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Preliminary Assessment of Water Chemistry Related to Groundwater Flooding in Wawarsing, New York, 2009–11

Scientific Investigations Report 2012–5144

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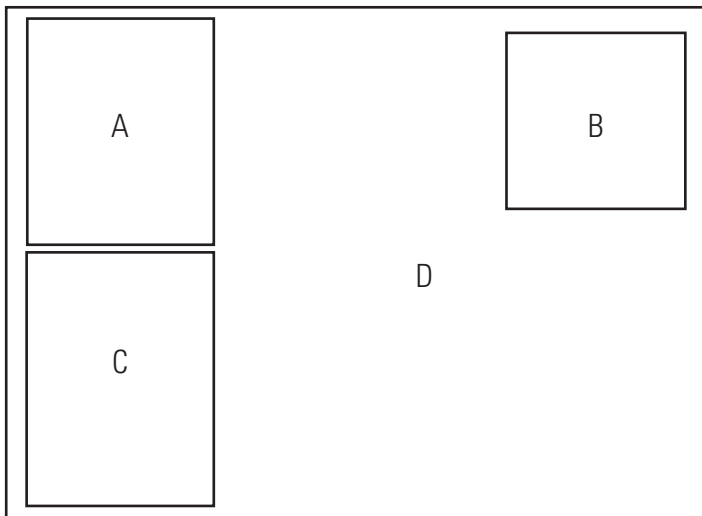
Cover. *A,* U.S. Geological Survey scientist sampling a domestic well in Wawarsing, New York. *B,* Basement flooding in Wawarsing, New York. *C,* U.S. Geological Survey scientists logging a domestic well in Wawarsing, New York. *D,* Basement pumpage discharging to a flooded street in Wawarsing, New York.

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KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

Acknowledgments

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Conversion Factors, Datum, and Abbreviations

Inch/Pound to SI

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square mile (mi^2)	2.590	square kilometer (km^2)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m^3)
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)
inch per year (in/yr)	25.4	millimeter per year (mm/yr)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
$$°F=(1.8×°C)+32$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88) or the National Geodetic Vertical Datum of 1929 (NGVD 29).

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

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

Concentrations of chemical constituents in water are given either in parts per trillion by volume (pptv), milligrams per liter (mg/L), picograms per liter (pg/L), molarity, or moles per liter (mol/L), milligrams per kilogram (mg/kg), picomoles per kilogram (pmol/kg), or femtomoles per kilogram (femtomol/kg), cubic centimeters per liter at standard temperature and pressure (cm^{3}STP/L), or picoCuries per liter (pCi/L).

Abbreviations

>	greater than
<	less than
δ	delta
E	estimated concentration
IAP/Ksp	ratio of ion activity product to solubility product coefficient
MCL	maximum contaminant levels
MRL	minimum reporting level
MVT	Mississippi Valley Type
MWL	meteoric water line
NAWQA	National Water Quality Assessment Program
NOAA	National Oceanic and Atmospheric Administration
NWQL	National Water Quality Laboratory
NWS	National Weather Service
NYC	New York City
NYCDEP	New York City Department of Environmental Protection
RWB	Rondout–West Branch
TEAP	terminal electron-accepting processes
USGS	U.S. Geological Survey
VCDT	Vienna Canyon Diablo Troilite
VOC	volatile organic compound
VPDB	Vienna Pee Dee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
Ag	silver
Ar	argon
As	arsenic
B	boron
Ba	barium
Be	beryllium
Br^-	bromide
Ca	calcium
Cd	cadmium
CH_4	methane
CFCs	chlorofluorocarbons
Co	cobalt
CO_2	carbon dioxide
Cr	chromium
Cu	copper
DIC	dissolved inorganic carbon

DO	dissolved oxygen
E. coli	*Escherichia coli*
F^-	fluoride
Fe	iron
H	hydrogen
^2H	deuterium
^3H	tritium
H_2S, HS^-	hydrogen sulfide species
He	helium
HNO_3	nitric acid
K	potassium
Li	lithium
Mb	molybdenum
Mg	magnesium
Mn	manganese
N, N_2	nitrogen
Na	sodium
NH_4^+	ammonium
Ni	nickel
NO_2^-	nitrite
NO_3^-	nitrate
O_2	oxygen
P	phosphorus
Pb	lead
PO_4^{2-}	phosphate
S	sulfur
Se	selenium
SF_6	sulfur hexafluoride
SO_4^{2-}	sulfate
SiO_2	silica
Sr	strontium
Tl	thallium
U	uranium
V	vanadium
Zn	zinc

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Abstract

Water-quality samples collected in an area prone to groundwater flooding in Wawarsing, New York, were analyzed and assessed to better understand the hydrologic system and to aid in the assessment of contributing water sources. Above average rainfall over the past decade, and the presence of a pressurized water tunnel that passes about 700 feet beneath Wawarsing, could both contribute to groundwater flooding. Water samples were collected from surface-water bodies, springs, and wells and analyzed for major and trace inorganic constituents, dissolved gases, age tracers, and stable isotopes. Distinct differences in chemistry exist between tunnel water and groundwater in unconsolidated deposits and in bedrock, and among groundwater samples collected from some bedrock wells during high head pressure and low head pressure of the Rondout–West Branch Tunnel. Samples from bedrock wells generally had relatively higher concentrations of sulfate (SO_4^{2-}), strontium (Sr), barium (Ba), and lower concentrations of calcium (Ca) and bicarbonate (HCO_3^-), as compared to unconsolidated wells. Differences in stable-isotope ratios among oxygen-18 to oxygen-16 ($\delta^{18}O$), hydrogen-2 to hydrogen-1 (δ^2H), sulfur-34 to sulfur-32 ($\delta^{34}S$) of SO_4^{2-}, Sr-87 to Sr-86 ($^{87}Sr/^{86}Sr$), and C-13 to C-12 ($\delta^{13}C$) of dissolved inorganic carbon (DIC) indicate a potential for distinguishing water in the Delaware–West Branch Tunnel from native groundwater. For example, $^{87}Sr/^{86}Sr$ ratios were more depleted in groundwater samples from most bedrock wells, as compared to samples from surface-water sources, springs, and wells screened in unconsolidated deposits in the study area.

Age-tracer data provided useful information on pathways of the groundwater-flow system, but were limited by inherent problems with dissolved gases in bedrock wells. The sulfur hexafluoride (SF_6) and (or) chlorofluorocarbons (CFCs) apparent recharge years of most water samples from wells screened in unconsolidated deposits and springs ranged from 2003 to 2010 (current) and indicate short flow paths from the point of groundwater recharge. All but three of the samples from bedrock wells had interference problems with dissolved gases, mainly caused by excess air from degassing of hydrogen sulfide and methane. The SF_6 and (or) CFC apparent recharge years of samples from three of the bedrock

wells ranged from the 1940s to the early 2000s; the sample with the early 2000s recharge year was from a flowing artesian well that was chemically similar to water samples collected at the influent to the tunnel at Rondout Reservoir and the most hydraulically responsive to water tunnel pressure compared to other bedrock wells.

Data described in this report can be used, together with hydrogeologic data, to improve the understanding of source waters and groundwater-flow patterns and pathways, and to help assess the mixing of different source waters in water samples. Differences in stable isotope ratios, major and trace constituent concentrations, saturation indexes, tritium concentrations, and apparent groundwater ages will be used to estimate the proportion of water that originates from Rondout–West Branch Tunnel leakage.

Introduction

Groundwater flooding of streets and residential basements during fall 2008 in the Rondout Valley near the town of Wawarsing, Ulster County, New York, prompted the New York City Department of Environmental Protection (NYCDEP) to ask the U.S. Geological Survey (USGS) to characterize the groundwater-flow system of the area. Precipitation records indicate that above average rainfall over much of the past two decades, particularly over the past decade, has aggravated flooding problems (Stumm and others, 2012). Additionally, a segment of the Rondout–West Branch (RWB) Tunnel, which is an underground concrete-lined structure that passes about 700 feet (ft) beneath Wawarsing and carries pressurized water through from the Catskill Mountains to New York City (NYC), is leaking and also could be contributing to groundwater flooding (Stumm and others, 2012). This 44-mile (mi) long, 13.5-ft diameter water tunnel between the Rondout Reservoir and the Catskill Aqueduct carries about one-half of the NYC water supply and has a capacity of about 1.03 billion gallons per day (gal/d) (New York City Department of Environmental Protection, 2010). One of the two primary areas of leakage along the RWB Tunnel is beneath Wawarsing; during construction of the RWB Tunnel, this section of bedrock beneath the Rondout Valley was observed to be highly faulted and

weathered, had over 9,000 gallons per minute (gal/min) of inflow, and required over 20,000 bags of concrete and steel reinforcements to stabilize the bedrock. The total estimated leakage out of the RWB Tunnel is 15 to 35 million gallons per day (Mgal/d) (James Canale, New York City Department of Environmental Protection, written commun., 2011; DiNapoli, 2007). In 2003 and 2009, an autonomous underwater vehicle was used to inspect the interior of the RWB Tunnel and recorded 8,200 linear feet of cracking throughout the tunnel (James Canale, New York City Department of Environmental Protection, written commun., 2011). Most of the cracking was observed in the sections of the tunnel that are within the limestone units underlying Roseton and Wawarsing, N.Y.

Water-chemistry data were interpreted with hydrogeologic data, which are detailed in a companion report (Stumm and others, 2012), to help identify and distinguish between water sources that may contribute to the groundwater flooding observed in Wawarsing. Inorganic constituents, stable isotopes, and age tracers in groundwater and springs are useful indicators of different sources of water, including surface water or anthropogenic sources, as well as geochemical processes in different parts of the aquifer system. Water-chemistry data were interpreted with hydrogeologic data, which are detailed in a companion report (Stumm and others, 2012), to help identify and distinguish between water sources that may contribute to the groundwater flooding observed in Wawarsing.

In 2008, the USGS was tasked by the NYCDEP to characterize the hydrogeologic conditions in the Wawarsing area and investigate the possible relation between groundwater flooding and leakage from the adjacent RWB Tunnel. A companion report (Stumm and others, 2012) describes the hydrology of the Wawarsing study area. Together, the reports serve as a foundation for understanding the hydrologic system and how it is affected by precipitation and pressurized water leaking from the RWB Tunnel.

Purpose and Scope

The purposes of this report are to describe the collection and analysis of water samples and to present some general interpretation of water-chemistry data in order to better understand the hydrologic system and to aid in the assessment of sources of groundwater flooding in the town of Wawarsing, N.Y. The report presents information on the hydrogeologic setting, the occurrence and distribution of chemical constituents and characteristics, and groundwater-age estimates for groundwater samples in the study area. Hydrogeologic data from a companion report (Stumm and others, 2012) are used in this analysis. The report presented herein describes general water-chemistry characteristics, such as oxidation-reduction (redox) conditions, pH, and water types at the Rondout Reservoir inflow to the RWB Tunnel, Lippman Lake, 4 springs, and 19 wells, including 9 wells screened in unconsolidated deposits and 10 wells completed in bedrock. A description of the design of the monitoring network and methods of data collection and analysis of water-level fluctuations are included. The interpretive steps for estimating groundwater ages using atmospheric tracers are described, along with the distribution of the interpreted groundwater ages in selected wells.

The level of interpretation in this report is limited because additional information is required for a detailed assessment. Information on the geology, hydrogeology, and additional water-quality sample analysis in the study area is required to assess the sources of water in the aquifer system related to flooding.

Description of Study Area

The study area encompasses a 12-square mile (mi^2) area in Wawarsing, N.Y., that is prone to frequent groundwater flooding. A sampling site at Rondout Reservoir at Lackawack (station 01366400; fig. 1), where reservoir water enters the RWB Tunnel portion of the Delaware Aqueduct was used to represent water from the RWB Tunnel. The Rondout Valley near the town of Wawarsing, Ulster County, N.Y., is part of the Port Jervis Trough, which is a deep, glaciated valley that extends about 100 mi southwestward from Kingston through Kerhonkson, N.Y., and continues into Pennsylvania. The Port Jervis Trough separates the Shawangunk Mountains to the east from the Catskill Front (eastern side of the Catskill Mountains) to the west (Reynolds, 2007). The valley in the study area is underlain by gravel, sand, silt, and clay of Pleistocene and Holocene age (Cadwell and others, 1989) and bedrock sequences of limestone, sandstone, and shale with substantial fracturing and faulting (Dibbell, 1944).

The population of Wawarsing was 13,157, according to the 2010 U.S. Census (U.S. Census Bureau, 2010), and land use is predominantly residential. Wawarsing lies to the west of the Shawangunk Mountains, which are the north-easternmost expression of the Valley and Ridge province of the central Appalachians. Land-surface altitudes range from about 270 ft in the flood-prone area in Wawarsing to about 730 ft at the "mixing chamber" from the Rondout Reservoir to the Delaware Aqueduct (in this report, altitudes are referenced to the North American Vertical Datum of 1988, unless otherwise specified). The sampling network in Wawarsing and the Delaware Aqueduct water sampled in Lackawack are herein described as the "study area."

The study area is underlain by unconsolidated deposits of variable thickness, including Pleistocene till and stratified drift, and Holocene alluvium. Much of the stratified drift is glacial lake silt and clay, which, along with the till, impedes infiltration and groundwater flow. The surrounding bedrock highlands rise about 150 ft to the west of the valley and about 300 ft to the east.

Previous Investigations

Several studies have focused on the NYC water-supply system and, more specifically, the RWB Tunnel. Merguerian (2000) described the history of the NYC water-supply system. Stumm and others (2012) studied the hydrologic effects of temporary shutdowns of the RWB Tunnel on the groundwater-flow system in Wawarsing. A drainage study (Chadd Hodgkinson, Malcolm Pirnie, written commun., 2009) indicated that higher than average rainfall and poor drainage contributed to flooding of streets and basements in the study area.

The surficial and bedrock geology of the study area is described in several published reports. Drilling logs for wells in the study area were compiled by Frimpter (1970), who later characterized the hydrogeologic units in the study area (Frimpter, 1972). Reynolds (2007) mapped the surficial geology of the southern part of the study area and described the major unconsolidated units. Berkey (1911) described the unconsolidated deposits, bedrock geology, and possible faults within the Rondout Valley. Dibbell (1944) compiled the construction, geology, and hydrology of the RWB Tunnel within the study area. Fluhr (1950, 1953) described the results of exploration drilling by the NYCDEP in the study area.

Methods of Data Collection and Analysis

The design of the sampling network of surface water, springs, monitoring wells, and supply wells; the water-quality sampling and analyses; age dating of groundwater; methods of quality assurance; and data interpretation are described in this section.

Design of Monitoring Network

The monitoring network includes sites for water-level measurements and water-quality sampling. The water-level monitoring network is discussed in detail by Stumm and others (2012) (fig. 2, table 1); water levels were measured at 31 sites to help determine the potentiometric surface and direction of groundwater flow (Stumm and others, 2012). Most of the wells in the monitoring network are used for private or public water supply, but monitoring wells were specifically drilled in the unconsolidated deposits during 2009–10 to monitor water levels and for potential water-quality sampling (Stumm and others, 2012).

Water-quality monitoring includes surface-water sites (Rondout Reservoir, Lippman Lake), supply and monitoring wells, and springs (table 1, figs. 1 and 2). The springs include two basement sites associated with flooding (U1665 and U1666), in addition to other springs (U1667, U1668) or well points installed at springs or "spring wells" (U1632 and

U1633) in the hills to the east. The sampled wells include both monitoring and domestic and public supply wells in the unconsolidated aquifer and domestic and public supply wells in fractured bedrock.

Collection and Analysis of Water Samples

Water-quality samples were collected during conditions in which (1) basements were flooding in the Wawarsing areas and the water tunnel was under typical high-pressure conditions, (2) basements were not flooding and the water tunnel was under typical high-pressure conditions, and (3) basements were not flooding and the water tunnel was depressurized for repair work. Sites were sampled for an extensive list of constituents, including major ions and trace elements, dissolved gases, age tracers, and stable isotopes (tables 2–5). Surface-water bodies generally were not analyzed for dissolved gases, chlorofluorocarbons (CFCs), or sulfur hexafluoride (SF_6), which were used to estimate groundwater age, because they are sensitive to atmospheric interaction; however, these constituents were analyzed in some cases to provide source end members for mixing. Field characteristics, which include water temperature, pH, and specific conductance, were measured during sample collection in accordance with USGS procedures described by Koterba and others (1995).

