

Ground-Water Quality in the Appalachian Plateaus, Kanawha River Basin, West Virginia

National Water-Quality Assessment Program

Water-Resources Investigations Report 99-4269

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By Charlynn J. Sheets and Mark D. Kozar

U.S. Department of the Interior U.S. Geological Survey

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National Water-Quality Assessment Program

Charleston, West Virginia

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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by waterresources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for a specific contamination problem; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing waterquality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- •Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- •Describe how water quality is changing over time.
- •Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through investigations of 59 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 59 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.

Robert M. Hirsch Chief Hydrologist

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CONVERSION FACTORS, VERTICAL DATUM AND ABBREVIATED WATER-QUALITY UNITS

Multiply	Ву	To obtain	
	Length		
inch (in.)	25.4	millimeter	
foot (ft)	0.3048	meter	
foot squared per day (ft ² /d)	0.09290	meter squared per day	
gallon per minute	0.06308	liter per second	
liter (L)	0.2642	gallon	
mile (mi)	1.609	kilometer	
milliliter (mL)	0.0610	cubic inch	
square foot (ft ²)	0.09290	square meter	
square mile (mi ²)	2.590	square kilometer	

Temperature in degrees Celsius (°C) can be converted to degrees Fahrenheit (°F), and conversely, by use of the following equations:

$${}^{o}F = (1.8 \times {}^{o}C) + 32$$
 ${}^{o}C = ({}^{o}F-32) \times 0.5555$

VERTICAL DATUM

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

ABBREVIATED WATER-QUALITY UNITS:

Chemical concentration and temperature are given in metric units. Chemical concentration is expressed in milligrams $(1x10^{-3}\text{grams})$ per liter [mg/L], micrograms $(1x10^{-6}\text{ grams})$ per liter [µg/L], picocuries $(1x10^{-12}\text{ curies})$ per liter [pCi/L], and microsiemens per centimeter at 25 degrees Celsius [µS/cm]. Bacteria is expressed in colonies per 100 milliliters [col/100 mL], and turbidity is expressed as nephelometric turbidity units [NTU].

Ground-Water Quality in the Appalachian Plateaus, Kanawha River Basin, West Virginia

By Charlynn J. Sheets and Mark D. Kozar

Abstract

Water samples collected from 30 privately-owned and small public-supply wells in the Appalachian Plateaus of the Kanawha River Basin were analyzed for a wide range of constituents, including bacteria, major ions, nutrients, trace elements, radon, pesticides, and volatile organic compounds. Concentrations of most constituents from samples analyzed did not exceed U.S. Environmental Protection Agency (USEPA) standards.

Constituents that exceeded drinking-water standards in at least one sample were total coliform bacteria, *Escherichia coli* (*E. coli*), iron, manganese, and sulfate. Total coliform bacteria were present in samples from five sites, and *E. coli* were present at only one site. USEPA secondary maximum contaminant levels (SMCLs) were exceeded for three constituents -- sulfate exceeded the SMCL of 250 mg/L (milligrams per liter) in samples from 2 of 30 wells; iron exceeded the SMCL of 300 µg/L (micrograms per liter) in samples from 12 of the wells, and manganese exceeded the SMCL of 50 µg/L in samples from 17 of the wells sampled.

None of the samples contained concentrations of nutrients that exceeded the USEPA maximum contaminant levels (MCLs) for these constituents. The maximum concentration of nitrate detected was only 4.1 mg/L, which is below the MCL of 10 mg/L. Concentrations of

nitrate in precipitation and shallow ground water are similar, potentially indicating that precipitation may be a source of nitrate in shallow ground water in the study area.

Radon concentrations exceeded the recently proposed maximum contaminant level of 300 pCi/L at 50 percent of the sites sampled. The median concentration of radon was only 290 pCi/L. Radon-222 is a naturally occurring, carcinogenic, radioactive decay product of uranium. Concentrations, however, did not exceed the alternate maximum contaminant level (AMCL) for radon of 4,000 pCi/L in any of the 30 samples.

Arsenic concentrations exceeded the proposed MCL of 5 μ g/L at 4 of the 30 sites. No samples exceeded the current MCL of 50 μ g/L.

Neither pesticides nor volatile organic compounds (VOCs) were prevalent in the study area, and the concentrations of the compounds that were detected did not exceed any USEPA MCLs. Pesticides were detected in only two of the 30 wells sampled, but four pesticides -- atrazine, carbofuran, DCPA, and deethylatrazine -- were detected in one well; molinate was detected in the other well. All of the pesticides detected were at estimated concentrations of only $0.002~\mu g/L$. Of the VOCs detected, trihalomethane compounds (THMs), which can result from chlorination of a well, were the most common. THMs were detected in 13 of the 30 wells sampled. Gasoline by-products, such as benzene, toluene, ethylben-

zene, and xylene (BTEX compounds) were detected in 10 of the 30 wells sampled. The maximum concentration of any of the VOCs detected in this study, however, was only $1.040~\mu g/L$, for the THM dichlorofluoromethane.

Water samples from 25 of the wells were analyzed for chlorofluorocarbons (CFCs) to estimate the apparent age of ground water. The analyses indicated that age of water ranged from 10 to greater than 57 years, and that the age of ground water could be correlated with the topographic setting of the wells sampled. Thus the apparent age of water in wells on hilltops was youngest (median of 13 years) and that of water in wells in valleys was oldest (median of 42 years). Water from wells on hillsides was intermediate in age (median of 29 years). These data can be used to define contributing areas to wells, corroborate or revise conceptual ground-water flow models, estimate contaminant travel times from spills to other sources such as nearby domestic or public supply wells, and to manage point and nonpoint source activities that may affect critical aquifers.

Introduction

As part of the National Water-Quality Assessment (NAWQA) Program, the U.S. Geological Survey (USGS) investigated ground-water quality in the Appalachian Plateaus Physiographic Province portion of the Kanawha River Basin in West Virginia (fig. 1). The overall goal of the NAWQA Program is to describe the status and trends in the quality of the ground- and surface-water resources of the United States and to develop an understanding of the natural and human factors that affect the quality of these resources (Hirsch and others, 1988). The NAWQA Program integrates water-quality information from local and regional scale studies to address national issues. Major components of the ground-water part of the program are to assess the quality of ground water in major ground-water regions throughout the United States and to determine the factors that affect the quality of water in these aquifer systems. This goal is achieved primarily by conducting "land-use surveys" and "study-unit surveys." Land-use surveys link the quality of shallow ground water to natural and human factors that affect the quality of water within the aquifer. Study-unit surveys assess the areal occurrence and distribution of water-quality constituents within an aquifer.

The Appalachian Plateaus Physiographic Province was chosen for investigation due to the lack of data in the region, especially with respect to organic compounds such as pesticides and volatile organic compounds (VOCs). Also, approximately 35.1% of rural home owners in the region obtain their water from wells completed in fractured bedrock aquifers throughout the region (McColloch and Kramer, 1993). The 30 wells selected for sampling were chosen randomly, by use of a computer randomization program. As a result of field inventories, wells of appropriate construction within a two mile radius of points determined by the randomization program were selected. Thus, wells selected were not chosen on the basis of particular land-use settings.

Purpose and Scope

This report describes the occurrence and distribution of water-quality constituents in ground water within the Appalachian Plateaus portion of the Kanawha River Basin. Thirty wells were sampled within the region for the following constituents: bacteria, major ions, trace elements, nutrients, selected radioactive elements, pesticides, volatile organic compounds, and dissolved organic carbon. Analyses of water-quality data were used to determine the prevalence of these constituents in ground water. Chlorofluorocarbons (CFCs) were collected to determine the ages of ground water sampled from wells. Finally, water-quality data were evaluated with respect to geochemical processes and human activities.

