells are mostly reported by well drillers at precise depths such as 65 ft, 115 ft, and 150 ft.

water string See intermediate casing string.

water table The upper surface of the zone of saturation.

water year October 1 through September 30 of the designated year. For example, water year 1989 starts October 1, 1988 and ends September 30, 1989.

X

Y

Z