Water was sampled according to protocols by Koterba and others (1995). Wells were purged, and field measurements of temperature, specific conductance, pH, turbidity, and dissolved oxygen (DO) concentrations were monitored until stable. Concentrations of total dissolved sulfides (H_2S plus HS^-, herein referred to as "H_2S") and low concentrations of DO (less than 1 milligram per liter (mg/L)) were measured onsite using colorimetric procedures (HACH Company, 2002). Water samples collected for analyses of major ions, trace elements, nutrients, and stable isotope ratios for $^{87}Sr/^{86}Sr$, $\delta^{34}S$ of SO_4^{2-}, and $\delta^{13}C$ of dissolved inorganic carbon (DIC) were filtered with a 0.45-micrometer (μm) inline filter. For water with low concentrations of SO_4^{2-}, samples were collected on an anion-exchange resin column (Carmody and others, 1998). Water samples for $\delta^{13}C$ of DIC analysis were collected in 40 milliliter (mL) glass vials, which were preserved with 5 to 10 milligrams (mg) of copper sulfate and sealed with a Teflon/silicon septa cap.

Water samples to be analyzed for dissolved gases were collected in 160-mL septum bottles (sealed in a large beaker under flow of evacuated well water). Dissolved gases (N_2, Ar, CO_2, CH_4, and O_2) were analyzed by gas chromatography after extraction from sample headspaces (Busenberg and others, 1998). The resulting data were used to define recharge temperatures for age dating because the solubility of atmospheric tracers varies as a function of temperature and for determining concentrations of excess air. Excess air consists of air trapped in pores that dissolves in groundwater, typically after a rapid rise in the water table. Recharge temperatures were calculated
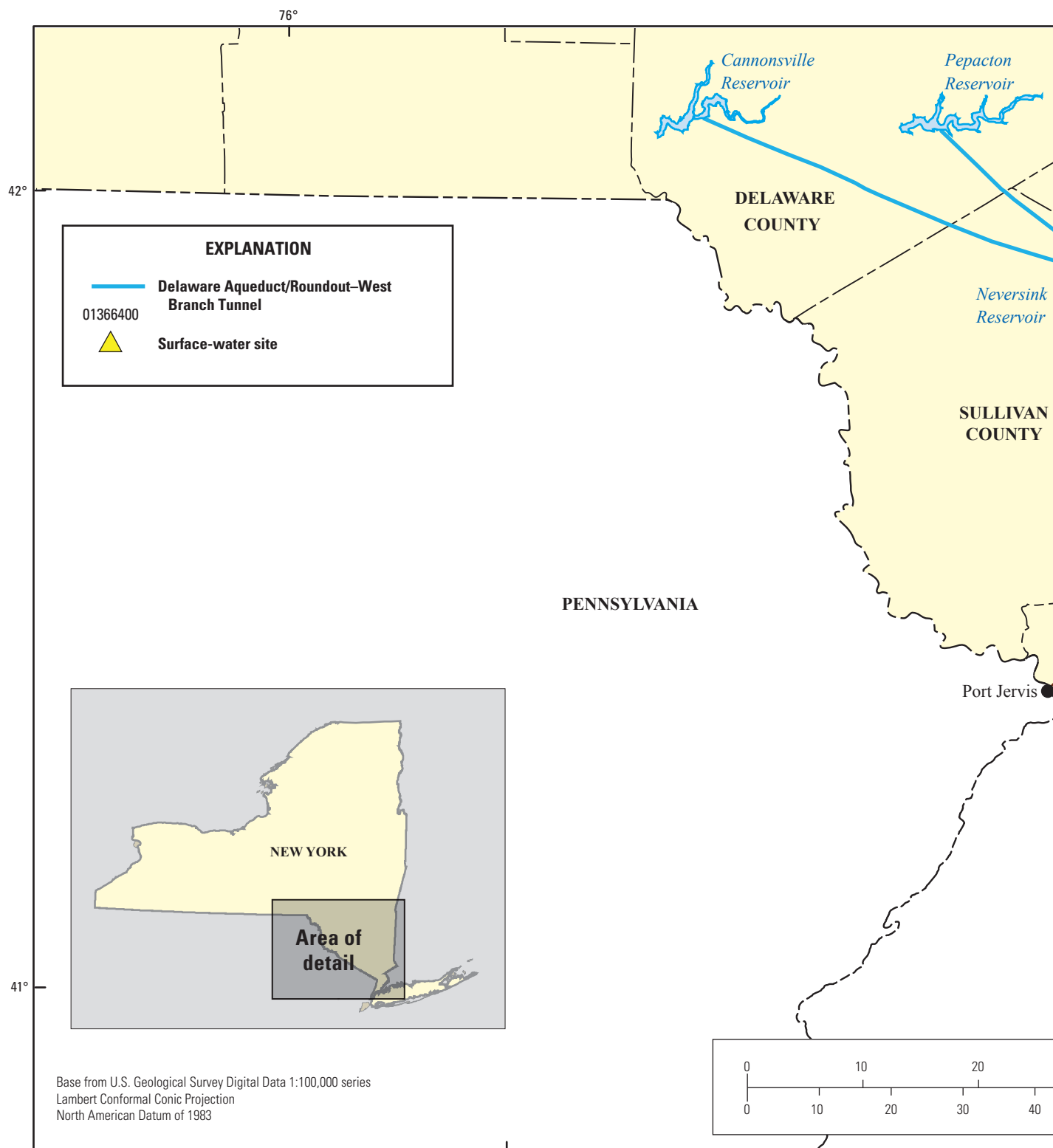
Figure 1.   Wawarsing study area, including Port Jervis Trough (Kingston to Port Jervis), four reservoirs (Cannonsville, Pepacton, Neversink, and Rondout), Delaware Aqueduct, Roundout Reservoir sampling site 01366400 at the influent to Rondout–West Branch Tunnel, and Kensico Reservoir, in Westchester County, New York.
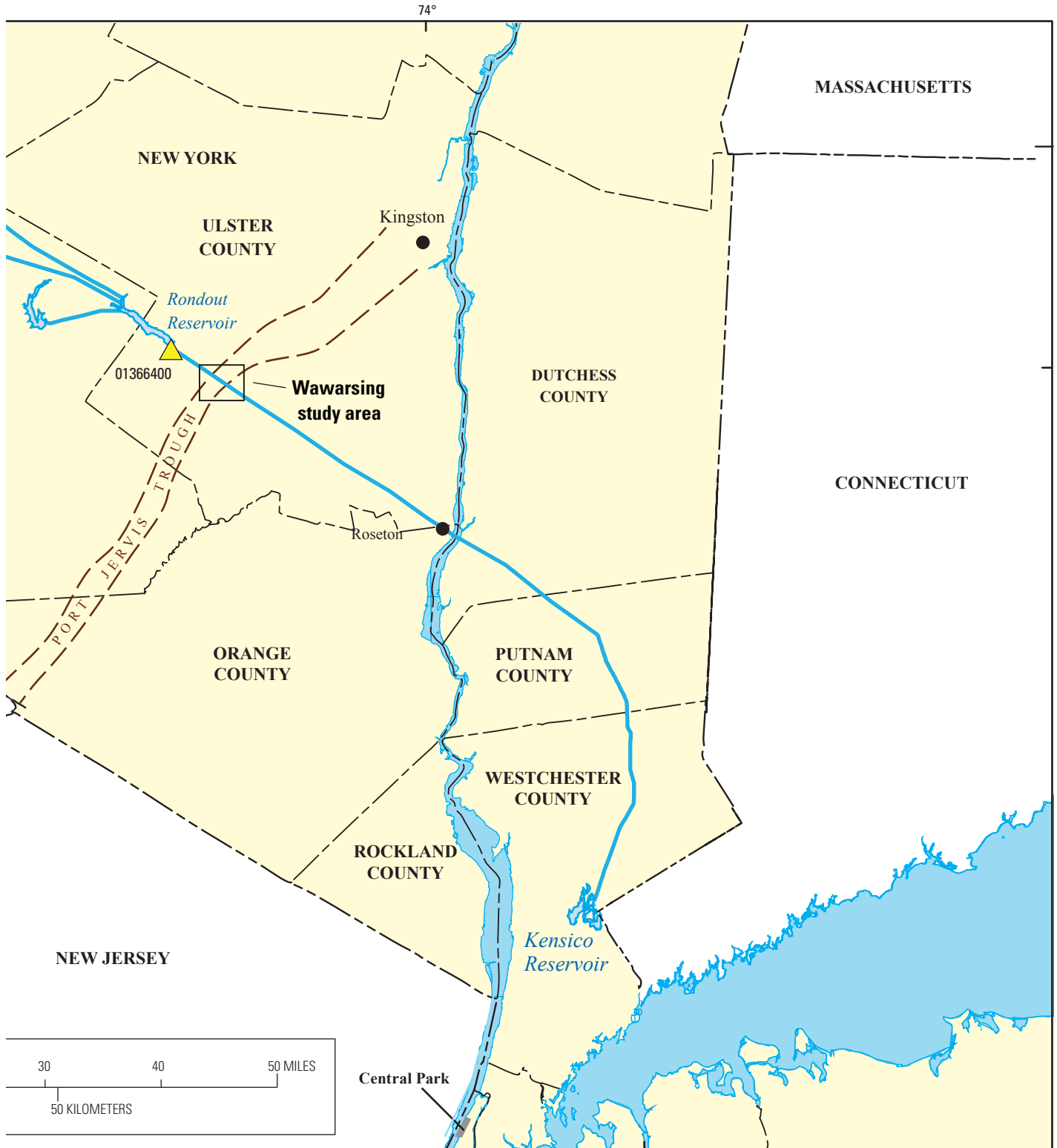
Figure 1. Wawarsing study area, including Port Jervis Trough (Kingston to Port Jervis), four reservoirs (Cannonsville, Pepacton, Neversink, and Rondout), Delaware Aqueduct, Roundout Reservoir sampling site 01366400 at the influent to Rondout–West Branch Tunnel, and Kensico Reservoir, in Westchester County, New York.—Continued
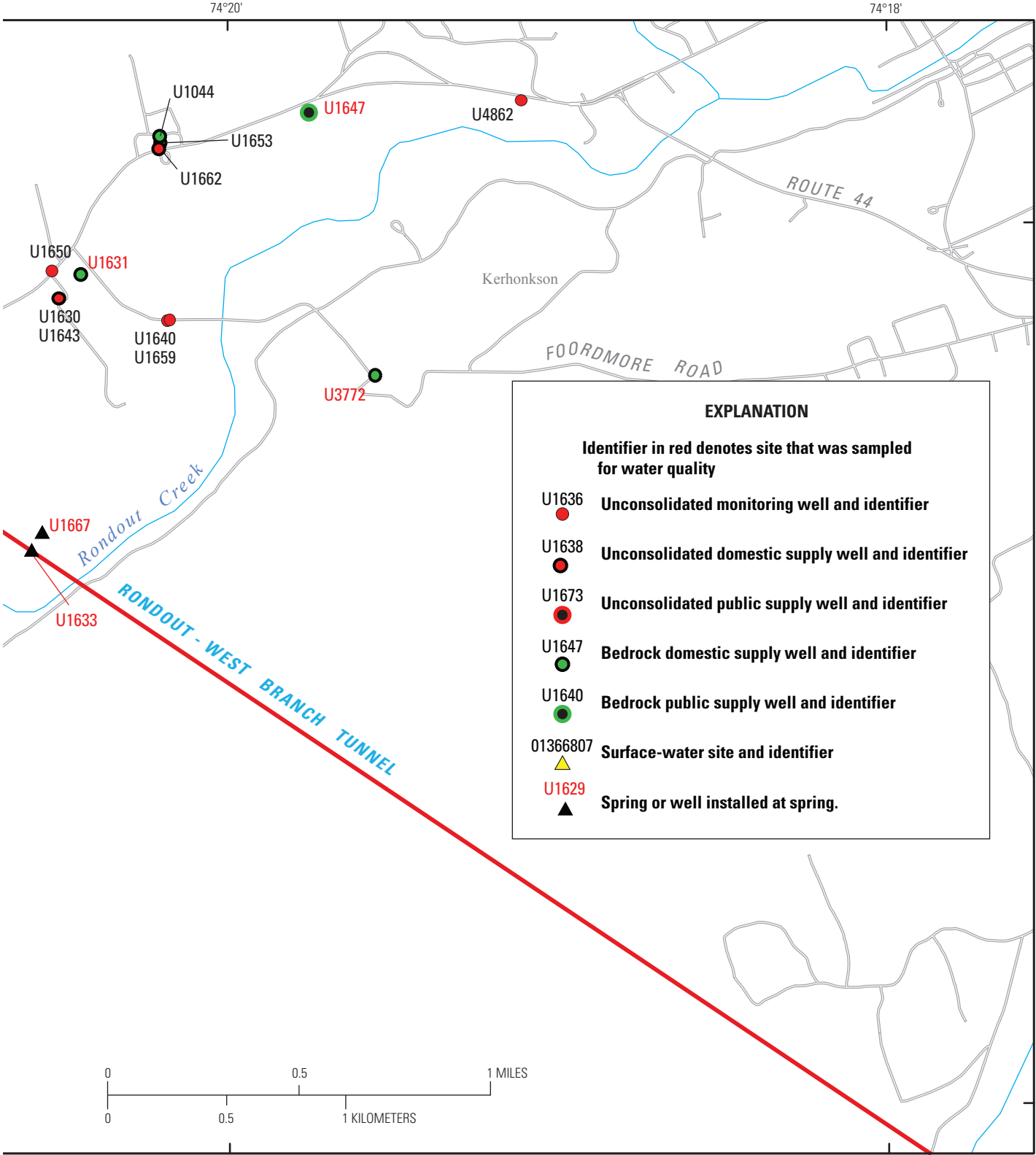
Figure 2. Monitoring sites at a lake (Lippman Lake), springs, unconsolidated monitoring and supply wells, and bedrock supply wells in Wawarsing, Ulster County, New York. (Location is shown in figure 1)

Figure 2.   Monitoring sites at a lake (Lippman Lake), springs, unconsolidated monitoring and supply wells, and bedrock supply wells in Wawarsing, Ulster County, New York. (Location is shown in figure 1)—Continued

Table 1.   Data on the sampling-site locations and construction of wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster County, New York, 2009–11.

[NAVD 88, North American Vertical Datum of 1988; DSW, domestic supply well; RWB, Rondout–West Branch Tunnel; --, no data; NA, not applicable; MW, monitoring well; CSW, community supply well; NCSW, non-community supply well; SPR, spring; SW, surface water; datum of gage is North American Vertical Datum of 1988]

Well identifier	Well or site type	Depth (feet)	Land surface altitude (feet above NAVD 88)	Aquifer-screened well type	Summary description
U1625	DSW	275	278.4	Bedrock	Flowing artesian well 1,820 feet from the RWB tunnel, extremely high transmissivity; large, rapid water-level response to tunnel.
U1626	DSW	10	275.7	Unconsolidated	Located 1,460 feet from the RWB tunnel. The hydrograph at this well responds well to rainfall events and also to tunnel leakage.
U1627	DSW	15	279.3	Unconsolidated	Responds well to rainfall events and also to tunnel leakage; tunnel (1,460 feet away) leakage inflows were estimated to have caused a 0.5 to 1 foot increase in water levels.
U1628	DSW	200	275.7	Bedrock	Near the tunnel trace and appears to be drilled within the Esopus Shale.
U1629	NCSW	118	300.1	Bedrock	Located 945 feet from RWB tunnel; moderately transmissive fracture network; with tunnel depressurization, water levels at U1628 dropped 5 to 6 feet, with delay of 48 hours.
U1630	DSW	--	266.1	Bedrock	Artesian flowing domestic bedrock well in the north-central part of the valley, where an upward flow gradient of 6.8 feet was recorded.
U1631	DSW	--	262.5	Bedrock	Flowing artesian well about 1,820 feet from the RWB tunnel; groundwater discharges from well at about 70 gallons per minute.
U1632	MW	--	--	Unconsolidated	These spring wells discharge from the upper slopes of a hilly deltaic deposit during seasonal (spring) periods of high precipitation and appear to result from a perched aquifer.
U1633	MW	--	--	Unconsolidated	
U1667	SPR	NA	--	--	
U1668	SPR	NA	--	--	
U1637	MW	27	264.5	Unconsolidated	Screened in fine-grained material, low yield; depth to bedrock about 310 feet.
U1641	MW	134	264.5	Unconsolidated	
U1644	DSW	--	268.4	Bedrock	Hydraulic head values much lower than in nearby bedrock wells; probably owing to less transmissive rock.
U1645	DSW	--	288.2	Bedrock	Located along the trace of the aqueduct, trends along a line perpendicular to the strike of the bedrock units; an area of lowest water-level response to tunnel influence may coincide with the Esopus Shale. Water-level changes during the shutdowns were only 1.5 feet.
U1647	NCSW	--	279.1	Bedrock	One of the farthest measured wells (7,100 feet from the RWB tunnel) with an indicated tunnel leakage response.
U1663	MW	47	275.2	Unconsolidated	Screened in fine grained material, low yield.
U1665	SPR	NA	280	--	Water flows upward through basement cracks during flooding.
U1666	SPR	NA	280	--	Water flows upward through basement cracks during flooding.
U1670	CSW	180	86.0	Unconsolidated	Located 0.9 mile southwest of the tunnel trace, both wells screened in overburden, just above bedrock; well 2 has a better yield, with double the specific capacity of well 1; underlying bedrock likely Shawungunk Formation.
U1673	CSW	180	86.5	Unconsolidated	
U3772	DSW	283	--	Bedrock	Flowing artesian well northeast of the trace (possibly in the Hudson River Formation or Shawangunk Formation).
U7017	DSW	--	--	Bedrock	
Lippman Lake effluent	SW	NA	299.2	NA	Runoff from the lake discharges to a culvert during periods of high lake stage. The lake receives runoff from several small streams that flow from the adjacent hills.
01366400[1]	SW	NA	840	NA	Sampled at the influent to the RWB tunnel.