Description of Study Area

The Kanawha River Basin drains 8,424 mi² in West Virginia and includes 3,809 mi² drained by the New River in Virginia and North Carolina (Eychaner, 1994). The basin consists of the Appalachian Plateaus, Blue Ridge, and Valley and Ridge Physiographic Provinces. The area of the study described here is the 7,262 mi² area of the basin that lies within the Appalachian Plateaus Physiographic Province in West Virginia. The Appalachian Plateaus are characterized by relatively flat-lying but intensely eroded bedrock, which results in a mountainous terrain capped by resistant layers of bedrock with a dendritic drainage pattern (Fenneman, 1938; Fenneman and Johnson,

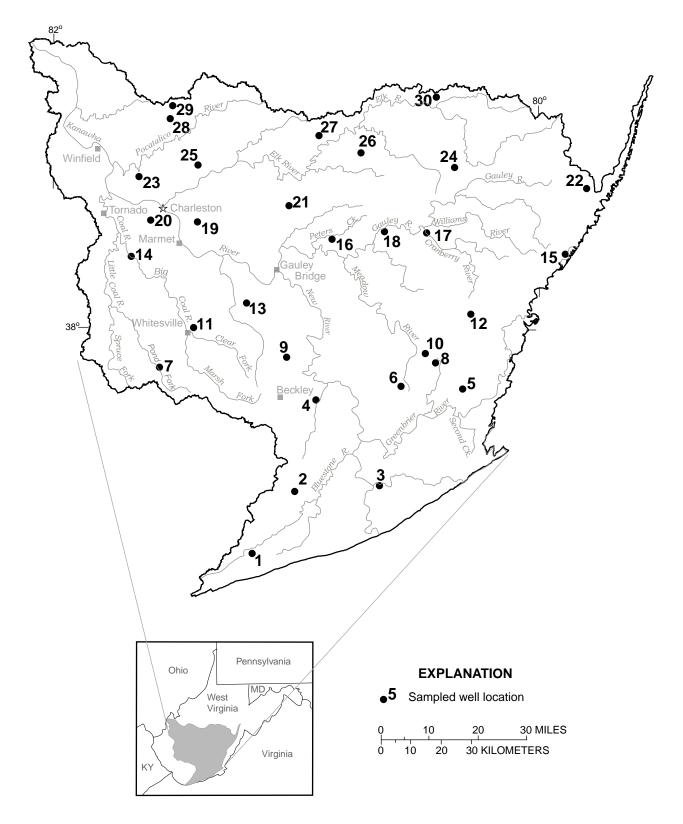


Figure 1. Location of the Appalachian Plateaus Physiographic Province within the Kanawha River Basin in West Virginia and location of wells sampled during the study.

1946). The Appalachian Plateaus portion of the basin was selected for study because of the relative lack of water-quality data (especially for organic constituents) available for characterizing water-quality conditions in the region. Also, the Potomac NAWQA conducted extensive investigations of ground-water quality in the Valley and Ridge Physiographic Province. Priority was therefore given to the Appalachian Plateaus portion of the basin.

Land-use data were collected in the early 1970's to characterize land use and land cover in West Virginia. The dominant land use in the study area is deciduous forest, which covers 60 percent of the land. Mixed forest, which consists of evergreen and deciduous trees, covers 24 percent of the study area. Cropland and pastures cover 10 percent of the study area, and urban or residential areas cover almost 2 percent. Strip mines, quarries, and gravel pits cover only 1 percent of the study area (U.S. Geological Survey, 1990).

Sampling and Analytical Methods

Ground-water samples were collected in May and June, 1997, from 30 wells (fig. 1). The wells selected for sampling were relatively new (less than 25 years old), of good construction (casings were not deteriorated or corroded), and distant from any known significant sources of contamination. The wells had reported yields of at least 5 gallons per minute (gpm), and adequate plumbing, pitless adaptors, and a clean spigot for sample collection. The sampling point was located as close to the well as possible, prior to any watertreatment systems or softeners, to avoid potential contamination (Lapham and others, 1995). Water levels were monitored throughout the purging and sampling process. Of the 30 wells sampled, seven are small public-supply wells, and the other 23 are privately owned household wells. All of the wells are drilled in fractured bedrock and have short casings. The median depth is 119 ft, and the median depth to water is 40 ft. All the wells sampled contained a submersible pump; were pumped to remove standing water, and then sampled according to USGS NAWQA protocols (Koterba and others, 1995). Quality-assurance and quality-control guidelines and protocols (Koterba and others, 1995) were followed to provide representative and accurate water-quality data and to assess sampling and analytical variability.

Field measurements of specific conductance, pH, turbidity, dissolved oxygen, oxidation-reduction potential, and water temperature were made at the time

of sampling. Samples for fecal and total coliform bacteria, Escherichia coli, and alkalinity (carbonate and bicarbonate) were analyzed on site. All samples for bacteria analysis were collected and analyzed according to standard USGS protocols -- mFC agar for fecal coliform, mEndo agar for total coliform, and NA-MUG agar for Escherichia coli (U. S. Geological Survey, 1997). Samples were analyzed for major ions, nutrients, trace elements, radon-222, uranium, pesticides, and VOCs at the USGS National Water-Quality Laboratory in Arvada, Colorado. To determine the relative age of ground water in the study area, 25 of the 30 sites were sampled for chlorofluorocarbons (CFCs). CFC analyses were completed by the USGS CFC laboratory in Reston, Va. Samples for CFC analysis were collected and analyzed according to standard guidelines and protocols (Busenberg and Plummer, 1998).

In addition to the collection of environmental samples, quality-assurance samples were also collected. Blanks were collected three times during sample collection for trace elements, common ions, nutrients, pesticides, volatile organic compounds, and dissolved organic carbon. Most constituents were not detected in the blanks. Trace-element blanks, however, had 1 detection of calcium (0.006 mg/L), chromium $(0.28 \mu g/L)$, and zinc $(1.8 \mu g/L)$. Aluminum was detected in all three blanks and was reported at concentrations close to the minimum reporting level. The range of aluminum concentrations detected in the blanks was 1.8 µg/L - 2.5 µg/L. Common ions had low level detections of dissolved solids, silica, and iron (2 mg/L, 0.017 mg/L, and 3.7 μg/L, respectively). Of the six nutrient compounds analyzed, two were detected in the blank samples. Ammonia was detected at a concentration of 0.022 mg/L, and nitrate was detected at a concentration of 0.054 mg/L.

There were no detections of pesticides in any of the blank samples analyzed. Of the 86 VOCs analyzed, three compounds were detected in both blank and environmental samples. Chloroform (0.01 $\mu g/L$), carbon disulfide (0.004 $\mu g/L$), and m-p- xylene (0.010 $\mu g/L$) were each detected in one of the three blank samples; these concentrations are much less than the respective reporting levels of 0.050, 0.080, and 0.064 $\mu g/L$ (table 1). Dissolved organic carbon was detected in the three blank samples at concentrations similar to concentrations in the environmental samples. The detections ranged from 0.1 mg/L - 0.2 mg/L.

Table 1. Volatile organic compounds detected in quality-assurance blank samples collected in the Appalachian Plateaus portion of the Kanawha River Basin, West Virginia

Volatile organic compound	Non-detect value	Units of measurement	Number of detections	Maximum concentration
Chloroform	0.050	μg/L	1	E0.010
Carbon-disulfide	0.050	$\mu g/L$	1	E0.004
l- and p-xylene	0.050	$\mu g/L$	1	E0.010

Quality-control samples were collected to quantify measurement bias and variability associated with the data-collection process (Koterba and others, 1995). Spikes and replicates were also collected as quality-control samples. A VOC and pesticide spike were collected, as well as two radon replicates. The spike recovery concentrations for the VOCs, pesticides, and radon replicates were all considered normal. Although there were a few low level detections of DOC and aluminum at concentrations near the minimum reporting level, the quality-assurance data do not indicate problems with any data except possibly for chloroform, which is a common laboratory and environmental contaminant.

Acknowledgments

The authors wish to thank the residents of West Virginia who allowed the USGS access to their properties for the collection of water samples and water-level measurements. This study could not have been completed without their cooperation.

Geohydrologic Setting

The streams in the Appalachian Plateaus flow in a dendritic drainage pattern and have eroded the flatlying sedimentary rocks into steep, sloping hills and narrow valleys and ridges. Ground water flows near the surface and moves through a series of fractures composed of joints, faults, and bedding planes. This section describes the geologic strata, a conceptual model of ground-water flow, ground-water age, and the depth of circulation.

Geohydrologic Framework

The Appalachian Plateaus consists of rugged, deeply incised mountainous terrain with uplifted plateaus capped by resistant layers of sandstone with shale (Fenneman, 1938; Fenneman and Johnson, 1946; and U.S. Geological Survey, 1970). This part of the Plateaus has moderate to high relief (300 to 1,000 ft) marked by deep, V-shaped valleys (Berg and others, 1989).

The generalized hydrogeologic framework of the Kanawha River Basin in West Virginia (fig. 2) is based on a stratigraphic succession of Mississippian, Pennsylvanian, and Permian age clastic rocks forming the predominate outcropping units in West Virginia (Schneider and others, 1965, sheet 3). The Pennsylvanian and Permian age units consist of sandstone, conglomerate, siltstone, shale, coal, limestone, and dolomite. The thickness of the stratigraphic column ranges from 3,000 to 3,800 ft in West Virginia and contains more than 68 separate coal seams (Ehlke and others, 1982). Structurally, the bedrock is almost horizontal to slightly folded with fractures and joints, and has a regional dip to the northwest. The Pennsylvanian and Permian clastic rocks are commonly overlain by a thin layer of regolith. Mississippian age strata in the study area consist primarily of sandstone and shale with a few thin limestone layers. The massive Mississippian age limestones of the Greenbrier Group also crop out within the study area.