[1]Sample generally collected from sample port at 730-feet altitude.

Table 2.   Classes of water-quality chemical characteristics and constituents measured in water samples from a lake, springs, and wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster County, New York, 2009–11.

[Water-quality field parameters: temperature, pH, specific conductance, dissolved oxygen, dissolved sulfides, alkalinity; O, oxygen; H, hydrogen; C, carbon; $^{87}Sr/^{86}Sr$, stable isotope ratio of strontium-87 to strontium-86; δ, delta; $δ^2H$ (or "δD"), stable isotope ratio of hydrogen-2 to hydrogen-1; $δ^{18}O$, stable isotope ratio of oxygen-18 to oxygen-16, relative to Vienna Standard Mean Ocean Water standard; $δ^{34}S$ of SO_4^{2-}, stable isotope ratio of sulfur-34 to sulfur-32 of sulfate relative to the Vienna Canyon Diablo Troilite standard; $δ^{13}C$ in DIC, stable isotope ratio of C-13 to C-12 in dissolved inorganic carbon relative to the Vienna Pee Dee Belemnite standard; CFCs, chlorofluorocarbons; analyses done by the U.S. Geological Survey (USGS) National Water Quality Laboratory, unless otherwise indicated]

Water-quality field parameters
Major inorganic constituents and nutrients
Trace elements
$^{87}Sr/^{86}Sr$ isotopes[1]
$δ^{18}O$ and $δ^2H$ (δD) isotopes[2]
$δ^{34}S$ of SO_4^{2-} isotopes[2]
$δ^{13}C$ isotopes[2]
Dissolved gases[3]
CFCs[4]
Sulfur hexafluoride[4] (SF_6)
^3H (tritium)[5]

[1]Analyzed at the USGS Isotope Laboratory, Menlo Park, Calif.

[2]Analyzed at the USGS Reston Stable Isotope Laboratory, Reston, Va.

[3]Analyzed at the USGS Dissolved Gas Laboratory, Reston, Va.

[4]Analyzed at the USGS CFC Laboratory, Reston, Va.

[5]Analyzed at the USGS Isotope Tracer Laboratory, Menlo Park, Calif.

from N_2 and Ar gas concentrations in samples. N_2 concentrations can be affected by denitrification under denitrifying conditions, but excess N_2 was not present.

Groundwater ages were estimated from concentrations of tritium (^3H), chlorofluorocarbons (CFCs, including CFC-11, CFC-12, and CFC-113), and sulfur hexafluoride (SF_6) tracers. Anthropogenic activities, such as industrial processes and atmospheric testing of thermonuclear devices, released ^3H, SF_6, and CFCs into the atmosphere in small but measurable concentrations. Precipitation that incorporates these gases from the atmosphere infiltrates into the ground and carries the particular chemical or isotopic signature of the atmospheric conditions at the time of recharge. These dating methods assume that gas exchange between the unsaturated zone and the atmosphere is fast but that shallow groundwater remains closed to gas exchange after recharge (Schlosser and others, 1989; Plummer and Busenberg, 1999; Busenberg and Plummer, 2000). Where possible, at least two age-dating indicators were measured at sampling sites. Apparent ages were estimated by assuming that piston flow prevails in the aquifer system. Age-tracer samples were collected without headspace, although bubbles of H_2S formed in several samples from bedrock wells. If an H_2S bubble formed in the sample bottle, the headspace volume was measured and a correction was applied

to the calculation of SF_6 or CFC concentrations. The percent uncertainty in sample concentrations was below 3 percent.

The ^3H in water was measured at the ^3H Laboratory, University of Miami, by internal gas proportional counting of H_2-gas made from the water samples. The ^3H that was released into the atmosphere between 1952 and 1963 during nuclear weapons tests provides a tracer for rainwater, which allows dates of recharge to be estimated. Although ^3H concentrations are approaching that of natural atmospheric production (6 to 15 pCi/L), they remain high enough to use in this analysis. The ^3H related to weapons testing can be used to infer some aspects of groundwater age; at the very least, water can be classified as being recharged before or after 1953.

The CFC samples were collected by inserting the end of the discharge tubing into the bottom of the bottle, allowing at least 2 liters (L) to overflow into a 2-L beaker, then capping the 125-mL glass bottles with special foil-lined caps under water within the beaker. Groundwater samples for SF_6 were collected by placing the sampling-discharge line in the bottom of the bottle and displacing the air in the bottle with groundwater. After approximately 2 L of overflow, the sampling line was removed. The bottles were tightly sealed without headspace using conical screw caps and wrapped with electrical tape.

Concentrations of trichlorofluoromethane (CFC-11), dichlorodifluoromethane (CFC-12), and 1,1,2-trichlorotrifluo-roethane (CFC-113) in water were determined at the USGS CFC Laboratory in Reston, Virginia, with a detection limit of about 0.3 picomole per kilogram using purge and trap, gas-chromatographic techniques with electron-capture detector (GC-ECD) (Bullister, 1984; Bullister and Weiss, 1988; Busenberg and Plummer, 1992). The CFC-dating technique is described in Busenberg and Plummer (1992). Samples were analyzed for SF_6 at the USGS CFC Laboratory using procedures described by Busenberg and Plummer (2000).

Stable isotopes were analyzed using several different methods. Analyses of the stable-isotope ratios oxygen-18 to oxygen-16 ($\delta^{18}O$), hydrogen-2 to hydrogen-1 (δ^2H), $\delta^{34}S$ of SO_4^{2-}, and $\delta^{13}C$ of DIC were done at the USGS Stable Isotope Laboratory in Reston, Virginia. A hydrogen equilibration method was used for δ^2H analysis (Coplen and others, 1991), and the CO_2 equilibration technique (Epstein and Mayeda, 1953) was used for analysis of $\delta^{18}O$. The 2-sigma analytical uncertainties for δ^2H and $\delta^{18}O$ values are 2 and 0.2 per mil, respectively. The $\delta^{34}S$ of SO_4^{2-} was analyzed for $BaSO_4$ precipitates using procedures described in Carmody and others (1998). Results are reported in per mil relative to the Vienna Canyon Diablo Troilite (VCDT) standard. The uncertainty associated with $\delta^{34}S$ values is ±0.2 per mil. Water samples were analyzed for $\delta^{13}C$ using mass-spectrometry techniques at the University of Waterloo Environmental Isotope Laboratory, Waterloo, Ontario, Canada, and are reported relative to the Vienna Pee Dee Belemnite (VPDB) standard. The uncertainty associated with the $\delta^{13}C$ values is ±0.2 per mil. Ratios of $^{87}Sr/^{86}Sr$ were determined by thermal ionization mass spectrometry as described by Bullen and others (1997).

Quality Assurance

Field probes were cleaned and calibrated with standard solutions and checked periodically with independent field and laboratory probes. Field quality-control procedures included the collection and analysis of replicate samples, which provided information on the variability of analytical results caused by sample collection, processing, and analysis. The charge balances for major ion analyses generally were within ±5 percent, although 9 of the 40 samples that were analyzed for major and trace ions had greater imbalances (table 3, in back of report) and could result from (1) ions not included in the analyses, (2) error in laboratory analyses, and (or) (3) error caused by exsolution (degassing) or dissolution of carbon dioxide before sample analysis.

Hydrogeologic Setting

The geology and hydrology of the bedrock and unconsolidated deposits are discussed in the following section.

Geology

Bedrock

A complex series of fractured sedimentary bedrock units of Silurian and Devonian age underlie the unconsolidated deposits in the study area. The bedrock generally strikes northeast and dips about 45 degrees to the northwest. The bedrock units as delineated by Berkey and Fluhr (1936) and Dibbell (1944) include the Marcellus Shale, Onondaga Limestone, Esopus-Schoharie Shale, Helderberg Limestones (Port Ewen-Becraft, New Scotland, Coeymans), Manlius Limestone, Binnewater Limestone and Sandstone, High Falls Shale and Limestone, Wawarsing Wedge complex, Shawangunk Sandstone, and Hudson River Shale. The Marcellus Shale is estimated to have relatively high gas-production potential and is being considered for extraction in parts of New York, as well as Ohio, Maryland, and large parts of Pennsylvania and eastern West Virginia (Kargbo and others, 2010). The Shawangunk Formation, which caps the Shawangunk Mountains to the east, contacts the overlying Wawarsing Wedge to the west and the underlying Hudson River Shale to the east. Dibbell (1944) describes the bedrock sequences as having sections with substantial fracturing, and faulting in the subsurface below the study area. Many of these fracture and fault zones produced groundwater in thousands of gallons per minute during construction of the RWB Tunnel (figs. 3A and B).

Leakage of water from the RWB Tunnel appears to be from cracks in the liner allowing pressurized tunnel water to flow behind and (or) through the liner where transmissive voids may exist, including solution cavities in limestone, as well as through fractures, faults, and geologic contacts. Sustained leakage of pressurized tunnel water through limestone that contains dissolution features could induce further dissolution of the limestone surrounding the tunnel liner. The Onondaga Limestone was described as being cavernous in many places and members of the Helderberg and Manlius Limestones exhibited a tendency to develop cavernous structures (Berkey and Fluhr, 1936). Transmissive fractures, faults, and bedrock contacts eventually crop out in the subsurface where the unconsolidated deposits may impede or transmit the pressurized RWB Tunnel leakage.

Some of the minerals in the fractured bedrock aquifer system are particularly pertinent to water-chemistry constituents, such as H_2S, CH_4, SO_4^{2-}, Sr, and several stable isotopes. For example, evaporites formed during the arid conditions in the late Silurian and the Silurian sedimentary sequence probably functioned as a paleoaquifer (Kesler and others, 1997). Sulfur (S) isotope compositions indicate that the lower part of the paleoaquifer contained reduced S formed by thermochemical reduction, whereas the upper part of the paleoaquifer contained reduced S formed by bacterial reduction of SO_4^{2-} derived from overlying Salina Group evaporites. These constraints, along with Na-Cl-Br leachate

data, indicate that Mississippi Valley Type mineralization in the Lockport Dolomite formed when rising, metal-bearing brines mixed with descending, sulfur-bearing brines from the Salina Group above (Kesler and others, 1997). Vein deposits of zinc, lead, and copper sulfides are present to the east, on the west slope of the Shawangunk Mountains (Heusser, 1976), in a northeast-trending belt 24 mi long, extending from Guymard to Ellenville, N.Y. (Wilbur and others, 1990). These deposits mark the eastern margin of the evaporite-bearing Silurian sedimentary basin and were observed during completion of the Delaware Aqueduct (Bird, 1944).

Unconsolidated Deposits

The valley in the study area is underlain by surficial deposits of gravel, sand, silt, and clay, and include Pleistocene glacial stratified and till deposits, and Holocene alluvium deposits, which are present primarily in stream channels. The major unconsolidated hydrogeologic units consist of till, ice-contact stratified drift, outwash, glacial lake clays, recent alluvium, and colluvium. Reynolds (2007) and Frimpter (1972) described a sand and gravel aquifer buried beneath glacial lake sediments. Geologic data from 14 USGS-drilled monitoring wells within the study area indicate highly variable deposits ranging from sand and gravel to silt and clay and lacustrine clay deposits that exceed 140 ft in thickness in some areas (Frederick Stumm, U.S. Geological Survey, written commun., 2010). Preliminary analysis of unpublished USGS passive seismic surveys and deep electromagnetic geophysical surveys of the study area indicate that the bedrock contact is undulating with areas of deep erosional troughs. These deep troughs are northeast-southwest trending and extend more than 300 ft below land surface.

Hydrology

Randall (1996) studied the precipitation variations in upstate New York and determined that the Wawarsing study area averaged about 44 inches (in.) of precipitation annually during 1951–80. This study is consistent with the long-term daily precipitation records recorded by the National Weather Service (NWS) at Central Park in New York City (National Oceanic and Atmospheric Administration, 2010), and indicates only slight variations owing to localized storms. Annual precipitation exceeded the long-term mean every year during 2002–10. The increase in precipitation has caused increased groundwater levels and contributed to surface flooding when the rate of precipitation exceeded drainage from roadways or recharge into surficial deposits (Stumm and others, 2012).

Groundwater generally flows from the surrounding hills east and west of the valley and from southwest of the valley toward the central and ultimately northeastern part of the valley. Hydrographs from wells screened in unconsolidated deposits indicate a direct correlation to precipitation but also some effects caused by tunnel leakages from underlying

bedrock (Stumm and others, 2012). Analysis of the vertical gradients between the deeper and shallower parts of the unconsolidated aquifer indicate an upward-flow gradient, particularly in the central parts of the valley where the water table discharges to Rondout Creek and the deposits are thickest (Stumm and others, 2012).

For bedrock wells, the highest water levels were recorded in March and April of 2009 and 2010 during periods of elevated precipitation (Stumm and others, 2012). The bedrock potentiometric surface was higher locally in the area along State Route 209 as a result of tunnel leakage (Stumm and others, 2012). Most bedrock wells affected by tunnel leakage had upward-flow gradients from the bedrock to the unconsolidated aquifer. The head differential between the bedrock and unconsolidated aquifers at wells U1627 and U1625 was 10.6 ft, and the flow gradient direction was upward (Stumm and others, 2012).

The majority of homes in Wawarsing rely upon domestic-supply wells in the unconsolidated and bedrock aquifers. Major municipal-water users in this area include the Village of Ellenville (4,400) and the Eastern New York Correctional Facility (700), totaling about 5,000 municipal groundwater users (New York State Department of Health, 1982). The transmissivity of the aquifer near Ellenville appears to be very high, as evidenced by a 39-ft deep supply well for the village of Ellenville that initially had a pumping rate of 1,000 gal/min (Frimpter, 1972).

Water-Quality Monitoring Sites

Water-quality monitoring sites sampled in Wawarsing include four springs, seven wells screened in unconsolidated deposits, and six wells in bedrock, in addition to the lake site at Lippman Park. Manual measurements of groundwater levels were completed monthly, and levels at selected wells were recorded hourly with pressure transducers and data loggers, as described in Stumm and others (2012). Groundwater temperatures in wells U1625, U1630, U1649, and U1651 were the lowest among the monitored bedrock wells and are consistent with the leakage of colder tunnel water into the surrounding fractured-bedrock groundwater-flow system along highly transmissive sections (Stumm and others, 2012). Bedrock wells with the coldest groundwater temperatures were the same wells that had the largest water-level changes and shortest delay times to tunnel influences.

Rondout Reservoir and the Rondout–West Branch Water Tunnel

Rondout Reservoir water was sampled at the influent to the RWB Tunnel, which carries water from the Rondout Reservoir to the Kensico Reservoir and then on to NYC (fig. 1). Sample analysis of this water was used to represent water chemistry in the tunnel. Water in the Rondout Reservoir results from precipitation in the contributing Delaware and
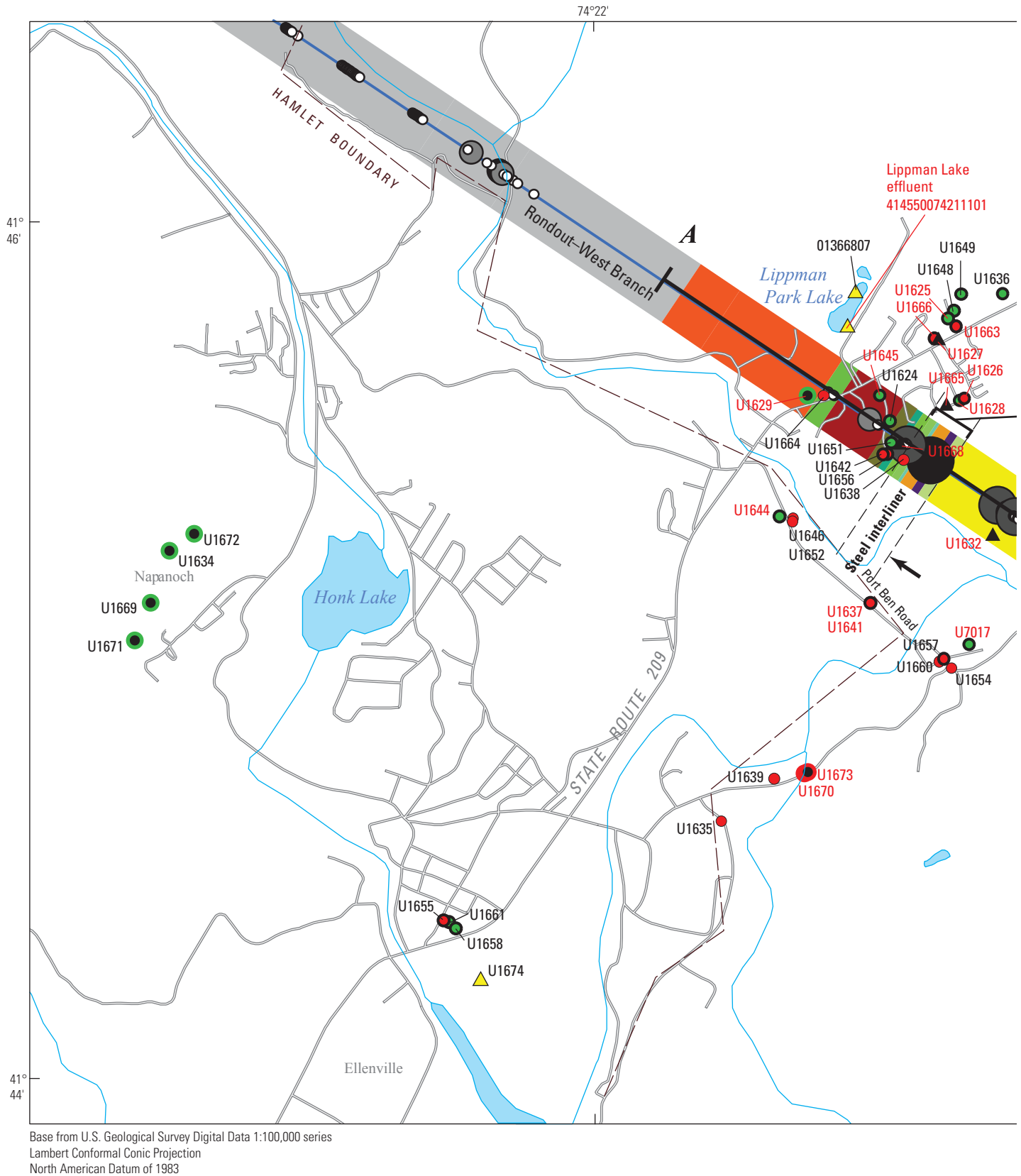
Figure 3. *A.* Locations of wells and surface-water sites; Rondout–West Branch Tunnel geology; and water-inflow rates documented during tunnel construction in the Wawarsing study area, Ulster County, New York (Location is shown in figure 1; LS, limestone; SS, sandstone; SH, shale).
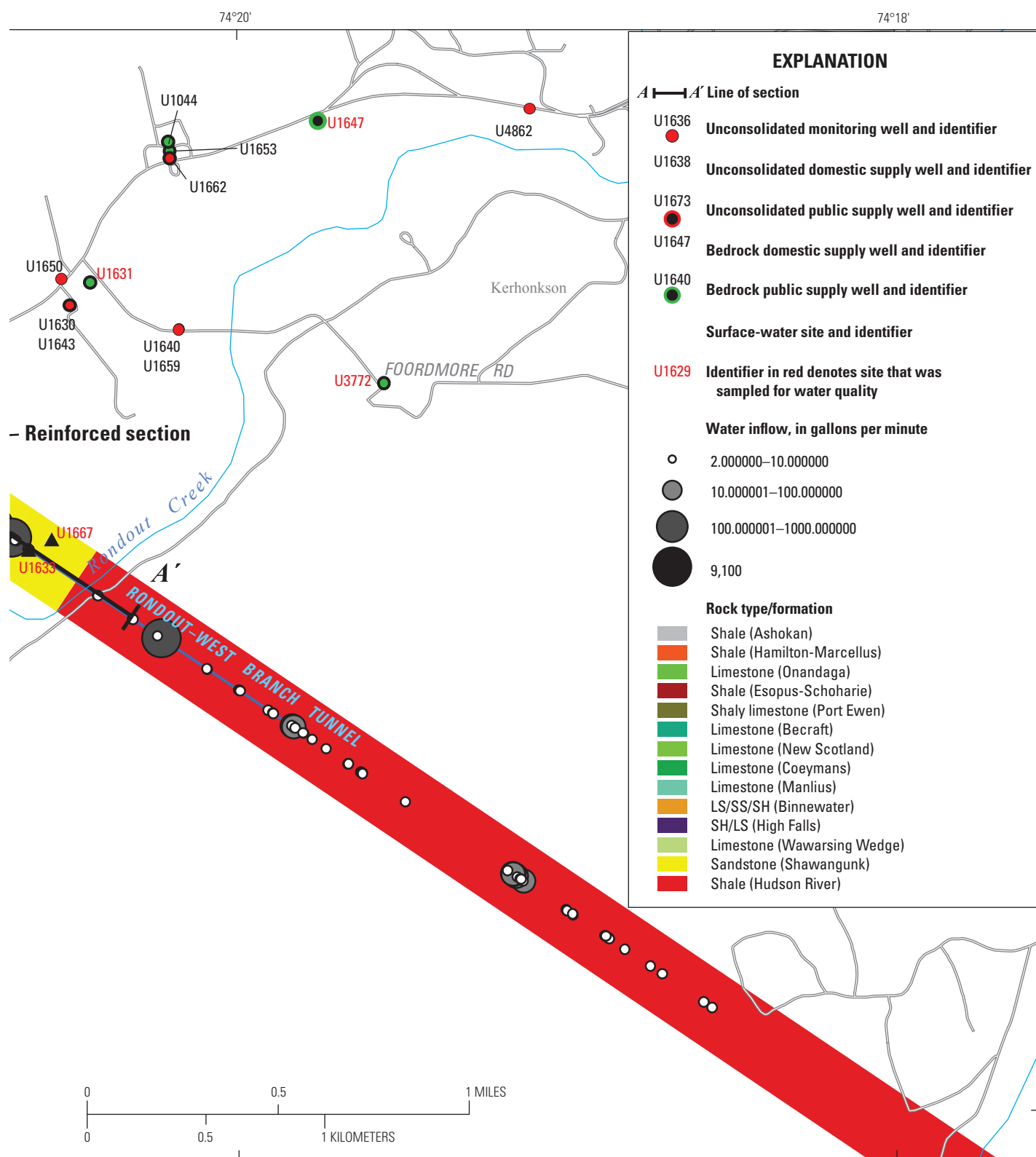
Figure 3. *A.* Locations of wells and surface-water sites; Rondout–West Branch Tunnel geology; and water-inflow rates documented during tunnel construction in the Wawarsing study area, Ulster County, New York (Location is shown in figure 1; LS, limestone; SS, sandstone; SH, shale).—Continued
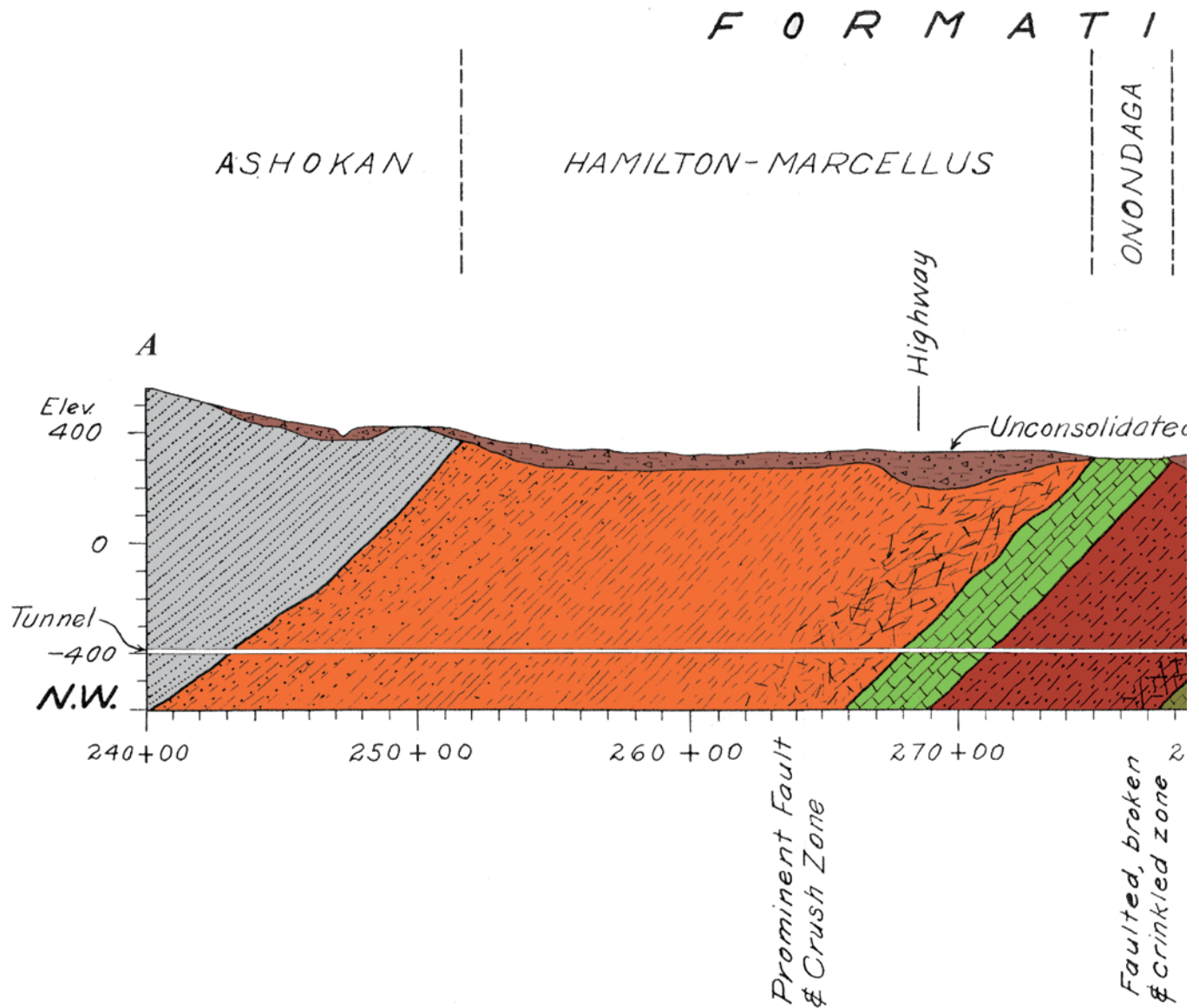
Figure 3. *B.* Geology observed during New York City Board of Water Supply test borings and Rondout–West Branch Tunnel construction from A to A' within the study area, Town of Wawarsing, Ulster County, New York. (Location is shown in figure 3A) (The Helderberg Group has been divided into the Port Ewen, Becraft, New Scotland, and Coeymans Formations; vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). (Modified from Berkey and Fluhr, 1936).

Figure 3. *B.* Geology observed during New York City Board of Water Supply test borings and Rondout–West Branch Tunnel construction from A to A′ within the study area, Town of Wawarsing, Ulster County, New York. (Location is shown in figure 3A) (The Helderberg Group has been divided into the Port Ewen, Becraft, New Scotland, and Coeymans Formations; vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). (Modified from Berkey and Fluhr, 1936).—Continued

Catskill watersheds. The Rondout Reservoir is located 75 mi northwest of NYC in the Catskill Mountains between the towns of Wawarsing in Ulster County and Neversink in Sullivan County. The reservoir is the central collection point for the Delaware System and provides about one-half of the daily consumption for NYC.

The Rondout Reservoir is 6.5 mi long and 3.2 mi² in area and reaches a maximum depth of 175 ft near the dam; the mean depth is 73.8 ft, and the altitude is 840 ft above NAVD 88 (Effler and others, 2001). The Rondout Reservoir holds 49.6 billion gallons, which comes from the 95-mi² Rondout Creek watershed, as well as from the Cannonsville, Neversink, and Pepacton Reservoirs via the Delaware and Neversink Tunnels. Because those three reservoirs are in the Delaware River watershed, Rondout is considered by the city's Department of Environmental Protection to be part of the Delaware System despite being entirely within the Hudson River watershed. Rondout is circumscribed by State Routes 55 and 55A, but access to the actual reservoir is tightly restricted.

Specific conductance in the Rondout Reservoir generally is lower than in the Pepacton and Cannonsville Reservoirs, but higher than in the Neversink Reservoir (Owens, 1998; Effler and others, 2001). Specific conductance and temperature in the Rondout Reservoir did not vary substantially in lateral directions (Effler and O'Donnell, 2001). The Rondout Reservoir undergoes thermal stratification during summer, although not extensively because of the large contributions of cold water received from the upstream reservoirs. The Rondout Reservoir has a drawdown of 35 ft (10.8 meters) and a flushing rate of 6.8 times per year (Effler and others, 2001).

Hydrologic Effects of Temporary Rondout–West Branch Water Tunnel Shutdowns

The NYCDEP shut down the RWB Tunnel on four separate occasions from October 2008 to December 2010 (Stumm and others, 2012) and three times during the period of water-quality sampling, December 2009 to April 2010. The four shutdowns occurred (1) October 25–November 26, 2008, (2) November 5–19, 2009, (3) December 4–16, 2009, and (4) January 13–26, 2010. During each of the shutdowns, the tunnel pressure was slowly reduced from about 600 to about 75 ft above NAVD 88 over a period of 34 to 56 hours, as measured in a nearby tunnel shaft. The re-pressurization process was accomplished in the same manner, by increasing the pressure in the RWB Tunnel from about 75 to about 600 ft above NAVD 88, over a period of 43 to 54 hours.

A number of wells screened in unconsolidated deposits and in bedrock in Wawarsing indicated water-level changes in response to tunnel pressure (Stumm and others, 2012). The location of unconsolidated aquifer wells with measureable changes to tunnel leakage correlated with those in the bedrock. Water levels in the bedrock changed as much as 12 ft within 0.5 hour during tunnel shutdowns, although the majority of bedrock wells influenced by tunnel leakage indicated lag times

of 21 to 33 hours. RWB Tunnel leakage has been documented to enter the bedrock units adjacent to the tunnel and cause increases in the bedrock water levels by as much as 10.5 ft (Stumm and others, 2012). Transmissive fractures in the bedrock near the contact between the unconsolidated and bedrock aquifers can transmit this increased pressure to the overlying unconsolidated aquifer.

Water-level changes in bedrock wells during the shutdowns ranged from 12 ft at U1625 to 1.5 ft at U1645, and well U1629 indicated no change (Stumm and others, 2012). The greater water-level responses in units on either side of these wells appear to correlate with the limestone units in contact with the shale (Stumm and others, 2012). Analysis of the hydrographs at U1625 during the tunnel shutdowns indicates the bedrock in this area responds within about 0.5 hour of tunnel depressurization or re-pressurization (fig. 11B in Stumm and others, 2012). The rapid response times to changes in tunnel pressure, the large water-level changes, and the considerable distance from the tunnel may indicate the existence of an interconnected cave or dissolution fracture system with large storage and transmissivity characteristics. Well U1647, located 7,100 ft from the RWB Tunnel, was one of the farthest measured wells with a tunnel-leakage response. Bedrock wells U1628 and U1631 had among the longest lag times: 48 and 60 hours, respectively (Stumm and others, 2012). Well U1628 is near the tunnel and appears to be drilled within the Esopus Shale, a fine-grained rock unit that could have limited transmissivity and connectivity (fig. 3).