Ground-water flow in the Appalachian Plateaus is affected by geology and weathering processes. Topography, lithology, and structural geology control the occurrence, movement, storage, and flow of ground water and also affect ground-water quality. Ground-water flowpaths are short and confined to two principal aquifer systems: unconsolidated alluvial aquifers, composed of sand, silt, clay, and gravel; and

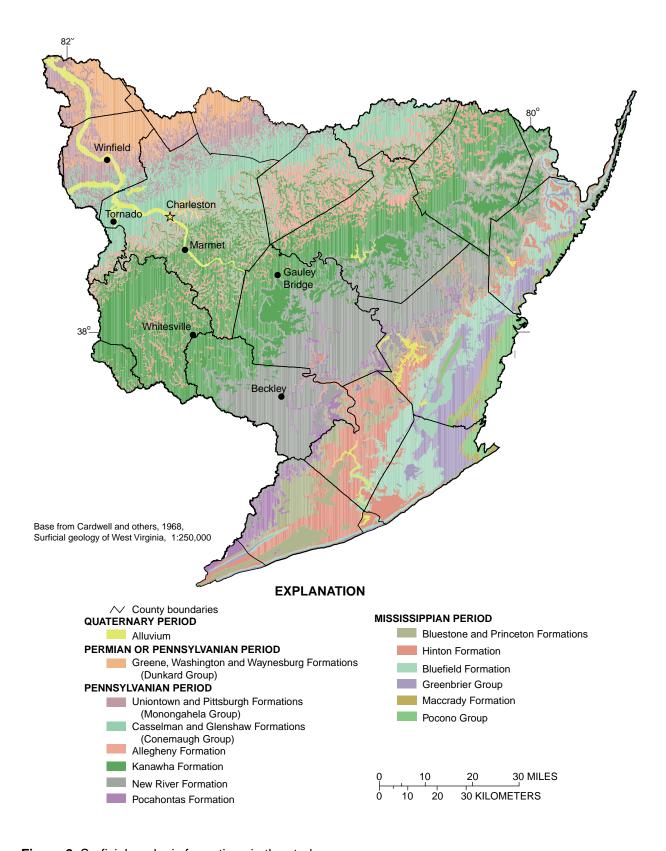


Figure 2. Surficial geologic formations in the study area.

fractured bedrock aquifers, composed of sedimentary rocks (Puente, 1984). The major-ion chemistry, pH, and hardness of ground water varies with the mineralogy of the sandstone, shale, coal, limestone and other bedrock which constitute the fractured bedrock aquifers of the region.

Bedrock aquifers generally occur in Pennsylvanian and Permian age sedimentary rocks (fig. 2). Upper and Lower Pennsylvanian age formations have nearly horizontal layers of sandstone, siltstone, shale, limestone, and coal (Puente, 1984). Ground water flows primarily through fractures or bedding-plane separations. Locally, the regolith (weathered surficial material) is thin with low permeability, allowing little ground-water storage. Secondary permeability is due to joint and stress-release fractures. Intergranular porosity has been significantly reduced by calcium carbonate or silica cementation (Wyrick and Borchers, 1981).

Regionally, coal deposits accompany Pennsylvanian to Lower Permian clastic rocks of the Appalachian Plateaus (fig. 2). The Lower Pennsylvanian Pocahontas, New River, and Kanawha Formations generally contain less pyrite and sulfur than coal-bearing rocks in the Upper Pennsylvanian Allegheny Formation, Conemaugh, and Monongahela Groups and Permian Dunkard Group (Watts and others, 1994). The boundary between the high and low sulfur coal regions, referred to as the "hinge line," trends northeast to southwest from Tucker County, through Charleston to Wayne County, West Virginia and into Kentucky (Keystone Coal Industry Manual, 1994). Coal from the southern coal fields contains low total sulfur (less than 1.5 percent), although the sulfur content of coal can vary significantly within a single mine. Most of the wells sampled as part of this study are south of the hinge line, in or adjacent to the southern coal fields.

Conceptual Model of Ground-Water Flow

Ground-water flow in the Appalachian Plateaus is not fully understood, but two conceptual models have been formulated (Wyrick and Borchers, 1981; Harlow and LeCain, 1993). The models vary somewhat in their representation of ground-water flow in the region. According to the first model, ground water in the Appalachian Plateaus flows primarily in bedding-plane separations beneath valley floors and in nearly vertical and horizontal slump fractures along valley walls (Wyrick and Borchers, 1981). The fractures are

formed primarily from the release of overburden stress, which results from isostatic rebound. As valleys are formed by erosion, the unloading of compressional stress, known as "stress relief," results in upward arching of rocks near the center of the valley, causing enlargement of bedding-plane separations that can increase secondary permeability. Stress relief also causes nearly vertical and horizontal fractures and slumping of the valley walls. Ground water, therefore, flows primarily near the surface along a network of fractures in the valley and hillsides. This theory does not fully explore the possibility that ground water can flow in lower permeability bedding-plane separations, faults, or joints that are present deep beneath the surface in the core of the hillside or mountain. It assumes that ground-water flow is primarily a shallow process.

According to the second model for typical sequences of sandstone, siltstone, shale, and coal throughout the Appalachian Plateaus, transmissivity decreases with increasing depth (Harlow and LeCain, 1993). Most rocks are permeable (transmissivity greater than $0.001 \text{ ft}^2/\text{d}$) to a depth of approximately 100 ft. Coal seams, however, can be permeable at depths greater than 200 ft. Additionally, ground-water flow in coal seams is primarily horizontal because of greater hydraulic conductivity in the coal seam, rather than vertical connection with adjacent sandstone, siltstone, or shale layers. Potentiometric head measurements indicate that recharge occurs primarily in topographically high areas (ridges) and ground water flows laterally and downward through shallow fractures in the bedrock. Vertical hydraulic conductivity can be negligible, resulting in lateral ground-water flow that discharges as springs and seeps in hillsides and in valleys. Where vertical and horizontal hydraulic conductivity are variable, ground water flows through a stair-step pattern alternating among vertical joints, faults, fractures, and horizontal bedding-plane separations. Ground water flows from ridges towards valleys, but can also recharge underlying coal seams. Because overburden pressure beneath ridges can be high, hydraulic conductivity of coal seams and fractured bedrock can be relatively low in these areas. Ground-water flow patterns in the Appalachian Plateaus are most likely affected by all the processes discussed in these conceptual ground-water flow models.

To understand ground-water flow in the Appalachian Plateaus, the distinction between local and regional aquifers must also be made. Local aquifers can be and commonly are components of larger

regional aquifer systems. Ground water can flow in deep regional aquifer systems as well as in local shallow aguifers (Heath, 1983). Local fractured-bedrock aquifers of less than 0.5 to 5.0 mi² in area are common within the Appalachian Plateaus. Each small valley contains a separate disconnected aquifer that discharges ground water to a nearby stream. The ridges surrounding the valley define the lateral boundaries and the principal recharge area of the local aquifer. Depth to saline water (brines) has been used to infer the depth of aquifers containing potable fresh ground water (Foster, 1980). The depth to saline water ranges from a maximum in excess of 1,700 ft near the southwestern part of the study area to a minimum of less than 50 ft in the northwestern part of the study area. Most regional aquifers are susceptible to contamination by saline water, especially in the northwestern part of the study area, so larger regional aquifers are not typically used for domestic or public supply. The fresh and saline water interface may indicate the boundary between regional and sub-regional aquifers.

Small local aquifers, therefore, provide most of the ground water used by rural home owners and businesses. Not all the water in the local aquifers discharges to nearby streams. Some water from these small disconnected aquifers is believed to recharge deeper and larger sub-regional or regional aquifers. Smaller, local disconnected aquifers typically discharge to small headwater streams or to sub-regional aquifers, and regional aquifers discharge to larger streams or rivers. The conceptual model of groundwater flow in the Appalachian Plateaus in West Virginia is summarized in figure 3.

The ground-water-age data used to corroborate the conceptual model of ground-water flow is based on CFC data from 25 wells that range in depth from 46 to 523 ft. The ground-water-age data are considered indicative of the local ground-water flow system, but are not applicable to shallow ground water present in the unsaturated zone, the regolith, or in sub-regional or regional aquifers. Ground water in the unsaturated zone and regolith probably is younger, and water in

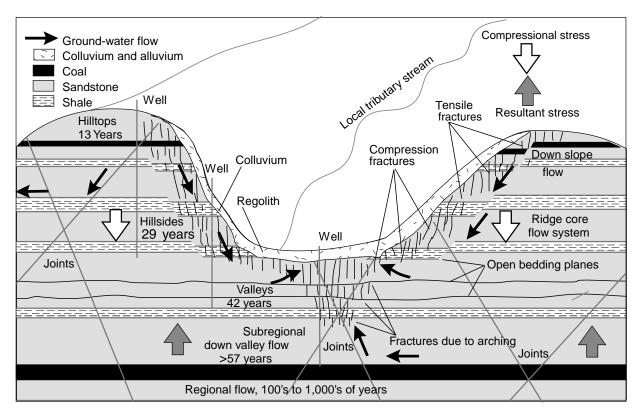


Figure 3. Revised conceptual model of ground-water flow in an Appalachian Plateaus fractured-bedrock aquifer including apparent age of ground water (Modified from Wyrick and Borchers, fig. 3.2-1, 1981 and Kozar, 1998).

regional aquifers probably is much older than the age estimates presented in this report. Further study, however, is needed to determine the age of ground water in these systems.