Water levels in the unconsolidated deposits changed as much as 2.5 ft within 18 hours during tunnel shutdowns (Stumm and others, 2012). The location of wells in the unconsolidated aquifer with measurable changes caused by tunnel leakage correlated with those in the bedrock, including some at distances of 7,000 ft from the RWB Tunnel (Stumm and others, 2012). A hydrograph of well U1641 indicates a drop in water levels of 2 to 2.5 ft during each of the last three shutdowns. The tunnel-leakage influence lag time at this overburden well was only about 18 hours, indicating that the bedrock, which is about 170 ft deeper than well U1641, must consist of highly transmissive fractures that respond quickly to tunnel-pressure changes (Stumm and others, 2012). Tunnel-leakage inflows at U1626 were estimated to have caused a 0.5 to 1 ft increase in water levels in the unconsolidated aquifer at this well (Stumm and others, 2012).

Water Sources and Chemistry

Anthropogenic and natural sources of water can be characterized based on water chemistry, age tracers, and stable isotopes. Data analysis included graphical plotting of concentrations of water-quality constituents and pertinent plots of constituent and isotope ratios.

Sources of Water

Groundwater chemistry is primarily affected by atmospheric deposition; weathering of soil and aquifer material; and anthropogenic sources, such as road salt, septic-system leachate, leaking underground-storage tanks, landfills, chemical spills, and storm-water runoff from roads and parking lots. Several analysis tools were used to help distinguish (1) anthropogenic sources or pathways from natural ones and (2) surface water or shallow groundwater from deep groundwater, including Piper diagrams, scatterplots (not shown), saturation indexes for calcite and gypsum, stable isotopes, dissolved gases, and groundwater-age tracers. Differences in chemical signatures among the parts of the hydrologic system were used to improve the understanding of source waters and groundwater-flow patterns and pathways and can be used to assess mixing of the different source waters in samples.

Major Constituents and Nutrients

Major-ion concentrations in water samples collected during the study show differences depending on the sample type, depth, and location (table 3, in back of report). The Piper diagram (Piper, 1944) is used to show the clustering of samples by water type and the effects of aquifer weathering and anthropogenic activities on major-ion concentrations; samples are represented by the percentages of total cations and total anions, plotted on separate trilinear plots, and then projected onto a central diamond (fig. 4).

The anion percentages in water samples from most unconsolidated aquifer wells and springs were greater in HCO_3^- and carbonate (CO_3^{2-}) than in SO_4^{2-} and chloride compared to the bedrock well samples; the lower concentrations of HCO_3^- in deep groundwater could result from the precipitation of calcite. Similarly, water samples from most unconsolidated aquifer wells and springs had a greater percentage of calcium (Ca) compared to other cations than did bedrock well samples. The exception was the water sample from U1625, which had high ratios of HCO_3 and Ca relative to other ions, and similar to other samples, such as unconsolidated aquifer well samples and surface-water samples (fig. 4). Water samples from bedrock wells generally had relatively high concentrations of SO_4^{2-} compared to other anions; samples from two bedrock wells that did not have high concentrations of SO_4^{2-} were reducing and had high concentrations of dissolved H_2S. High concentrations of SO_4^{2-} are not uncommon in groundwater from the Silurian-Devonian bedrock, which is likely due to the presence of gypsum in the upper part of the Silurian sequence (Williams and Eckhardt, 1987).

Nitrate (NO_3^-) plus nitrite (NO_2^-) in water samples can be derived from several sources, including microbial decay of organic matter in soils, animal waste, septic-system leachate, synthetic fertilizers, and rainfall. Concentrations of NO_3^- plus NO_2^- ranged from less than the minimum reporting levels

(MRLs) in water samples with reducing redox characteristics to 0.88 mg/L as N for a domestic well in a residential area with onsite septic-tank drainfields (table 3, in back of report). Concentrations of NO_2^- were less than the MRL of 0.008 mg/L as N in all but two samples; therefore, NO_3^- plus NO_2^- is hereafter referred to as NO_3^-. The median concentration of NO_3^- for wells in the study area was less than 0.5 mg/L as N, and samples at more than one-half of the sites were below the reporting level of 0.04 mg/L as N. Urban septic-system leachate and lawn fertilizer are the major sources of NO_3^- in the study area and can affect shallow groundwater quality. Although NO_3^- from septic systems does not appear to be a health concern, bacterial contamination of private-supply wells with *Escherichia coli* (*E. coli*) is a recurring problem in the Rondout Valley near the town of Wawarsing (J.T. Rodden, Jr., Ulster County Health Department, written commun., 2009). The presence of *E. coli* in domestic well water is likely caused by the mobilization of septic-system leachate by the high water table associated with seasonal flooding.

Saturation indexes, which are represented by the logarithms of the ratios of the ion activity products to the solubility product constants, or log (IAP/Ksp), indicated that groundwater samples from bedrock wells were at or near saturation with respect to gaseous CO_2, quartz, calcite, and dolomite, and undersaturated with respect to gypsum and fluorite (table 3, in back of report). Groundwater samples from most bedrock wells generally were nearer to saturation of calcite and gypsum than groundwater samples from unconsolidated wells (fig. 5). The U1625 well sample that was collected at the RWB Tunnel during low-head pressure on December 14, 2009, shows similar chemistry to that of other bedrock wells; however, samples that were collected on June 24, 2009, and April 7, 2011, from well U1625 under normal tunnel-pressure conditions, when the tunnel pressure was high, had chemistry that was similar to shallow groundwater or surface water (fig. 5). Similarly, the U1631 well sample that was collected at the RWB Tunnel during low-head pressure on December 14, 2009, was supersaturated with respect to calcite, yet was undersaturated in the sample collected on September 16, 2009, when the tunnel pressure was high. These differences in bedrock groundwater chemistry between normal and depressurized tunnel conditions indicate that tunnel water does influence native groundwater under normally pressurized tunnel conditions.

Redox Conditions

Redox reactions affect many chemical processes in aquifers, including the concentrations of dissolved gases, such as O_2, N_2, H_2S, and CH_4; speciation and mobility of naturally occurring elements, such as Fe, Mn, S, As, and U; and the transformation of anthropogenic compounds, such as NO_3^-, chloroform, and trichloroethylene. Redox conditions tend to proceed along a well-documented sequence of zones dominated by a single electron-accepting process. Water-quality
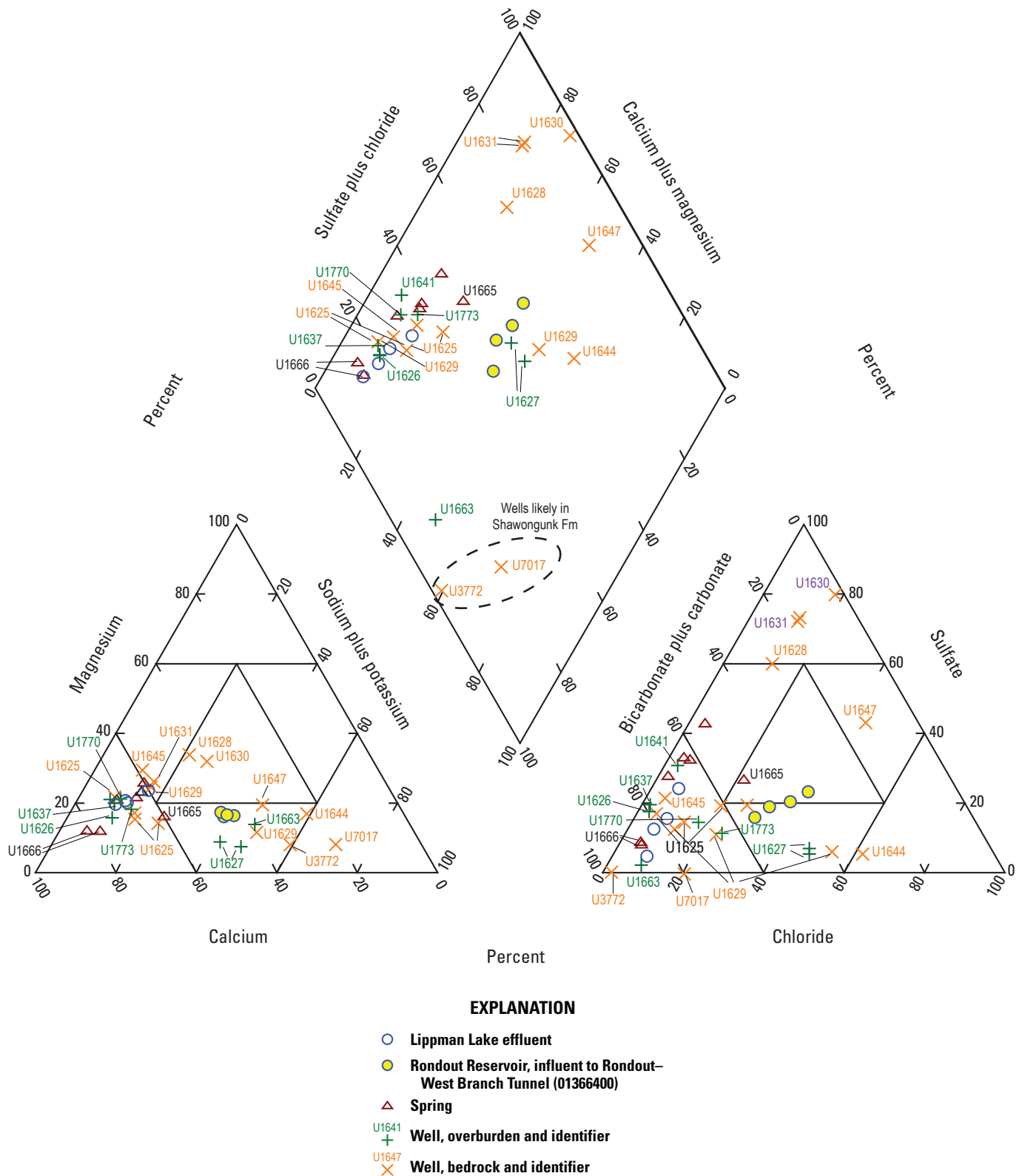
Figure 4.   The percentage of total equivalents of major cations and anions in surface-water and groundwater samples collected from a lake, springs, and wells in Wawarsing and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster County, New York, 2009–11.
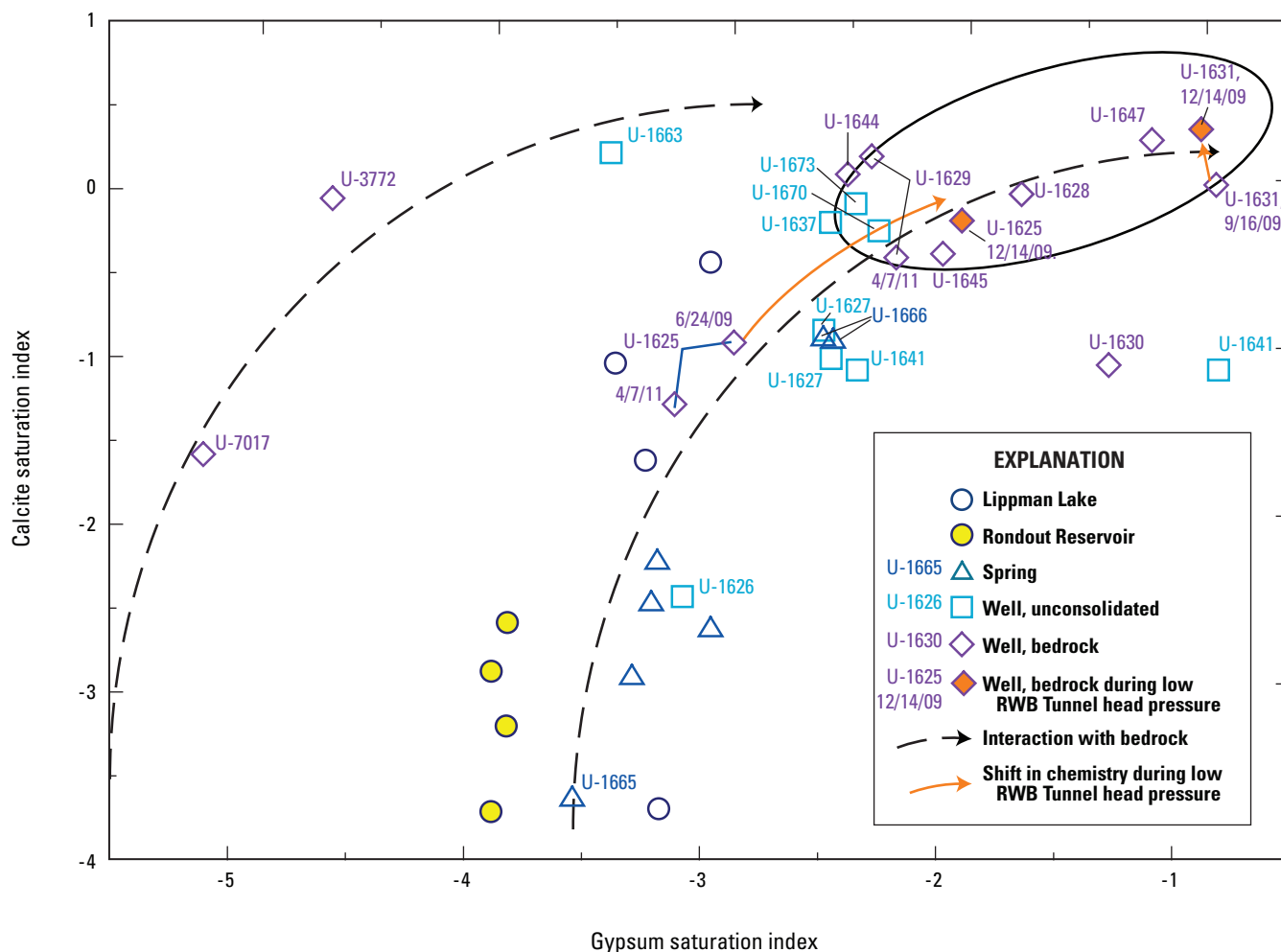
Figure 5. Saturation indexes for calcite and gypsum in surface-water and groundwater samples collected from a lake, springs, and wells in the study area, Wawarsing, New York, and for the Rondout Reservoir at the influent to the Rondout–West Branch (RWB) Tunnel in Lackawack, Ulster County, New York, 2009–11.

data can be used to assess ambient-redox processes in groundwater systems (McMahon and Chapelle, 2007). DO produces more energy per mole of organic carbon oxidized than any other commonly available electron acceptor; thus, it is used preferentially by surface and subsurface microorganisms. Because groundwater systems can be isolated from the atmosphere, however, O_2 tends to be consumed along aquifer flow paths. Under anoxic conditions, the next most energetically favorable naturally available electron acceptor is NO_3^-, followed by manganese (IV) [Mn(IV)], ferric iron [Fe(III)], sulfate (SO_4^{2-}), and finally carbon dioxide (CO_2). This order of preferential electron acceptor utilization—$O_2 > NO_3^- > Mn(IV) > Fe(III) > SO_4^{2-} > CO_2$—is referred to as the ecological succession of terminal electron-accepting processes (TEAPs). These predominant TEAPs, from more oxidizing to reducing, are O_2-reducing (also referred to as oxic in this report), NO_3^--reducing, Mn-reducing, Fe-reducing, SO_4^{2-}-reducing, and

methanogenic (containing methane or CH_4). Some common contaminants of groundwater systems, such as chlorinated ethenes, also may act as electron acceptors.

A redox classification scheme described by McMahon and Chapelle (2007) and modified by Chapelle and others (2009) uses various chemical indicator species to classify redox conditions in each groundwater sample. The scheme has been modified for this study based on available data for N_2, H_2S, and CH_4 (table 4, in back of report). In several instances, conflicting or overlapping indicators of redox conditions occur and are related to mixtures of water with different redox indicators but also may indicate disequilibrium among redox indicators; therefore, the term is used whereby Y/Z indicates waters with different redox ranging from most oxidized (Y) to most reduced (Z). CH_4 was present in water samples from bedrock wells, including high concentrations (greater than 1 mg/L) in samples from U1629, U1647, U7017,

U3772, and U1644 (table 4, in back of report). The Devonian bedrock sequence includes the black shales of the Esopus and Marcellus Formations, which are organic rich, so the presence of CH_4 is not surprising.

Redox conditions in the study area ranged from oxic in surface water and most wells screened in unconsolidated deposits to reducing in those wells screened in poorly permeable unconsolidated deposits and in bedrock (table 4, in back of report). Bedrock wells typically have long, open sections that could have had water contributed from several fractures with different flow-path histories. For example, bedrock well U1631 had DO concentrations greater than 1 mg/L, yet also had high concentrations of reduced species, including dissolved Fe, Mn, H_2S, and CH_4. CH_4 is not included as a redox variable for the redox classification system used, but its presence in groundwater indicates a contribution of water with very reducing conditions. Most of the bedrock wells were reducing, with the exception of well U1625; concentrations of DO were greater than 2 mg/L in well U1625, but CH_4 was present in the second sample collected on December 14, 2009, during a tunnel shutdown (table 4, in back of report).

Trace Constituents

Concentrations of trace constituents, including Fe, Mn, As, Sr, Ba, B, Li, Ni, and Pb, were generally higher in water samples from bedrock wells than in water samples from wells screened in unconsolidated deposits, RWB Tunnel water, or Lippman Lake (table 5, in back of report). High concentrations of dissolved Mn and (or) Fe reflect anoxic conditions, and one or both exceeded U.S. Environmental Protection Agency secondary drinking-water standards of 50 micrograms per liter (μg/L) and 300 μg/L, respectively, at several wells (table 5, in back of report; U.S. Environmental Protection Agency, 2006a). Mn concentrations in water samples ranged from less than 0.2 to 660 μg/L; samples from 7 of the 10 bedrock wells and 5 of the 7 unconsolidated wells had exceedances of the secondary maximum contaminant level (MCL) (table 5, in back of report). Fe concentrations in water samples ranged from less than 4 to 1,800 μg/L; samples from 4 of the 10 bedrock wells and only 1 of the 7 unconsolidated wells had exceedances of the secondary MCL (table 5, in back of report). Concentrations of dissolved As in water sampled from domestic bedrock well U1645 was at the MCL of 10 μg/L (U.S. Environmental Protection Agency, 2006b). Sr concentrations were high in several bedrock wells, ranging up to 20 mg/L at U1630 and U1631. High concentrations (greater than 1 mg/L) of dissolved Zn were observed in groundwater samples from drive-point wells that were previously installed by a consultant. Zn concentrations in samples from U1632 (spring) and U1633 (spring) were 2 and 5.3 mg/L, respectively, whereas Zn concentrations detected in all other samples were below 6 μg/L. These high Zn concentrations in the springs likely originated from the galvanized drive-point wells.

Stable Isotopes

Stable isotopes were analyzed to help determine different chemical sources that affect flooding and the amount of mixing of the waters. The sources may have different isotopic signatures because of the type of source or chemical fractionation related to evaporative or chemical processes. Stable isotopes measured from constituents in water samples include $\delta^{18}O$, δ^2H, $\delta^{34}S$ of SO_4^{2-}, $^{87}Sr/^{86}Sr$, and $\delta^{13}C$ of DIC (table 5, in back of report).

The $\delta^{18}O$ and δ^2H data for the study area generally plotted along an inferred local meteoric water line (LMWL) that was drawn through groundwater samples collected from sites in Wawarsing (not shown); the LMWL reflects the isotopic signature of local precipitation (Kendall and Coplen, 2000). Most groundwater and surface-water samples from Wawarsing plotted along a line with a slope of about 7.5. Water samples from the Rondout Reservoir plot along a slightly different meteoric water line (MWL), mostly due to seasonal evaporation that varies in intensity as summer progresses, which causes a linear pattern that deviates from the local line. The $\delta^{18}O$ and δ^2H values in RWB Tunnel water vary seasonally as a result of evaporative concentration of the heavier isotopes, ^{18}O and ^2H. Water samples collected during the warmer months are distinctly heavier in $\delta^{18}O$ and δ^2H values than those in water from the RWB Tunnel and water from bedrock wells. Values of $\delta^{18}O$ and δ^2H in rainfall also vary locally and at different altitudes (Coplen and Kendall, 2000); the higher altitude at the Rondout Reservoir (840 ft NAVD 88) compared to the Wawarsing study area (about 280 ft NAVD 88) could account for part of this deviation.

The isotope ratios of $\delta^{34}S$ of SO_4^{2-} in groundwater samples ranged from -11.5 to 31.6 per mil (table 5, in back of report) and appear to reflect several processes and mixtures of sources. The $\delta^{34}S$ of SO_4^{2-} in water samples from most bedrock wells are much heavier and have higher SO_4^{2-} concentrations, as compared to water samples from wells screened in unconsolidated deposits, springs, and surface water.

Strontium (Sr) is a useful isotope for tracing water sources because the $^{87}Sr/^{86}Sr$ ratio does not fractionate during evaporation or precipitation and because Sr derived from any mineral will retain the same ratio in water (Bullen and Kendall, 1995). Sr in groundwater results from its interaction with aquifer material and should have a range of $^{87}Sr/^{86}Sr$ ratios similar to geologic material. Strontium concentrations are greater and $^{87}Sr/^{86}Sr$ ratios more depleted in groundwater samples from some bedrock wells (U1630, U1631, and U1647), as compared to other samples (table 5, in back of report), and likely reflect the isotopic signature from a different aquifer source and (or) the extent of water-rock interaction of this source.

The $\delta^{13}C$ values for DIC in groundwater samples ranged from -23.5 to -8.17 per mil with a median of -14 per mil (table 5, in back of report). The slightly heavier $\delta^{13}C$ of DIC in water samples from bedrock wells (-13.1 per mil at U1628; table 5, in back of report) could be related to the weathering of

calcite in carbonate rocks, which contain heavier $\delta^{13}C$ values. Many of the bedrock well samples are at or near saturation with respect to calcite (table 3, in back of report) and may indicate dissolution of calcite at some point along their flow paths. The $\delta^{13}C$ of DIC in surface-water samples (median of -13.5 for all Lippman Lake and Rondout Reservoir samples) also could be enriched during summer months by algal blooms; the $\delta^{13}C$ values for DIC in the Lippman Lake sample collected on July 2, 2009, was -8.17 per mil.

Groundwater Age

Samples were collected to estimate groundwater ages using the following tracers: ^3H, SF_6, and CFCs. Apparent groundwater age is defined as the time elapsed since recharge of a sampled parcel of water. Concentrations of ^3H were measured in several wells to determine whether the water was older than 1953 (prior to nuclear atmospheric weapons testing) or younger.

Dissolved gas concentrations were measured to esti-mate the temperature of groundwater at the time of recharge, because the solubility of atmospheric tracers varies as a func-tion of temperature, and to calculate the amounts of excess air and N_2 (table 4, in back of report). Recharge temperatures estimated from Ar and N_2 dissolved gas concentrations varied among wells. The ratio of these dissolved gases (N_2 and Ar) in water samples from several bedrock wells, including U1628, U1631, and U1630, indicate large amounts of excess air. Excess air consists of air trapped in pores that dissolves in groundwater, typically after a rapid rise in the water table, or some other source of atmospheric gases. Dissolved gas concentrations in all samples indicate that there was little or no excess N_2, which can result from the reduction of NO_3^-, con-tributing to excess air. The ratio of dissolved gases in samples from several wells and a spring also appeared to be altered by degassing. The degassing was possibly caused by the genera-tion of CH_4 and H_2S gas bubbles resulting from organic-matter decomposition or other microbial processes that preferentially remove N_2, which is less soluble than Ar. As a result of these gas problems in the samples (as described in "age tracer notes" in table 4, in back of report), the recharge temperatures, excess air volumes, and age-tracer concentrations of several bedrock wells could not be determined with confidence. These bedrock wells include U1628, U1631, U1630, and U1647.

Dating groundwater with ^3H is qualitative at best, but can be useful in recognizing post-nuclear testing water, and can be used together with other tracers to estimate mixing of groundwater from various sources. Concentrations of ^3H in samples from springs or wells screened in the unconsolidated deposits ranged from less than 0.03 picoCuries per liter (pCi/L) in well U1637, which had an upward-flow gradient, to 60 pCi/L in well U1666, a basement spring sample collected on June 23, 2009 (table 4, in back of report). These ranges in values reflect, in part, the high seasonal and annual variations of ^3H observed in precipitation (Clark and Fritz,

1997). Concentrations of ^3H in samples from bedrock wells ranged from <0.03 to 60 pCi/L. Samples from wells that had low ^3H concentrations (<10 pCi/L) could be current or have substantial components of old water that were recharged before 1953. The low ^3H concentration (<0.03 pCi/L) in the groundwater sample from unconsolidated aquifer well U1637 indicates that the water likely was recharged before 1953. The sample from U1641—the adjacent, deeper well screened in unconsolidated deposits—also had a low ^3H concentration (1.1 pCi/L) compared to other unconsolidated aquifer wells and is consistent with the upward-head gradient at that location, indicating that older groundwater is flowing upward from bedrock. The upper range value of 60 pCi/L in a sample from the well U1666 basement spring indicates that either the water was recharged during the ^3H peak in the early 1960s or that the water was affected by ^3H contamination, possibly from a nearby landfill. The early 1960s recharge date is unlikely, given the young apparent recharge years indicated by the age tracers SF_6, CFC-11, CFC-12, and CFC-113, as discussed later in this section.

Results of the CFC and SF_6 age tracers for samples from several of the wells screened in unconsolidated deposits and springs showed conflicting apparent ages and recharge years. The apparent SF_6 ages generally were younger than those of CFC ages, apparently caused by the degradation of CFCs, which results in erroneously young apparent ages. The CFC-11 and CFC-113 tracers are prone to degradation under reduc-ing conditions. Other limitations of CFCs include problems with dating extremely young waters (Hunt and others, 2005), issues with mixing of waters of varying age (Goode, 1996; Bethke and Johnson, 2002; Weissman and others, 2002), and the leveling off or declining of atmospheric concentrations over time (Plummer and Busenberg, 1999). The SF_6 ages of samples from wells screened in unconsolidated deposits and springs seemed more reasonable; recharge years of most springs or wells ranged from 2003.0 to 2009.5 and indicate short flow paths from the point of groundwater recharge. The exception is the sample from well U1641, which had an appar-ent SF_6 recharge year of 1975–76. Adequate flow could not be obtained from nearby well U1637 to produce dissolved-gas or age-tracer samples, but the upward-flow gradient at this location is consistent with the older recharge year and a longer flow path.

CFC age-tracer samples also were collected from Lippman Lake and Rondout Reservoir because they could be important sources of groundwater in the study area. The presence of CFC-11, CFC-12, and CFC-113 in samples from both surface-water bodies showed degradation, which is common in northern temperate lakes owing to organic-rich sediments and anoxic conditions (Walker and others, 2007). Recharge temperatures were estimated for Lippman Lake effluent and Rondout Reservoir samples because dissolved gas samples were not collected at these sites. The water-sample temperature at the time of collection was used for recharge temperatures at Rondout Reservoir. At Lippman Lake, the mean annual air temperature (10°C) was used for the sample

collected on June 23, 2009; for the sample collected on December 22, 2009, the mean air temperature for the previous 2 months, November and December (7°C), was used for the estimated recharge temperature because it was judged to be more representative of water in this shallow water body during this time of year (table 4, in back of report).

As discussed earlier in this section, most of the samples from bedrock wells had interference problems with dissolved gases, either because of excess air from trapped bubbles in recharge water or degassing from high concentrations of H_2S and CH_4. Water samples from three wells, U1629, U1625, and U1645, did not appear to have these problems, at least enough to prevent apparent-age estimates. A sample from U1629, which is located near the RWB Tunnel, had an apparent "piston recharge" year of early 1950s, consistent with other chemistry that showed little or no similarity to the tunnel water chemistry. "Piston recharge" assumes that a tracer becomes incorporated in a parcel of water that moves from the recharge area with the mean velocity of groundwater. The CFC apparent-recharge year based on CFCs was similar to that based on SF_6. Well U1625 was sampled on two occasions. The June 24, 2009 sample, collected during a period of nearby basement flooding, indicated consistency between the SF_6 recharge year of 2003 and the CFC-12 apparent-recharge year of 2002.8. CFC-11 and CFC-113 are more prone to degradation under reducing conditions and likely are not as reliable in this sample. The degradation of these CFCs indicates that some component of reducing water contributes to the well. The later sample was collected on December 14, 2009, during a period of lower head pressure in the tunnel (Stumm and others, 2012), and the apparent SF_6 recharge year of 2000.5 indicates a greater component of older water, apparently caused by a lower contribution of water from the RWB Tunnel and a greater contribution from ambient groundwater. The reducing properties of ambient water from bedrock also might have resulted in degradation of CFCs in the sample collected on December 14, 2009, at well U1625. A sample from U1645 had an SF_6 apparent recharge year of 1970, but one or more of the CFCs was degraded and yielded older ages.

Summary and Conclusions

The U.S. Geological Survey and the New York City Department of Environmental Protection conducted a cooperative study to evaluate the water chemistry and potential effects of flooding in Wawarsing, N.Y. These data, together with hydrogeologic data, can be used to improve the understanding of source waters and groundwater-flow patterns and pathways and to help assess mixing of the different source waters in water samples.

Major-ion concentrations in water samples collected during the study show differences depending on the sample type, depth, and location. Water samples from most wells screened in unconsolidated deposits and springs had a greater percentage of calcium as compared to other cations than samples from

bedrock wells. The exception was well U1625, which had high ratios of bicarbonate and calcium relative to other ions similar to samples from the unconsolidated aquifer wells and the surface-water samples. Samples from bedrock wells generally had relatively higher concentrations of sulfate (SO_4^{2-}) as compared to other anions. Water samples from most wells screened in unconsolidated deposits and springs were greater in bicarbonate and carbonate than in SO_4^{2-} and chloride, as compared to samples from bedrock wells. Differences in calcite and gypsum saturation indexes in water samples were evident among (1) most bedrock wells and wells screened in unconsolidated aquifer wells and (2) water samples collected from two bedrock wells during high head pressure and water samples collected during low head pressure of the Rondout–West Branch (RWB) Tunnel. Concentrations of trace constituents, including strontium (Sr), barium (Ba), arsenic (As), boron (B), lithium (Li), nickel (Ni), and lead (Pb), generally were higher in samples from bedrock wells than in samples from wells screened in unconsolidated deposits and in water from RWB Tunnel or in the lake at Lippman Park.

Nitrate (NO_3^-) plus nitrite (NO_2^-) concentrations ranged from less than minimum reporting levels (MRLs) in water samples with reducing redox characteristics to 0.88 milligram per liter (mg/L) as nitrogen (N) for a domestic well in a residential area with onsite septic-tank drainfields (table 3, in back of report). Concentrations of NO_2^- were less than the MRL of 0.008 mg/L in all but two samples; therefore, NO_3^- plus NO_2^- is referred to herein as "NO_3^-." The median concentration of NO_3^- for wells in the study area was less than 0.5 mg/L as N, and samples at more than one-half of the sites were below the reporting level of 0.04 mg/L as N. Urban septic-system leachate and lawn fertilizer are the major sources of NO_3^- in the study area and can affect shallow groundwater quality.

Dissolved gas concentrations were measured to estimate the temperature of groundwater at the time of recharge, because the solubility of atmospheric tracers varies as a function of temperature, and to calculate the amount of excess air and excess nitrogen (N_2). Recharge temperatures estimated from argon (Ar) and N_2 dissolved gas concentrations varied among wells. Most of the samples from bedrock wells had interference problems with dissolved gases, either because of excess air from trapped bubbles in recharge water or degassing from high concentrations of hydrogen sulfide (H_2S) and methane (CH_4). The ratio of N_2 and Ar in water samples from several bedrock wells, including U1628, U1631, and U1630, indicated large amounts of excess air and (or) degassing.

Age-tracer data provided useful information on pathways of the groundwater-flow system but were limited by inherent problems with dissolved gas data. Tritium concentrations in samples from springs or wells screened in unconsolidated deposits ranged from less than 0.03 picoCurie per liter (pCi/L) in an unconsolidated aquifer well with an upward-flow gradient to 60 pCi/L in a basement spring sample. Results of the chlorofluorocarbon (CFC) and sulfur hexafluoride (SF_6) age tracers for some of the wells screened in unconsolidated deposits and springs showed conflicting apparent ages and

recharge years. The apparent SF_6 ages generally were younger than those of CFC ages, apparently caused by the degradation of CFCs that resulted in erroneously young apparent ages. The SF_6 ages of the wells screened in unconsolidated deposits and springs seemed more reasonable; recharge years of most springs or shallow wells ranged from 2003 to 2010 (current) and indicate short flow paths from the point of groundwater recharge. The exception is an apparent age of early to mid-1970s for a sample from well U1641 that is screened in poorly permeable sediments and had an upward-flow gradient.