Ground-Water Age and Depth of Circulation

Chlorofluorocarbons (CFCs) are relatively stable, synthetic compounds that can be used for determining the age of young ground water. Chlorofluorocarbons were first manufactured and introduced to the environment in 1930, and today are used as refrigerants, aerosol propellants, cleaning agents, and solvents (Dunkle and others, 1993). The analysis of water samples for chlorofluorocarbons was used to estimate apparent ages of ground water, which is based on the time since recharge was isolated from the atmosphere. Water in fractured bedrock aquifers of the study area exists primarily in thin zones of nearly vertical stress-relief fractures, horizontal bedding planes, and coal seams. Ground water can flow both vertically and horizontally, commonly in a stair-step pattern. The age of water from 25 selected wells ranged from 10 years to greater than 57 years, with a median age of 30 years, and is much older than previously believed. Statistical analyses of available well-construction, CFC, and water-quality data show that topographic setting is the only factor that correlates with ground-water age (Kozar, 1998). Water from hilltop wells was the youngest, having a median age of 13 years. Water from hillside wells was older, with a median apparent age of 29 years. Water from valley wells was oldest, having a median apparent age in excess of 42 years (Kozar, 1998).

Estimates of circulation depth were analyzed with respect to topographic setting (Kozar, 1998). Depth of ground-water circulation was found to be greatest in valley wells (median circulation depth of 317 ft). Hilltop wells had the shallowest depths of ground-water circulation (median circulation depth of 133 ft). Hillside wells had an intermediate depth of ground-water circulation (median circulation depth of 200 ft) (Kozar, 1998). This data can be used to better define ground-water contributing areas, confirm or revise ground-water flow models, estimate contaminant travel times from spills to nearby water-supply wells, and to better manage point- and nonpoint-source activities that may affect critical aquifers.

Ground-Water Quality

The data collected from wells sampled in the Appalachian Plateaus portion of the Kanawha River Basin were used to assess the quality of water in aquifers within the study area and to assess the effects of land use on ground-water quality. These data are statistically summarized in table 2 and are described in the following sections of this report.

Bacteria

Ground-water samples were tested for fecal coliform bacteria, total coliform bacteria, and *Escherichia coli* (*E. coli*). These microorganisms are indicators of potential contamination by feces of warm-blooded animals or humans, which can introduce harmful bacteria, viruses, or other pathogens to the ground-water system. *E. coli* is a particular concern because it can cause health problems such as fever and diarrhea. Fecal coliforms were not detected in samples from any of the 30 wells sampled in the study area (table 2). Total coliforms were detected in five wells at concentrations of 1, 1, 3, 4, and 420 col/100 mL. The sample from one well contained *E. coli* at a concentration of 1 col/100 mL (Sheets and Kozar, 1997).

The absence of bacteria in the water from most of the wells sampled is probably due to a lack of fecal source material near the wells and general good condition of the wells. Most of the wells sampled were recently constructed and were generally less than 25 years old. The casings of the wells sampled were in good condition. Currently, state regulations do not require domestic wells be grouted, but do require that a concrete pad be installed around the casing at the surface (West Virginia Bureau for Public Health, 1984). Proper grouting and sealing of wells at the surface by installation of a concrete pad helps to reduce contamination of wells by retarding the transport of fecally contaminated soil or other contaminants along the annular space between the well and casing. Only 12 percent of grouted wells had bacteria present. Of the ungrouted wells, 31 percent contained indicator bacteria. These findings suggest that proper grouting and sealing of the wells can reduce bacterial contamination. Of the 30 wells sampled, 57 percent were grouted, and 43 percent of the wells were not grouted. Bacteria data from the 30 wells sampled show no significant bacteriological problems in ground water within the study area.

Table 2. Summary of water-quality data for 30 wells sampled in the study area

[μS/cm, microsiemens per centimeter; NTU, nephelometric turbidity units; mg/L, milligrams per liter; col/100mL, colonies per 100 milliliters; μg/L,micrograms per liter; pCi/L, picocuries per liter; <, less than; USEPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; MCLG, maximum contaminant level goal; PMCL, proposed maximum contaminant level; N/A, not applicable; °C, degrees Celsius; mV, millivolts; E, estimated value; #, only one site had a detection.]

Constituent	Non- detect value	Units of measurement	Percent of sites with detections	Median value	Maximum concentration	USEPA drinking-water standards: MCL ¹ , SMCL ² , MCLG ³ or PMCL ⁴	Percent of sites exceeding drinking- water standards
Field measurements							
Specific conductance	1.0	μS/cm	100	360	1,090	N/A	N/A
pH	0.1	pH units	100	7.0	8.9	$6.5 - 8.5^2$	27
Turbidity	0.01	NTU	100	1.4	500	N/A	N/A
Water temperature	0.1	°C	100	13.2	14.8	N/A	N/A
Oxidation reduction potential	N/A	mV	100	144.	910.	N/A	N/A
Dissolved oxygen	0.1	mg/L	77	0.2	8.3	N/A	N/A
Bacteria							
Total coliform	1	col/100 mL	20	<1	420	0^3	20
Escherichia coli	1	col/100 mL	3#	<1	1	0^3	3
Fecal coliform	1	col/100 mL	0	<1	<1	0^3	0
Inorganic constituents							
Major ions and constituents							
Hardness (CaCO ₃)	1	mg/L	100	82	560	N/A	N/A
Calcium (Ca)	0.02	mg/L	100	24	190	N/A	N/A
Magnesium (Mg)	0.004	mg/L	100	5.8	32	N/A	N/A
Sodium (Na)	0.1	mg/L	100	19	117	N/A	N/A
Potassium (K)	0.1	mg/L	100	1.4	4.5	N/A	N/A
Bicarbonate (HCO ₃)	1	mg/L	100	168	419	N/A	N/A
Carbonate (CO ₃)	1.0	mg/L	3#	<1	18	N/A	N/A

Ground-Water Quality

Table 2. Summary of water-quality data for 30 wells sampled in the study area —Continued

[μS/cm, microsiemens per centimeter; NTU, nephelometric turbidity units; mg/L, milligrams per liter; col/100mL, colonies per 100 milliliters; μg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; USEPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; MCLG, maximum contaminant level goal; PMCL, proposed maximum contaminant level; N/A, not applicable; °C, degrees Celsius; mV, millivolts; E, estimated value; #, only one site had a detection.]

Constituent	Non- detect value	Units of measurement	Percent of sites with detections	Median value	Maximum concentration	USEPA drinking-water standards: MCL ¹ , SMCL ² , MCLG ³ or PMCL ⁴	Percent of sites exceeding drinking- water standards
Alkalinity (CaCO ₃)	1	mg/L	100	138	344	N/A	N/A
Sulfate (SO4)	0.1	mg/L	97	8.6	410	250^{2}	7
Chloride (Cl)	0.1	mg/L	100	3.3	95	250^{2}	0
Bromide (Br)	0.010	mg/L	90	0.03	0.37	N/A	N/A
Fluoride (F)	0.1	mg/L	77	0.155	1.4	2^2	0
Silica (SiO ₂)	0.10	mg/L	100	12	21	N/A	N/A
Dissolved solids	10	mg/L	100	212	836	500^{2}	7
Nutrients							
Nitrite (NO ₂ , as N)	0.010	mg/L	7	< 0.010	0.014	1^1	0
Nitrate + nitrite (NO ₃ +NO ₂ , as N)	0.050	mg/L	37	0.025	4.09	10^{1}	0
Ammonia (NH ₄ , as N)	0.015	mg/L	73	0.109	0.96	N/A	N/A
Ammonia + organic (N)	0.20	mg/L	33	< 0.20	1.00	N/A	N/A
Phosphorus (P)	0.010	mg/L	53	0.011	0.199	N/A	N/A
Ortho-Phosphate (P)	0.010	mg/L	50	0.008	0.158	N/A	N/A
Dissolved organic carbon (C)	0.1	mg/L	93	0.35	1.80	N/A	N/A
Trace elements							
Aluminum (Al)	5	μg/L	97	3.1	20	50-200 ²	0
Antimony (Sb)	1	μg/L	0	N/A	N/A	6^{1}	0
Arsenic (As)	1	$\mu g/L$	37	<1	16	50 ¹ 5 ⁴	0 13
Barium (Ba)	1	$\mu g/L$	100	206	1,230	$2,000^{1}$	0
Beryllium (Be)	1	$\mu g/L$	0	N/A	N/A	4^{1}	0

Table 2. Summary of water-quality data for 30 wells sampled in the study area —Continued Ground-Water Quality in the Appalachian Plateaus, Kanawha RIver Basin, West Virginia

[µS/cm, microsiemens per centimeter; NTU, nephelometric turbidity units; mg/L, milligrams per liter; col/100mL, colonies per 100 milliliters; µg/L, micrograms per liter; pCi/L, picocuries per liter; <, less than; USEPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; SMCL, secondary maximum contaminant level; MCLG, maximum contaminant level goal; PMCL, proposed maximum contaminant level; N/A, not applicable; O, degrees Celsius; mV, millivolts; E, estimated value; #, only one site had a detection.]