Water samples from three bedrock wells, U1629, U1625, and U1645, did not appear to have a problem with dissolved gases that prevented apparent-age estimates. A sample from U1629, which is located near the RWB Tunnel, had an apparent piston recharge date of early 1950s, consistent with other chemistry that showed little or no similarity to the water chemistry in the tunnel. The apparent recharge year based on CFCs was similar to that of SF_6. Well U1625 was sampled on two occasions. The sample collected June 24, 2009, during a period of nearby basement flooding, indicated consistency between the SF_6 recharge year of 2003 and the CFC-12 apparent recharge year of 2002.8. CFC-11 and CFC-113 are more prone to degradation under reducing conditions and likely are not as reliable in this sample. The degradation of these CFCs indicates that some component of reducing water contributes to the well. The later sample was collected on December 14, 2009, during a period of lower head pressure in the tunnel (Stumm and others, 2012), and the apparent SF_6 recharge year of 2000.5 indicates a greater component of older water, apparently caused by less contribution of water from the RWB Tunnel and greater contribution from ambient groundwater. A sample from U1645 had an SF_6 apparent recharge year of 1970.

Stable isotopes were analyzed to help determine different chemical sources that affect flooding and the amount of mixing of the waters. Differences in stable-isotope ratios among $\delta^{18}O$, ^2H, $\delta^{34}S$ of SO_4^{2-}, $^{87}Sr/^{86}Sr$, and $\delta^{13}C$ of dissolved inorganic carbon (DIC) indicate potential for distinguishing water in Delaware–West Branch Tunnel from native groundwater. The $\delta^{18}O$ and δ^2H values in water from the RWB Tunnel vary seasonally as a result of evaporative concentration of the heavier isotopes, ^{18}O and ^2H. Water samples collected during the warmer months showed distinct differences between water from the RWB Tunnel and water from bedrock wells. The $\delta^{34}S$ of SO_4^{2-} in water samples from most bedrock wells are much heavier and have higher SO_4^{2-} concentrations, as compared to water samples from wells screened in unconsolidated deposits, springs, and surface water. Strontium concentrations are greater and $^{87}Sr/^{86}Sr$ ratios are more depleted in groundwater samples from most bedrock wells, as compared to samples from surface-water sources, springs, and wells screened in unconsolidated deposits in the study area. The heavier $\delta^{13}C$ of DIC in water samples from bedrock wells could be related to the weathering of calcite in carbonate rocks, which contain heavier $\delta^{13}C$ values. Many of the bedrock well samples were at or near saturation with respect to calcite and may indicate dissolution of calcite at some point along their flow paths.

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Tables 3–5

Table 3. General chemical characteristics, concentrations of major elements and nutrients, saturation indexes, and percent charge balance error in surface-Branch Tunnel in Lackawack, Ulster County, New York, 2009–11.

[μS/cm, microsiemens per centimeter at 25 degrees Celsius; SI, saturation index; concentrations in milligrams per literunless indicated otherwise; Ca, calcium; Mg, magne-N, nitrogen; PO_4^{3-}, orthophosphate; --, not measured; NA, not applicable; <, less than; E, estimated value below minimum reporting level]

Well identifier	Date	Sample time	Temperature, water (degrees Celsius)	pH	Specific conductance (μS/cm)	Depth of well (feet below land surface)	Dissolved solids	Hardness, as CaCO3	Ca	Mg	K	Na	Alkalinity	HCO3-	CO3 2-	Cl-	Br-	Cl.Br mass ratio
U1626	12/15/2009	1500	8.8	6.3	94	10	67	43	14	1.9	0.43	2.3	41	50	<0.1	1.2	0.01	120
U1627	6/23/2009	1200	15.8	6.8	499	15	338	160	56	6.0	1.35	52	--	160	<0.1	96	0.04	2,400
U1627	4/1/2010	0900	6.8	6.9	551	15	281	130	45	4.5	0.94	53	120	140	<0.1	86	0.03	2,867
U1637	8/31/2010	1400	15.6	7.8	226	26.5	135	104	32	5.6	1.25	4.2	90	110	<0.1	1.6	0.011	145
U1641	4/20/2010	1300	11.6	8.0	224	117	137	110	34	6.1	0.94	3.8	60	73	<0.1	1.9	0.01	190
U1641	4/20/2010	1301	--	8.0	224	117	140	110	33	6.0	0.86	3.8	60	73	<0.1	1.9	0.01	190
U1663	8/31/2010	1400	14.5	8.2	286	47	167	79	23	5.1	1.9	32	130	160	<0.1	9.0	0.065	138
U1673	11/30/2011	1200	11.6	7.7	345	180	188	160	50	9.3	0.68	8.4	120	150	<0.1	21	0.02	1,050
U1670	11/30/2011	1000	12.2	8.0	350	180	197	160	49	8.3	0.77	12	120	140	<0.1	30	0.02	1,500
U1632	9/14/2009	1730	11.3	6.2	105	NA	54	38	12	2.1	0.43	1.7	37	46	<0.1	1.1	0.01	110
U1633	9/15/2009	1200	16.1	6.3	85	NA	43	22	6.7	1.4	0.96	1.2	22	27	<0.1	1.1	0.01	110
U1667	9/15/2009	1400	13.4	6.9	66	NA	41	23	6.8	1.5	0.69	1.5	16	21	<0.1	1.1	0.01	110
U1668	7/1/2009	1300	14.8	6.9	78	NA	53	29	8.3	2.1	0.47	2.0	22	28	<0.1	1.4	0.01	140
U1666	6/23/2009	1400	13.6	6.7	284	NA	195	160	55	5.0	1.6	7.3	150	180	<0.1	7.3	0.01	730
U1666	3/31/2010	1600	7.5	6.8	332	NA	189	150	54	4.7	1.3	4.5	150	180	<0.1	6.2	0.01	620
U1665	3/31/2010	1200	6.4	6.0	60	NA	46	18	5.8	0.92	1.2	2.0	13	16	<0.1	4.1	0.01	410
Lippman Lake effluent	6/24/2009	1330	--	--	--	NA	--	--	--	--	--	--	--	--	--	--	--	--
Lippman Lake effluent	7/2/2009	1300	22.7	7.6	52	NA	53	41	13	2.4	0.50	2.3	36	43	<0.1	1.9	0.01	190
Lippman Lake effluent	9/1/2009	1230	--	--	--	NA	--	--	--	--	--	--	--	--	--	--	--	--
Lippman Lake effluent	9/16/2009	1300	21.2	7.3	217	NA	157	120	38	6.4	0.90	5.7	110	140	1	7.7	0.04	193
Lippman Lake effluent	10/13/2009	1515	13.8	7.4	231	NA	--	--	--	--	--	--	--	--	<0.1	--	--	--
Lippman Lake effluent	12/15/2009	1000	0.8	5.5	86	NA	60	32	9.3	2.2	0.37	2.7	29	35	<0.1	2.2	0.01	220
Lippman Lake effluent	4/1/2010	1200	11.2	7.2	97	NA	65	39	12	2.2	0.42	2.4	36	44	<0.1	2.7	0.01	270
01366400	6/23/2009	0930	10.3	6.4	60	NA	36	14	4	0.95	0.43	4.2	17	21	<0.1	6.9	0.01	690
01366400	9/1/2009	1030	15.4	6.2	45	NA	26	13	3.8	0.82	0.44	3.5	7.0	9.0	<0.1	5.7	0.01	570
01366400	10/13/2009	1420	15.9	7.4	50	NA	--	--	--	--	--	--	--	--	--	--	--	--
01366400	10/13/2009	1425	--	--	--	NA	--	--	--	--	--	--	--	--	--	--	--	--
01366400	12/22/2009	1110	6.7	7.2	53	NA	38	15	4.2	0.98	0.51	3.7	12	14	<0.1	5.8	0.01	580
01366400	4/1/2010	1000	5.4	7.1	51	NA	37	12	3.6	0.82	0.49	3.4	10	12	<0.1	6.0	0.01	600
U1625	6/24/2009	1100	11	7.5	134	275	84	63	20	2.8	0.65	5.5	57	70	0.1	7.5	0.02	375
U1625	12/14/2009	1000	10.8	7.2	413	275	306	250	75	14	1.1	10	210	260	<0.1	9.3	0.04	233
U1625	4/7/2011	1900	--	7.6	109	275	63	--	12	1.7	0.59	5.2	30	37	<0.1	7.3	<.01	1,450
U1629	6/24/2009	0800	11.8	7.8	780	118	480	200	61	11	1.0	87	160	190	0.4	150	1.4	107
U1629	4/7/2011	1100	--	7.0	370	118	260	--	64	10	1.0	18	160	190	--	40	0.32	125
U1629	4/7/2011	0900	--	7.3	370	118	240	--	64	10	0.96	9.1	160	200	--	19	0.11	173
U1628	7/2/2009	1000	12.8	8.1	409	200	320	190	44	20	1.0	23	66	80	0.4	20	0.15	133
U1630	9/15/2009	1700	12.8	7.9	797	NA	580	290	65	31	1.5	48	8	9.8	<0.1	45	0.45	100
U1631	9/16/2009	1000	12.8	7.6	1,170	NA	930	540	150	37	2.3	46	96	120	<0.1	58	0.53	109
U1631	9/16/2009	1001	12.8	7.6	1,170	NA	920	540	150	37	2.3	46	96	120	<0.1	57	0.54	106
U1631	12/14/2009	1630	11.5	8.0	905	NA	850	500	130	36	2.2	42	95	120	<0.1	54	0.52	104
U1647	4/21/2010	1300	15.8	7.9	1,640	NA	1,100	460	110	39	5.4	170	100	130	<0.1	250	2.2	114
U7017	9/20/2011	1200	12.1	6.9	236	NA	140	36	10	2.4	1.7	37	99	120	<0.1	18	0.13	138
U3772	9/20/2011	1200	11.6	6.8	232	NA	140	49	15	2.3	2.3	30	120	140	<0.1	1.7	<0.01	680
U1645	9/21/2011	1200	12.9	7.2	443	NA	20	200	53	16	1.1	11	170	210	<0.1	7.6	0.036	210
U1644	9/21/2011	1200	14.3	7.8	1,060	NA	550	200	46	20	1.2	130	160	190	<0.1	210	1.7	120

Table 3   29

water and groundwater samples from a lake, springs, and wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West

sium; K, potassium; Na, sodium; HCO_3^-, bicarbonate; Cl^-, chloride; Br^-, bromide; F^-, fluoride; SiO_2, silica; SO_4^{2-}, sulfate; NH_4^+, ammonia; NO_3^-, nitrate; NO_2^-, nitrite;

F^-	SiO_2	SO_4^{2-}	NH_4^+	NO_3^- plus NO_2^- as N	NO_2^- as N	Ortho-PO_4^{3-} as P	Total N	Water type	log [Ca^{+2}]	log [Mg^{+2}]	SI (Calcite)	SI (Dolo-mite)	SI (Gypsum)	SI (Fluorite)	SI (Quartz)	Charge balance error (per-cent)
<.08	9.4	8.7	<.020	0.14	<.002	E.005	0.21	Ca-HCO$_3$	-3.5275	-4.1936	-2.4306	-5.6473	-3.073	-3.5058	0.4295	-3.2
E.05	5.2	14	<.020	0.51	<.002	0.031	0.60	Ca-Na-Cl-HCO$_3$	-3.0207	-3.7667	-0.8423	-2.4281	-2.4732	-3.5589	0.0565	-0.21
E.06	4.4	17	<.020	0.71	<.002	0.024	0.80	Na-Ca-Cl-HCO$_3$	-3.1021	-3.8803	-1.0107	-2.9587	-2.4423	-3.3503	0.1292	-1.7
0.135	2.5	21	0.039	<0.04	<0.002	0.016	<.10	Ca-HCO$_3$	-3.2221	-3.7646	-0.1996	-0.9424	-2.4445	-2.8685	-0.2635	0.12
0.1	12	27	0.033	<0.04	<.002	0.013	<.10	Ca-Mg-HCO$_3$-SO$_4$	-3.2025	-3.7301	-1.0795	-2.6212	-2.331	-3.169	0.3483	14
0.1	12	27	0.032	<0.04	<.002	0.012	<.10	--	-2.7452	-3.1179	-1.0795	-2.6212	-0.8018	-2.2993	0.5134	13
0.44	1.6	3.4	0.092	<0.04	<0.002	0.02	<.10	Na-Ca-HCO$_3$	-3.3642	-3.8067	0.2152	-0.0306	-3.3739	-1.9723	-0.43	0.12
<.04	8.6	25	0.013	<0.04	<.001	0.006	<.05	Ca-HCO$_3$-Cl	-3.0528	-3.5639	-0.2499	-0.0689	-2.2404	-4.9295	0.3296	-1.1
0.06	8.6	20	0.018	<0.04	<.001	0.006	<.05	Ca-Mg-HCO$_3$	-3.0567	-3.6092	-0.0889	-0.7896	-2.3377	-3.3666	0.3414	-1.5
<.08	7.1	14.2	<.020	E.03	<.002	0.020	<.10	Ca-HCO$_3$-SO$_4$	-3.6176	-4.146	-2.6175	-5.837	-2.9528	-3.6333	0.2627	-13
<.08	7.7	11.0	<.020	0.04	<.002	0.013	0.12	Ca-Zn-HCO$_3$-SO$_4$	-3.8477	-4.3262	-2.9039	-6.2791	-3.2865	-3.9474	0.2222	-15
<.08	8.3	12.6	<.020	<0.04	<.002	0.024	E.08	Ca-Mg-HCO$_3$-SO$_4$	-3.8373	-4.2704	-2.4642	-5.3985	-3.2048	-3.8786	0.2993	-6.5
E.04	8.2	11.4	E.014	E.02	<.002	0.026	0.19	Ca-Mg-HCO$_3$-SO$_4$	-3.7575	-4.1308	-2.2168	-4.8205	-3.1787	-4.4212	0.2729	-3.8
<.08	6.0	13.1	<.020	0.16	<.002	0.042	0.33	Ca-HCO$_3$	-3.0073	-3.8304	-0.8851	-2.6269	-2.4753	-3.0961	0.1585	-0.2
E.05	4.7	13.9	<.020	0.48	<.002	0.041	0.57	Ca-HCO$_3$	-3.0086	-3.8475	-0.8976	-2.7793	-2.4337	-3.4084	0.1498	-1.6
<.08	4.6	6.41	0.027	0.35	E.001	0.026	0.45	Ca-HCO$_3$-SO$_4$-Cl	-3.8997	-4.4761	-3.6296	-8.0028	-3.5388	-3.9239	0.1557	-5.4
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
E.04	4.7	5.22	<.020	<0.04	<.002	E.007	0.28	Ca-Mg-HCO$_3$	-3.5763	-4.0878	-1.0385	-2.4867	-3.3565	-4.3451	-0.0934	4.0
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
0.12	5.4	5.87	<.020	<0.04	<.002	E.004	0.25	Ca-HCO$_3$	-3.1497	-3.7022	-0.4377	-1.346	-2.9531	-2.9777	-0.0091	1.3
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
<.08	7.5	9.64	<.020	E.02	E.001	E.004	0.17	Ca-Mg-HCO$_3$-SO$_4$	-3.7075	-4.1121	-3.6966	-8.0853	-3.1722	-3.6651	0.4671	-4.4
E.04	4.8	7.10	<.020	<0.04	<.002	E.004	0.1	Ca-HCO$_3$	-3.5962	-4.119	-1.6173	-3.833	-3.2284	-4.2108	0.0928	-2.4
<.08	2.0	4.86	0.029	0.20	<.002	<.008	0.31	Ca-Na-HCO$_3$-Cl	-4.0529	-4.4652	-3.2022	-6.9085	-3.8186	-4.0851	-0.2784	-16
<.08	1.7	4.42	0.031	0.12	E.001	<.008	0.24	Ca-Na-Cl-HCO$_3$-SO$_4$	-4.0756	-4.5221	-3.7123	-7.8749	-3.8838	-4.3282	-0.4322	1.2
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
<.08	2.0	4.55	<.020	0.16	<.002	<.008	0.20	Ca-Na-HCO$_3$-Cl	-4.0297	-4.4461	-2.5853	-5.748	-3.8142	-3.9614	-0.202	-4.5
<.08	2.1	4.48	<.020	0.18	<.002	<.008	0.25	Ca-Na-HCO$_3$-Cl-SO$_4$	-4.098	-4.5207	-2.8753	-6.3607	-3.8822	-4.0124	-0.1634	-8.0
<.08	3.0	11.1	<.020	0.26	<.002	E.006	0.34	Ca-HCO$_3$	-3.3886	-4.0324	-0.9162	-2.5553	-2.8541	-3.409	-0.1131	-3.1
E.05	7.8	44.0	<.020	0.88	0.020	E.005	0.94	Ca-Mg-HCO$_3$	-2.9054	-3.4089	-0.1906	-0.9673	-1.8878	-3.3838	0.3132	-0.33
<0.04	2.7	9.2	<0.01	0.24	<0.001	0.0058	--	--	-3.5851	-4.2338	-1.285	-3.2977	-3.1062	-4.4468	-0.152	0.69
0.11	12	23	0.18	<0.04	<.002	0.048	0.20	Na-Ca-Cl-HCO$_3$	-3.0039	-3.5328	0.1928	-0.2079	-2.2709	-2.8165	0.4901	-1.0
0.1	11	25	--	--	--	--	--	Ca-HCO$_3$-Cl	-2.96	-3.5268	-55.03	-1.7322	-2.1732	-2.6838	0.447	-1.0
0.1	11	26	--	--	--	--	--	Ca-HCO$_3$	-2.96	-3.5477	-0.4101	-1.3424	-2.1662	-2.9534	0.3182	-0.87
0.19	10	140	0.16	<0.04	<.002	0.013	0.18	Ca-Mg-Na-SO$_4$-HCO$_3$	-3.1628	-3.281	-0.0319	-0.2293	-1.6361	-2.5125	0.4056	1.2
0.32	9.1	270	0.12	<0.04	<.002	E.006	0.12	Ca-Mg-Na-SO$_4$	-3.0424	-3.149	-1.0502	-2.2541	-1.2671	-1.967	0.345	5.2
0.16	13	470	0.16	<0.04	<.002	0.009	0.14	Ca-Mg-SO$_4$	-2.7527	-3.1256	0.0235	-0.3731	-0.8111	-2.1589	0.5135	-1.5
0.19	13	470	0.16	E.03	<.002	0.008	0.15	Ca-Mg-SO$_4$	--	--	--	--	--	--	--	-1.3
0.16	13	430	0.15	<0.04	<.002	E.006	0.15	Ca-Mg-SO$_4$	-2.7913	-3.1246	0.3555	0.3077	-0.8747	-2.3221	0.535	-1.6
0.38	9.9	330	0.58	<0.04	<.002	0.013	0.55	Na-Ca-Cl-SO$_4$	-2.8605	-3.0973	0.2891	0.344	-1.0832	-1.7175	0.3346	2.9
0.53	7.1	0.13	0.18	<0.02	<0.001	0.0079	0.21	Na-Ca-HCO$_3$-Cl	-3.7061	-4.1093	-1.5821	-3.6268	-5.1023	-2.1041	0.2516	3.1
0.31	6.7	0.31	0.4	<0.02	<.001	0.015	0.44	Na-Ca-HCO$_3$	-3.5308	-4.1321	-0.0561	-4.554	-4.554	-2.3871	0.2283	0.86
0.09	12	49	0.1	<0.02	<.001	0.005	0.13	Ca-Mg-HCO$_3$-SO$_4$	-3.0497	-3.405	-0.3878	-1.1118	-1.9684	-3.0443	0.4668	1.7
0.34	9.4	26	0.32	<0.02	<.001	0.099	0.36	Na-Ca-Cl-HCO$_3$	-3.139	-3.2759	0.0866	0.0144	-2.3723	-2.0249	0.3369	0.68