Constituent	Non- detect value	Units of measurement	Percent of sites with detections	Median value	Maximum concentration	USEPA drinking-water standards: MCL ¹ , SMCL ² , MCLG ³ or PMCL ⁴	Percent of sites exceeding drinking- water standards
Cadmium (Cd)	1	$\mu g/L$	0	N/A	N/A	51	0
Chromium (Cr)	1	$\mu g/L$	90	2.9	6.7	100^{1}	0
Cobalt (Co)	1	$\mu g/L$	10	<1	8.9	N/A	N/A
Copper (Cu)	1	$\mu g/L$	27	<1	85	$1,000^2$	0
Iron (Fe)	3	$\mu g/L$	80	145	22,200	300^{2}	40
Lead (Pb)	1	$\mu g/L$	7	<1	1.2	0^3	7
Manganese (Mn)	1	$\mu g/L$	87	98.5	1530	50^{2}	57
Molybdenum (Mo)	1	$\mu g/L$	27	<1	55	N/A	N/A
Nickel (Ni)	1	$\mu g/L$	20	<1	17	140^{1}	0
Selenium (Se)	1	$\mu g/L$	7	<1	7	50^{1}	0
Silver (Ag)	1	$\mu g/L$	0	N/A	N/A	100^{2}	0
Zinc (Zn)	1	$\mu g/L$	73	3.2	521	$5,000^2$	0
Radioactive elements							
Radon (Rn)	80	pCi/L	80	291	2,490	300^{4}	50
Uranium (U)	1	$\mu g/L$	10	<1	3.9	N/A	N/A
Pesticides							
Atrazine	0.001	$\mu g/L$	3#	N/A	E0.002	3^1	0
Carbofuran	0.003	$\mu g/L$	3#	N/A	E0.002	40^{1}	0
DCPA	0.002	$\mu g/L$	3#	N/A	E0.002	N/A	0
Deethylatrazine	0.002	$\mu g/L$	3#	N/A	E0.002	N/A	0
Molinate	0.004	$\mu g/L$	3#	N/A	E0.002	N/A	0

Inorganic Constituents

Water samples from the 30 wells were analyzed for inorganic constituents including trace elements, major ions, nutrients, and radioactive elements. Sulfate exceeded the USEPA SMCL of 250 mg/L at two wells, and no nutrients were found in the ground water at concentrations exceeding maximum contaminant levels (MCLs). Of the trace elements, only iron and manganese typically exceeded the U.S. Environmental Protection Agency secondary maximum contaminant level (SMCL) of 50 and 300 $\mu g/L$, respectively (table 2).

Major lons and Constituents. Moderately hard water with a hardness between 61-120 mg/L as CaCO₃ was present in 43 percent of the wells sampled. Soft water (0-60 mg/L) was common in 27 percent of sampled wells, hard water (121-180 mg/L) in 17 percent of the wells, and only four wells (13 percent) had very hard water (>180 mg/L) with a maximum hardness of 560 mg/L (table 2).

Concentrations of dissolved sulfate exceeded the SMCL of 250 mg/L at only 2 (7 percent) of the 30 wells sampled (fig. 4). The maximum concentration of sulfate was 410 mg/L with a median of 8.6 mg/L. Dissolved chloride and fluoride did not exceed USEPA drinking-water standards (fig. 4). Dissolved bromide does not have a USEPA drinking-water standard. Bromide was detected at 27 of the 30 sites sampled at a maximum concentration of only 0.37 mg/L and a median of 0.033 mg/L (fig. 4). The composition of water from wells sampled in the study area was primarily a calcium or sodium bicarbonate type (fig. 5), which may suggest a sodium for calcium cation exchange process.

Nutrients. None of the samples contained concentrations of nutrients that exceeded the USEPA MCLs for these constituents. The maximum nitrate concentration detected was only 4.1 mg/L as N, which is below the MCL of 10 mg/L (fig. 6). Ammonia was detected in 73 percent of the sites sampled, and concentrations ranged from 0.031 - 0.960 mg/L as N. Phosphorus was detected in 53 percent of the sites sampled, and concentrations ranged from 0.010 - 0.199 mg/L (fig. 6).

Trace Elements. Of the trace elements analyzed, only iron and manganese exceeded USEPA SMCLs. Iron was detected in 80 percent of the sites sampled, and 40 percent of sites sampled had concentrations greater than the SMCL of 300 μ g/L (fig. 7). Manganese was detected at 87 percent of the sites, and

57 percent of the sites sampled had concentrations higher than the SMCL of 50 μ g/L (fig. 7). The drinking-water standards established for iron and manganese by the USEPA are to prevent the staining of plumbing fixtures, discoloration of water, and to eliminate questionable taste (U.S. Environmental Protection Agency, 1996). In West Virginia, concentrations of iron and manganese in ground water commonly exceeded the USEPA secondary maximum contaminant level (Ferrell, 1986). In this study area, lead was detected at only two sites, at concentrations of 1.1 μ g/L and 1.2 μ g/L, respectively. The USEPA has a maximum contaminant level goal for lead of 0 μ g/L, but an action level is set at 15 μ g/L (table 2) (U.S. Environmental Protection Agency, 1998).

On May 24, 2000, USEPA proposed changing the permissible maximum contaminant level of arsenic in public drinking-water supplies from 50 µg/L to 5µg/L. Water samples from 4 of the 30 wells in this study, or 13 percent, contained more than 5µg/L of arsenic. Arsenic concentrations of at least 1 µg/L were detected in samples from 11 of the wells (37 percent) (table 2). Arsenic in ground water commonly results from natural minerals in rock units, which can differ at a local scale. The proposed standard reflects the previously unknown potential of arsenic to cause several cancers and other diseases. Current information on arsenic regulations for public drinking-water supplies can be found at http://www.epa.gov/safewater/arsenic.html/.

Radon. Radon-222, a radioactive gas, is a naturally occurring decay product of uranium. Radon can destroy lung tissue and cause lung cancer (Otton and others, 1993). Radon gas dissolved in water can enter homes when water valves are opened, especially when showers are in use. Granitic rocks, some volcanic rocks, dark shales, sedimentary rocks that contain phosphate, and metamorphic rocks derived from these rocks can have high uranium content (Otton and others, 1993). Uranium content, grain size, permeability, and the extent of fracturing in the host rock are factors that affect the accumulation and movement of radon.

In 1999, the U.S. Environmental Protection Agency (USEPA) reinstated a proposed maximum contaminant level (PMCL) for radon in drinking water of 300 picocuries per liter (pCi/L), but an alternate maximum contaminant level (AMCL) was also proposed at a level of 4,000 pCi/L (U.S. Environmental Protection Agency, 1999). The drinking-water standard that would apply for a public water system would

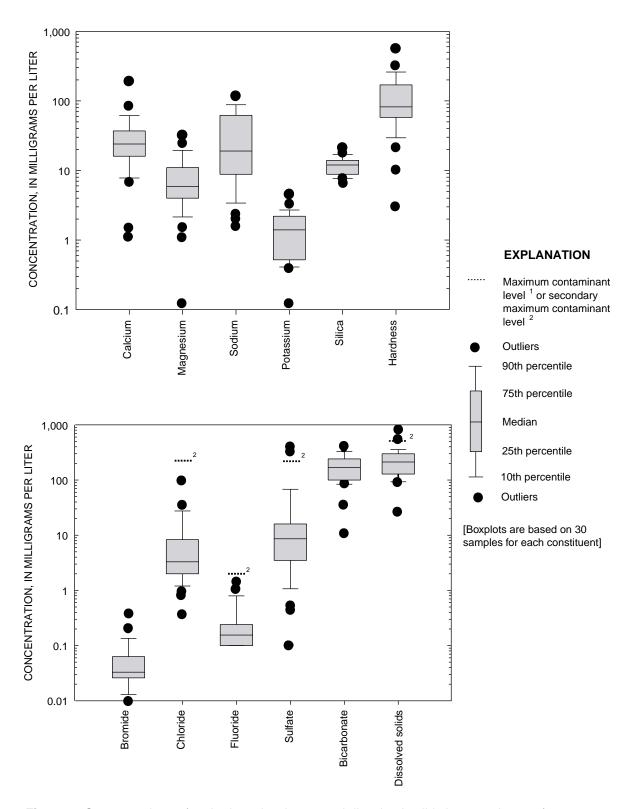


Figure 4. Concentrations of major ions, hardness, and dissolved solids in ground water from 30 wells sampled in the study area.

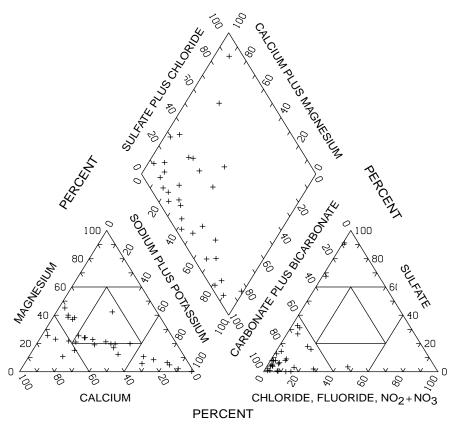


Figure 5. Diagram showing the composition of ground water in the study area.

depend on whether or not the State or public water system (PWS) develops a radon mitigation program. If a PWS serves 10,000 persons and either the State or the system has an approved radon mitigation program, then the 4,000 pCi/L AMCL would apply, otherwise the 300 pCi/L standard would apply. Radon concentrations exceeded the proposed USEPA MCL of 300 pCi/L for water in 15 of 30 (50 percent) wells sampled in the study area. The maximum concentration was 2,500 pCi/L with a median of 290 pCi/L. At six of the 30 sites, radon was not detected (Kozar and Sheets, 1997). None of the samples collected contained concentrations of radon greater than 4,000 pCi/L.

In the mid-Atlantic region, radon was sampled by the NAWQA Program in the Potomac and Lower Susquehanna River Basins of Pennsylvania, Maryland, Virginia, and West Virginia. Typically, median radon concentrations in the Kanawha-New River study area are among the lowest in the entire mid-Atlantic region. Of 267 samples collected in the mid-Atlantic region, 80 percent had concentrations greater than the 300 pCi/L PMCL, and 31 percent had concentrations greater than 1,000 pCi/L (Lindsey and Ator, 1996).

Only 50 percent of the 30 wells sampled as part of the Kanawha River Basin contained radon in concentrations greater than 300 pCi/L and, only 20 percent had concentrations greater than 1,000 pCi/L.

Organic Compounds

Water samples were also analyzed for organic constituents as part of the assessment of ground-water quality within the study area. The samples were analyzed for pesticides, volatile organic compounds (VOCs), and dissolved organic carbon (DOC). None of the pesticides or VOCs detected exceeded USEPA drinkingwater standards; however, only 2 of 5 pesticides and 11 of 16 VOCs detected have an MCL or health advisory level. Also, the effects of co-occurrence of contaminants was not addressed but should be considered when evaluating water-quality of an individual well.

Pesticides. Water samples collected from each well were analyzed for 47 pesticides (Ward and others, 1998). Five of the 47 pesticides were detected at two of the 30 sites sampled. Atrazine, carbofuran, DCPA, and deethyl atrazine were detected at estimated

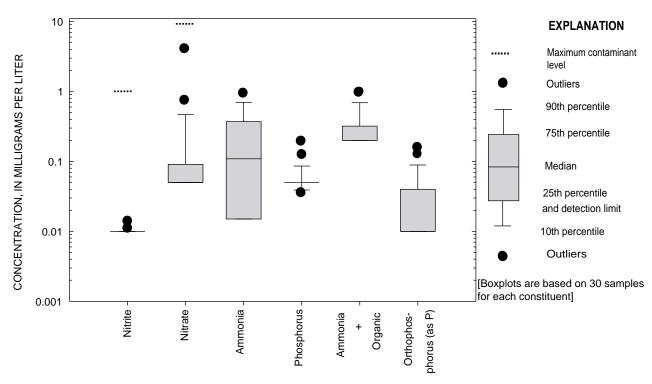


Figure 6. Concentrations of nutrients in ground water from 30 wells sampled in the study area.

concentrations of $0.002~\mu g/L$ at one site (table 2). An estimated concentration of $0.002~\mu g/L$ of molinate was detected at the second site. These concentrations are much lower than the USEPA MCLs of $3~\mu g/L$ for atrazine and $40~\mu g/L$ for carbofuran. The infrequent detection of pesticides in water from the 30 wells sampled reflects the land use within the study area. From a 1970 land-use census, only 10 percent of the land in the study area was considered cropland and pasture. Most of the study area was classified as deciduous and evergreen forest (U.S. Geological Survey, 1990), land on which pesticide usage is minimal.

Volatile Organic Compounds. Volatile organic compounds (VOCs) and dissolved organic carbon were collected at each of the 30 sites. Of 86 VOCs analyzed, 16 compounds were detected at very low concentrations (table 3). The complete suite of VOCs analyzed for this study is listed in the 1997 Water Resources Data report for West Virginia (Ward and others, 1998). At least one VOC was detected at 23 of the 30 sites. Many compounds were detected, but at concentrations below the reporting limit; thus their concentrations are shown as "estimated" in table 3. The majority of VOCs detected were components of two classes, trihalomethanes, and BTEX compounds.

Trihalomethanes (THMs) are compounds such as bromodichloromethane, bromoform, chloroform, and dibromochloromethane, which form as by-products of chlorination. THMs were detected in 11 of the 30 (37 percent) wells sampled. All were detected, however, at very low concentrations (table 3). The maximum concentration of any THM detected was for bromoform at a concentration of only 0.424 μ g/L. The maximum sum for combined THMs detected in a single well was only 1.36 μ g/L, almost 74 times lower than the combined THM MCL of 100 μ g/L.

Dissolved organic carbon (DOC) is considered a potential source of carbon for the formation of THMs. DOC concentrations measured in this study ranged from 0.1 to 1.8 mg/L, with a median of 0.35 mg/L. No correlation between dissolved organic carbon and the formation of trihalomethanes was seen in data collected for this study.

The compounds benzene, toluene, ethylbenzene, xylene (BTEX), and the fuel oxygenate methyl tert-butyl-ether (MTBE) also were commonly detected. The BTEX compounds and MTBE are common components of gasoline. The maximum detection among these compounds was methyl tert-butyl-ether at an estimated concentration of only 0.060 µg/L. BTEX

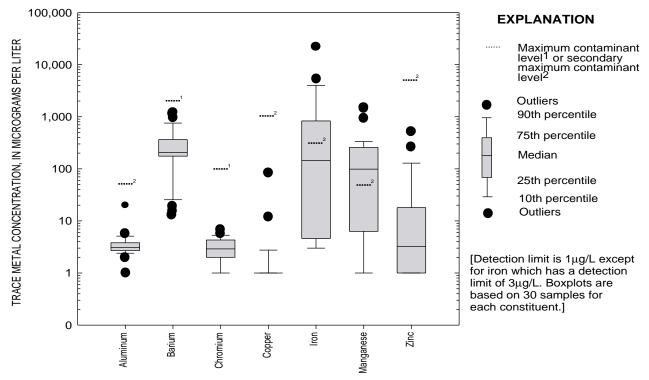


Figure 7. Concentrations of trace metals in ground water from 30 wells sampled in the study area.

compounds and MTBE were detected in 8 (27 percent) of the 30 wells sampled.

Carbon disulfide, present in 12 of the 30 (40 percent) wells sampled, was the most frequently detected VOC in the study area. It is widely used in the chemical industry in the manufacturing of flotation devices, cellophane, soil disinfectants, herbicides, grain fumigants, and as a solvent for fats, resins, phosphorus, sulfur, bromine, iodine, and rubber (Montgomery and Welkom, 1990). But concentrations of carbon disulfide were typically low; the maximum concentration was only 0.226 $\mu g/L$.

The results of VOC analyses of ground water from the Kanawha River Basin are compared to a recent NAWQA Program study of national VOC data collected nationally between 1985-1995. A reporting level of $0.2~\mu g/L$ was used to maintain consistency with national VOC data, although most concentrations for this study were quantified as being less than $0.2~\mu g/L$. Study area results are consistent with the national summary information for areas with similarly low population densities. In data from 2.542~wells in rural environments that were summarized in the national study, at least one VOC was detected in 14 percent of the wells. The Kanawha River Basin has a

low population density and is considered a rural area. At least one VOC was detected at 10 percent of the wells sampled, which is comparable to the national data. Nationally, sites with two or more VOC detections were detected in 6 percent of the samples. Two or more VOCs were detected at only 3 percent of the sites sampled in the Kanawha River study area. Only 1.5 percent of the sites in the national summary exceeded drinking-water criteria; none of the samples collected in the study area exceeded drinking-water criteria (Paul Squillace and others, U.S. Geological Survey, written commun. 1999).

Factors Affecting Water Quality

The quality of ground water in the Appalachian Plateaus portion of the study area is affected by a combination of geochemical and anthropogenic factors. Geochemical factors, the distribution and amount of chemical elements in minerals, ore, rock, soil, and the atmosphere, affect water quality in the hydrologic cycle as the chemical elements react with ground water. The most common geochemical processes occur as ground water comes in contact with rocks and dissolution of minerals takes place.

Table 3. Detections of volatile organic compounds in water samples collected from 30 wells sampled in the study area

[µg/L, micrograms per liter; E, estimated value; MCL, Maximum Contaminant Level; HAL, Health Advisory Level; n=number of wells sampled.]

Constituent	Number of sites with detections n=30	Detection limit (μg/L)	Maximum concentration detected (μg/L)	Drinking-water criteria	Median concentration detected in rural ground water nationwide n=2542 (µg/L)
1,4 Dichlorobenzene	1	0.050	E0.004	75 MCL	1.3
Benzene	6	0.050	E0.050	5 MCL	0.7
Bromodichloromethane	2	0.100	E0.070	100 MCL	0.5
Bromoform	1	0.200	0.424	100 MCL	0.4
Carbon disulfide	12	0.080	0.226		
Chloroform	7	0.052	0.248	100 MCL	0.5
Chloromethane	3	0.254	E0.060	3 HAL	0.35
Dibromochloromethane	1	0.182	0.142		0.4
Dichlorodifluoromethane	3	0.200	1.04	100 HAL	0.5
m- and p-xylene	1	0.064	E0.030	10,000 MCL	0.65
Methyl iodide	1	0.076	E0.010		
Ortho xylene	1	0.064	E0.010	10,000 MCL	0.65
Methyl tert-butyl-ether	1	0.112	E0.060		0.5
Tetrahydrofuran	1	5.0	E0.4		
Toluene	2	0.050	E0.010	1,000 MCL	0.3
Trichlorofluoromethane	1	0.100	E0.030	2,000 HAL	0.3

These processes include pyrite oxidation, resulting in sulfate production; radioactive decay of uranium and its daughter products, causing radon in ground waters; reduction of iron and manganese oxyhydroxide minerals, and dissolution of carbonate rock within bedrock aquifers, creating high concentrations of iron, manganese, and alkalinity in ground water. Anthropogenic factors include acid deposition, which results in a lower pH and conductivity of ground water on hill-tops; use of organic chemicals, fertilizers, manure, and pesticides for agriculture, which can introduce fecal bacteria, nitrate, ammonia, and pesticide contamination into the ground water; and septic-system effluent discharge to ground-water reservoirs, which also may result in bacterial contamination of aquifers.

Geochemical Factors

Water is sometimes referred to as the universal solvent because it has the ability to dissolve almost anything that it contacts. The presence of dissolved substances in ground water is affected by the chemical composition of precipitation, by biological and chemical reactions occurring in the soil zone, and by the mineral composition of the bedrock (Heath, 1983). Because of differences in these factors, ground water contains varying amounts of dissolved solids.

Hardness is primarily due to dissolved calcium and magnesium ions in ground water that are derived from weathering and dissolution of minerals in rock such as limestone, dolomite, and gypsum (Heath, 1983). Most ground water in the study area (43 percent of the sites sampled) is classified on a water hardness scale (table 2) as moderately hard (61-120 mg/L as

 $CaCO_3$). Of the remaining wells sampled, 27 percent had soft water (0-60 mg/L), 17 percent had hard water (121-180 mg/L), and only 13 percent had very hard water (greater than 180 mg/L).

In inland areas, sodium and chloride may be derived from brines, seawater trapped in sediments at the time of deposition. Dissolved calcium and magnesium can exchange for sodium in aquifers close to brines (Heath, 1983). Water with high concentrations of sodium and chloride tastes salty, increases the corrosiveness of water, and can affect people with cardiac difficulties and hypertension.

Cation and anion concentrations were converted to milliequivalents per liter and used to identify water types present in the study area. These water types include: calcium bicarbonate, calcium sulfate, sodium bicarbonate, and magnesium bicarbonate. Water type was compared to topographic setting of the well (table 4). Wells in valleys primarily had a sodium bicarbonate water. Water from wells on hillsides and hilltops was primarily a calcium bicarbonate type. The dominance of sodium bicarbonate waters in valley settings and calcium bicarbonate water on hillsides and hilltops suggests that cation exchange is occurring between calcium from calcium-rich recharge water and sodium present at shallow depths in brines beneath valleys.

The topographic setting of each well was compared to the calcium/sodium ratio of the water (fig. 8). The water in valley wells has a lower calcium/sodium ratio (higher sodium content) than water in hilltop and hillside wells, possibly indicating cation exchange processes are occurring in valley settings. Because of their topographic location, valley wells are closer to underlying connate brines, allowing for an easier exchange of calcium for sodium. As ground water infiltrates down hillsides into valleys it has an increas-

ingly longer contact time with the rocks and soils, which allows minerals to be dissolved. Water in hill-side wells has high calcium concentrations and high calcium to sodium ratios. Probably no cation exchange between calcium and sodium takes place on hillsides. Calcium is most likely being dissolved from the calcium-carbonate cement and minerals in the rocks as the ground water travels through the fractures, bedding-plane separations, and joints in the bedrock. Hill-top wells have a higher ratio of calcium to sodium (lower sodium content) than valley wells. Like hillside wells, there most likely is no cation exchange occurring in hilltop wells.

Precipitation is most likely a minor source of dissolved minerals in hilltop wells. The conductivity of rain water is usually low, with a median of only 22 uS/cm (table 5). Although calcium, magnesium, sodium, and potassium concentrations in precipitation are low, they may, to varying degrees and primarily in hilltop settings, affect ground-water quality (National Atmospheric Deposition Program, 1999). Median concentrations of ammonia and nitrate in precipitation are actually higher than those in ground water, indicating that precipitation may be a major source of these constituents in shallow recharge. Sulfate concentrations in precipitation, although not as high as those found in ground water, are significant enough to consider precipitation as a major source of sulfate in shallow ground water.

Anthropogenic Factors

Human activities can affect ground-water quality in an area. Nitrate is a common contaminant in ground water. Nitrate is a primary form of nitrogen and commonly is derived from human sewage, animal wastes, and fertilizers. Rainfall, however, can be a significant

lable 4. Water type with respect to	o topographic setting to	or 30 wells sampled in the
study area		

Topographic setting	Calcium bicarbonate number of sites (%)	Calcium sulfate number of sites (%)	Sodium bicarbonate number of sites (%)	Magnesium bicarbonate number of sites (%)
Hilltop	3 (10)	0 (0)	0 (0)	1 (3)
Hillside	7 (23)	1 (3)	3 (10)	0 (0)
Valley	5 (17)	1 (3)	9 (30)	0 (0)

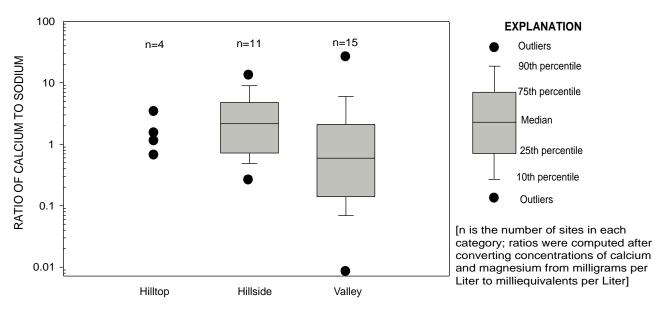


Figure 8. Ratio of calcium to sodium in ground water compared to topographic setting for 30 wells sampled in the study area.

source of nitrate in ground water (Kozar, 1996). The median concentration of nitrate in precipitation sampled during the past 10 years by the National Atmospheric Deposition Program Monitoring Station at Babcock State Park north of Beckley, West Virginia, is about six times greater than median concentrations typical of water in wells in hilltop settings and 26 times greater than median concentrations typical of water in wells in hillside and valley settings within the study area (table 5).

Low-level concentrations of nutrients in ground water could be due to atmospheric deposition (acid rain) of airborne nitrogen compounds emitted by industry and automobiles. Once nitrate dissolves into the water, it easily passes through soil and can persist for decades, accumulating to high concentrations in ground water (Nolan and others, 1998). Ingesting water with high concentrations of nitrate (greater than 10 mg/L) is not hazardous to adults, but may be fatal to infants by lowering oxygen levels in their blood, a condition known as methemoglobinemia, or "blue baby" syndrome (Nolan and Ruddy, 1996).

Of the 47 pesticides analyzed for in water samples from the 30 wells, only five were detected, but at concentrations below the analytical method reporting level. Atrazine, carbofuran, DCPA, and deethyl atrazine, a degradation by-product of atrazine, were detected in one well; molinate was detected in another well. Nationwide, as part of NAWQA investigations, atrazine was detected more frequently than any other

pesticide. This widespread detection could be due to the slow rate of atrazine transformation in the environment (Kolpin and others, 1998). Since the early 1970's, atrazine has been the most extensively used herbicide across the country. Carbofuran enters ground water from the leaching of soil fumigants used on corn, potatoes, alfalfa, rice, sorghum and other crops (Wangsness and Gilliom, 1997). Carbofuran can cause problems with blood and the nervous system and can cause reproductive difficulties (U.S. Environmental Protection Agency, 1998). Based on a nationwide data base of 2,600 ground-water wells sampled, carbofuran was detected only 17 times, at concentrations ranging from less than 0.003 to 2.8 µg/L (Wangsness and Gilliom, 1997). In the study area, carbofuran was detected in only one sample at a concentration of 0.002 µg/L. The virtual absence of pesticides detected in the thirty wells sampled reflects minimal pesticide use within the study area.

VOCs were more commonly detected than pesticides. Most of the VOCs detected were components of two classes: trihalomethanes and BTEX compounds (benzene, toluene, ethylbenzene, and xylene). Trihalomethanes form as by-products of disinfection (chlorination). Disinfection of rural domestic wells by addition of bleach (sodium hypochlorite) is a common practice and may be a potential process for production of THMs within the study area. BTEX compounds, as well as the fuel additive MTBE (methyl tert-butyl ether), are all common components of gasoline.

Factors Affecting Water Quality

Table 5. Statistical summary of concentrations of selected chemical constituents in 30 wells sampled in the study area and in precipitation from Babcock State Park, West Virginia

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

	pН	Specific Conductance (µS/cm)	Calcium (mg/L)	Magnesium (mg/L)	Potassium (mg/L)	Sodium (mg/L)	Ammonia (mg/L)	Nitrate (mg/L)	Chloride (mg/L)	Sulfate (mg/L)
				Hi	iltop wells - 4 wel	ls				
Median	6.9	297.	30.	9.4	0.67	13.	0.026	0.21	2.6	8.1
Maximum	7.7	445.	46.	18.	2.8	25.	0.050	0.56	3.1	15.
Minimum	5.4	31.	1.5	1.5	0.41	2.0	0.015	0.05	0.79	2.8
				Hil	lside wells - 11 we	lls				
Median	6.8	369.	32.	7.7	1.40	14.	0.050	0.05	2.3	10.
Maximum	7.7	752.	85.	32.	4.5	70.	0.920	4.09	95.	330.
Minimum	5.5	156.	16.	3.7	0.42	2.3	0.015	0.05	0.37	3.5
				Va	lley wells - 15 wel	ls				
Median	7.0	347.	20.	4.8	1.70	36.	0.14	0.05	5.1	5.1
Maximum	8.9	1,090.	190.	18.	2.6	117.	0.96	0.22	28.	410.
Minimum	6.3	169.	1.1	0.12	0.12	1.6	0.015	0.05	1.6	0.1
				Prec	ipitation (1988-19	97)				
Median	4.4	22.	0.09	0.014	0.021	0.048	0.20	1.28	0.11	1.83
Maximum	4.5	26.	0.13	0.023	0.047	0.064	0.23	1.44	0.13	2.48
Minimum	4.3	17.	0.07	0.010	0.014	0.037	0.11	1.07	0.08	1.36

These compounds may be responsible for minor, local ground-water contamination. Whether the BTEX compounds are entering ground water in precipitation or as a result of spills near the well head is not known. No VOCs, including the THM and BTEX compounds, were found in concentrations that exceeded USEPA drinking-water standards. MTBE and chloroform are two VOCs that were frequently detected in a recent national aggregation of NAWQA VOC data. (Paul Squillace and others, written commun., 1999). MTBE was detected at one site within the study area at an estimated concentration of 0.60 µg/L. Point sources that contribute MTBE to ground water are leaking underground gasoline storage tanks and gasoline spills on land. MTBE, however, also has been detected in precipitation. Once MTBE enters ground water, it is more resistant to decay than other gasoline components, such as benzene (Snow and Zogorski, 1995). MTBE is not required to be added to gasoline in West Virginia; therefore, it is infrequently detected in ground water within the study area.

Relation Between Precipitation and Ground Water

Nitrogen, although present in rocks in trace amounts, may also be derived from atmospheric sources and from human activities. Sources of nitrogen include production and use of synthetic fertilizers, septic systems, and nitrogenous organic waste from farm animals. The combustion of fossil fuels in gasoline and diesel engines releases nitrogen oxides into the atmosphere. In the atmosphere, chemical processes alter the nitrogen oxides into nitrate and nitric acid (Hem, 1992). These processes can lower the pH in precipitation, which eventually recharges the ground water. Water from wells located on hilltops have higher nitrate concentrations than ground water from wells in hillside and valley settings (fig. 9).

Rainfall analysis can provide an understanding of precipitation's effect on ground-water quality. Chemical data for precipitation samples collected at Babcock State Park were used to compare nitrate and other constituents in ground water to rainfall (table 5). Precipitation samples collected weekly at the park from 1988 to 1997 were analyzed for calcium, magnesium, potassium, sodium, ammonia, nitrate, chloride, sulfate, pH, and specific conductance. Precipitation at Babcock State Park has lower concentrations of these major ions, except for nitrate, than concentrations of these ions in ground water in the study area. Nitrate concen-

tration is usually much higher in precipitation than in ground water; therefore, nitrate affects ground-water quality, especially in hilltop recharge areas (fig. 9). The highest concentration of nitrate detected in either ground water or precipitation was detected in water sampled from a hillside well (fig. 9) completed in the karst Greenbrier limestone aquifer. The karst Greenbrier aquifer system is highly susceptible to contamination and is not characteristic of most wells sampled in the study area.

A comparison of chemical data for precipitation at Babcock State Park to similar data for ground water in various topographic settings in the study area shows that median concentrations of most constituents are highest in valley settings, and lowest and most similar to precipitation in hilltop settings. These data suggest that recharge from precipitation takes place primarily on hilltops and hillsides, and as ground water travels down hillsides through fractures in the bedrock and soils towards valleys, minerals are dissolved and concentrations of ions increase in ground water (table 5). This finding is supported by apparent median groundwater ages for ground water in hilltop, hillside, and valley settings of 13, 29, and 42 years, respectively.

Summary and Conclusions

The Appalachian Plateaus in the Kanawha River Basin of West Virginia were studied by the U.S. Geological Survey to determine water-quality characteristics of ground water. The Appalachian Plateaus are underlain by flat-lying, Pennsylvanian age sedimentary rocks. Ground water primarily flows down slopes to the valley through faults, joints, bedding-plane separations, and other fractures.

The results of analysis of samples for chlorofluorocarbons were used to determine the apparent age and depth of circulation of potable ground water. Statistical analysis shows that ground-water age and depths of ground-water circulation correlate with topographic setting. Hilltop wells had water with a median age of 13 years, and had the shallowest depth of circulation (median circulation depth of 133 ft). Water from hillside wells had a median age of 29 years and an intermediate circulation depth (median = 200 ft). Valley wells had the oldest water, with a median apparent age of 42 years and also had the deepest circulation depths of the three topographic settings (median = 317 ft).

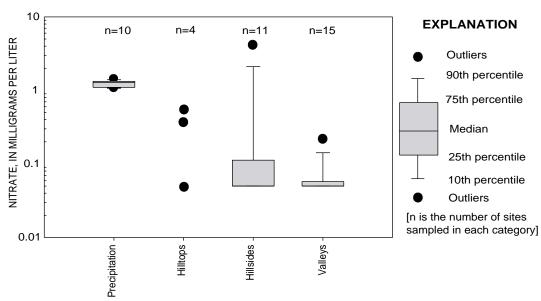


Figure 9. Nitrate concentrations in ground water sampled from 30 wells in hilltop, hillside, and valley settings compared with precipitation data from Babcock State Park, West Virginia.

Generally, ground-water quality in the study area meets U. S. Environmental Protection Agency (USEPA) maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs). Bacteria, sulfate, iron, manganese, and radon concentrations, however, exceed USEPA standards at some sites.

Bacteria were not routinely detected in ground water within the study area. Only five of the 30 sites sampled tested positive for the presence of total coliform bacteria, and only one site tested positive for *Escherichia coli* (*E. coli*). None of the sites sampled tested positive for fecal coliform bacteria. The general lack of agriculture in the study area explains the lack of bacterial contamination of ground water in the study area

Radon is another contaminant commonly found in ground water in the study area. Of the 30 sites sampled, 50 percent exceeded the proposed USEPA MCL of 300 pCi/L but none exceeded the 4,000 pCi/L proposed alternate maximum contaminant level (AMCL). The concentrations of radon are variable in the Appalachian Plateaus because of varying bedrock lithology within the region.

Arsenic is also a contaminant found in ground water. Of the 30 sites sampled, 4 samples exceeded the proposed MCL of 5 μ g/L. No samples exceeded the current MCL of 50 μ g/L.

Manganese concentrations exceeded the USEPA SMCL of $50 \mu g/L$ in 57 percent of the sites sampled and 40 percent of iron concentrations exceeded the USEPA SMCL of $300 \mu g/L$. The primary source of manganese, iron, and other dissolved constituents in ground water from the study area is minerals in the bedrock.

Precipitation is potentially a source of nitrate in ground water. Recently recharged shallow ground water located in hilltop wells has higher concentrations of nitrate than hillside or valley wells and is similar to nitrate concentrations in precipitation. Median nitrate concentrations were approximately six times higher in precipitation than in shallow ground water.

Pesticides and VOCs can enter ground water as a result of anthropogenic activities. Of 47 pesticides analyzed from 30 sites, five were detected, all at very low concentrations. Of the 30 sites sampled, only two had pesticide detections, but 23 (77 percent) had detections of at least one VOC. VOC detections were at very low concentrations or at estimated concentrations. BTEX and THMs were the most common VOCs detected. None of the pesticides or VOCs detected exceeded USEPA drinking-water standards, but only 2 of 5 pesticides and 11 of 16 VOCs detected have an MCL or health advisory level.

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