Table 4. Concentrations of dissolved gases and age tracers, redox properties, and apparent age of surface-water and groundwater samples from a lake, New York, 2009–11.

[--, not measured; <, less than; E, estimated value below minimum reporting level; NP, age estimate not possible; C, current age; apparent recharge years and ages for redox, oxidation–reduction; O_2, oxygen reducing, NO_3^-, nitrate reducing; Mn, manganese reducing; Fe, iron reducing; SO_4^{2-}, sulfate reducing; $FeSO_4$, iron- to sulfate-unless otherwise noted; mol/kg, moles per kilogram; pptv, parts per trillion by volume; pmol/kg, picomoles per kilogram; cm^3STP/L, cubic centimeters at standard

Well identifier	Date	Sample time	Dissolved oxygen (DO)	Sulfide (H_2S)[1]	Methane (CH_4)[1]	Nitrogen (N_2)[1]	Argon (Ar)[1]	Carbon dioxide (CO_2)[1]	Redox class category	Predominant redox process	Recharge temp (degrees Celsius)[1]	Excess air (cm^3 STP/L)[2]	Tritium, picocuries per liter[2]	SF_6 in water (femtomol/kg)[3]	Calculated SF_6 partial pressure (pptv)[3]
U1626	12/15/2009	1500	4.4	0.002	<0.001	21	0.74	42	Mixed (oxic/sulfidic)	O_2-SO_4^{2-}	8.6	2.3	26.1	2.86	5.55
U1627	6/23/2009	1200	5.6	<0.002	--	--	--	--	Oxic	O_2	--	--	--	--	--
U1627	4/1/2010	0900	8.6	<0.002	<0.001	23	0.86	30	Oxic	O_2	6	3.9	27.5	3.59	5.65
U1637	8/31/2010	1400	3	--	--	--	--	--	Mixed (oxic-methanogenic)	O_2-Fe(III)	--	--	<0.03	--	--
U1641	4/20/2010	1300	0.8	0.014	0.002	22	0.75	1.6	Mixed (oxic-methanogenic)	O_2-CH_4	10.1	4.1	1.1	0.273	0.479
U1641	4/20/2010	1301	--	--	--	--	--	--	--	--	10.1	4.1	1.1	0.279	0.489
U1663	8/31/2010	1400	2.9	--	--	--	--	--	Oxic	O_2	--	--	17.7	--	--
U1673	11/30/2011	1200	0.5	<0.002	0.0087	22.0	0.76	3.6	Mixed (oxic/methanogenic)	O_2-CH_4	7.8	3.8	0.20	1.03	1.77
U1670	11/30/2011	1000	0.6	<0.002	0.012	23.4	0.77	2.9	Mixed (oxic/methanogenic)	O_2-CH_4	9.6	6.0	0.30	--	--
U1632	9/14/2009	1730	5.9	--	<0.001	20	0.72	30	Oxic	O_2	10.0	0.7	14.8	2.50	6.25
U1633	9/15/2009	1200	8.5	--	--	--	--	--	Oxic	O_2	8.7	1.5	--	--	--
U1667	9/15/2009	1400	9.9	--	--	--	--	--	Mixed (oxic/anoxic)	O_2-Mn(IV)	--	--	--	--	--
U1668	7/1/2009	1300	9.5	--	--	--	--	--	Mixed (oxic/anoxic)	O_2-Mn(IV)	--	--	--	--	--
U1666	6/23/2009	1400	5.0	--	<0.001	17	0.64	74	Oxic	O_2	12.3	0	60	2.39	6.77
U1666	3/31/2010	1600	7.7	--	<0.001	23	0.84	44	Oxic	O_2	6	2.0	26.9	3.42	5.75
U1665	3/31/2010	1200	6.4	E0.001	<0.001	24	0.88	28	Oxic	O_2	1.2	2.2	24.8	3.72	5.55
Lippman Lake effluent	6/24/2009	1330	--	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	--	--	--	--	--	--
Lippman Lake effluent	7/2/2009	1300	8.9	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	O_2-Mn(IV)	10*	0	--	--	--
Lippman Lake effluent	9/1/2009	1230	--	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	--	--	--	--	--	--
Lippman Lake effluent	9/16/2009	1300	11	--	--	--	--	--	Oxic	O_2	--	--	--	--	--
Lippman Lake effluent	10/13/2009	1515	--	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	--	--	--	--	--	--
Lippman Lake effluent	12/15/2009	1000	7.3	--	--	--	--	--	Mixed (oxic/anoxic)	O_2-Mn(IV)	7#	0	--	--	--
Lippman Lake effluent	4/1/2010	1200	9.9	--	--	--	--	--	Mixed (oxic/anoxic)	O_2-Mn(IV)	--	--	--	--	--
01366400	6/23/2009	0930	9.6	--	--	--	--	--	Oxic	O_2	10*	0	--	--	--
01366400	9/1/2009	1030	--	--	--	--	--	--	Oxic	O_2	--	--	--	--	--
01366400	10/13/2009	1420	--	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	--	--	--	--	--	--
01366400	10/13/2009	1425	--	--	--	--	--	--	$O_2 \geq 0.5$ mg/L	--	--	--	--	--	--
01366400	12/22/2009	1110	--	--	--	--	--	--	Oxic	O_2	7*	0	--	--	--

Table 4   **31**

springs, and wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster County,

SF$_6$ and CFCs have been corrected for excess air; SF$_6$, Sulfur hexafluoride; CFC, chlorofluorocarbon; bold text indicates most reasonable apparent age or recharge year; reducing; CH$_4$, methanogenic; mixed (Y/Z) indicates waters with different redox ranging from most oxidized (Y) to most reduced (Z); concentrations in milligrams per liter, temperature and pressure per liter; pCi, picocuries per liter]

SF$_6$ Apparent recharge year, piston flow[3]	SF$_6$ Apparent age, piston flow[3]	CFC-11 corrected concentration (pmol/kg)[3]	CFC-12 corrected concentration (pmol/kg)[3]	CFC-113 corrected concentration (pmol/kg)[3]	CFC-11 Apparent age piston flow (years)[3]	CFC-12 Apparent age piston flow (years)[3]	CFC-113 Apparent age piston flow (years)[3]	CFC-11 Apparent recharge year, piston flow[3]	CFC-12 Apparent recharge year, piston flow[3]	CFC-113 Apparent recharge year, piston flow[3]	Dissolved gas notes	Age tracer notes
2004.0	**6.0**	0.742	1.46	0.141	44.0	34.0	31.2	1966	1976	1978.8		Age based on SF$_6$; CFCs could be degraded
--	--	--	--	--	--	--	--	--	--	--	Jet pump, not sampled	
2004.5	**5.8**	4.08	3.63	0.591	32.0	14.0	21.3	1978.3	1996.3	1989.0		Age based on SF$_6$; CFCs could be degraded
--	--	--	--	--	--	--	--	--	--	--	Poor yield, gas sample not possible	
1975.5	**34.8**	0.371	0.992	0.058	47.3	37.8	37.3	1963	1972.5	1973		Early-mid 1970s age based on SF$_6$, CFC-12, CFC-113
1976.0	**34.3**	0.373	0.955	0.058	47.3	37.8	37.3	1963	1972.5	1973		Early-mid 1970s age based on SF$_6$, CFC12, CFC-113
--	--	--	--	--	--	--	--	--	--	--	Poor yield, gas sample not possible	
1986.8	25.2	44.8	4,459	0.0298	NP	NP	**44.6**	NP	NP	**1967.3**	Trace CH$_4$	Age estimated using CFC-113; CFC-12 and -11 were contaminated
--	--	--	--	--	--	--	--	--	--	--	--	--
2007.2	**2.5**	5.06	2.85	0.438	**2.2**	C	21.2	**2007.5**	C	1988.5		Late 2000s age based on SF$_6$, CFC-11, -12
--	--	--	--	--	--	--	--	--	--	--	Poor yield, gas sample not possible	
--	--	--	--	--	--	--	--	--	--	--	Poor yield, gas sample not possible	
--	--	--	--	--	--	--	--	--	--	--	--	--
2009.5	**0**	5.59	2.60	0.485	C	**3.5**	14.0	C	**2006**	1995.5	Slight degassing	Late 2000s; CFCs could be degraded
2005.0	**5.2**	5.96	3.55	0.663	24.0	**0.2**	**5.2**	1986	**2010.1**	**2005.0**		Mid-late 2000s age based on SF$_6$, and CFC-12, -113
2004.3	**6.0**	4.41	3.79	0.619	35	NP	23	1975.5	NP	1986.8		Age based on SF$_6$; CFC-12 age not possible
--	--	--	--	--	--	--	--	--	--	--		
--	--	2.36	1.97	0.231	34.5	26.5	26.0	1975.0	1983.0	1983.5		Modern; degradation of CFCs in surface water
--	--	--	--	--	--	--	--	--	--	--		
--	--	--	--	--	--	--	--	--	--	--		
--	--	--	--	--	--	--	--	--	--	--		
--	--	5.07	4.59	0.651	25.5	C	11.8	1984.5	C	1998.2		Modern; surface water CFC-11,-12, and -113 degraded
--	--	--	--	--	--	--	--	--	--	--		
--	--	6.07	3.20	0.532	C	C	14.7	C	C	1994.8		CFCs slightly higher than modern water; CFC-12, -113 contaminated
--	--	--	--	--	--	--	--	--	--	--		
--	--	--	--	--	--	--	--	--	--	--		
--	--	--	--	--	--	--	--	--	--	--		
--	--	3.54	3.15	0.50	32.5	18.5	21.5	1977.5	1991.5	1988.5		Age uncertain; CFC-11,-12, and -113 degraded

Table 4.   Concentrations of dissolved gases and age tracers, redox properties, and apparent age of surface-water and groundwater samples from a lake, New York, 2009–11.—Continued

[--, not measured; <, less than; E, estimated value below minimum reporting level; NP, age estimate not possible; C, current age; apparent recharge years and ages for redox, oxidation–reduction; O_2, oxygen reducing, NO_3^-, nitrate reducing; Mn, manganese reducing; Fe, iron reducing; SO_4^{2-}, sulfate reducing; $FeSO_4$, iron- to sulfate-unless otherwise noted; mol/kg, moles per kilogram; pptv, parts per trillion by volume; pmol/kg, picomoles per kilogram; cm3STP/L, cubic centimeters at standard

Well identifier	Date	Sample time	Dissolved oxygen (DO)	Sulfide (H_2S)[1]	Methane (CH_4)[1]	Nitrogen (N_2)[1]	Argon (Ar)[1]	Carbon dioxide (CO_2)[1]	Redox class category	Predominant redox process	Recharge temp (degrees Celsius)[1]	Excess air (cm3 STP/L)[1]	Tritium, picocuries per liter[2]	SF_6 in water (femtomol/kg)[3]	Calculated SF_6 partial pressure (pptv)[3]
01366400	4/1/2010	1000	9.9	--	--	--	--	--	Oxic	O_2	5.4&	0	--	--	--
U1625	6/24/2009	1100	3.2	<0.002	<0.001	19.0	0.72	4.5	Oxic	O_2	8	0.65	27.2	2.4	5.32
U1625	12/14/2009	1000	2.1	0.093	0.022	22.5	0.8	23.1	Mixed (oxic/ methanogenic)	O_2-CH_4	9.4	4.5	25.3	2.85	4.75
U1629	6/24/2009	0800	<0.2	0.56	15	22.0	0.78	5.5	Anoxic	$Fe(III)$-SO_4^{2-}-CH_4	7.3	3.2	19.5	0.0282	0.05
U1628	7/2/2009	1000	0.6	1.2	0.16	31.0	0.98	1.2	Mixed (oxic/ methanogenic)	O_2-CH_4	NP	NP	8.3	0.13	0.13
U1630	9/15/2009	1700	1.5	0.012	<0.001	48.0	1.4	2.2	Mixed (oxic/ sulfidic)	O_2-$Mn(IV)$-SO_4^{2-}	NP	NP	3.7	1.17	1.37
U1631	9/16/2009	1000	1.4	0.65	0.51	34.0	1.07	3.8	Mixed (oxic/ methanogenic)	O_2-$Fe(III)$-CH_4	NP	NP	2.9	0.86	1.37
U1631	9/16/2009	1001	1.4	0.65	0.5	33.0	1.05	3.8	Mixed (oxic/ methanogenic)	O_2-$Fe(III)$-CH_4	NP	NP	2.6	0.50	1.30
U1631	12/14/2009	1630	1.8	2.3	0.34	33.0	1.05	2.2	Mixed (oxic/ methanogenic)	O_2-SO_4^{2-}-CH_4	NP	NP	2.8	0.50	0.47
U1647	4/21/2010	1300	<0.2	2.0	18	36.0	1.10	3.4	Anoxic	$Mn(IV)$-CH_4	NP	NP	<0.3	0.32	0.26
U7017	9/20/2011	1200	<0.2	0.039	13	25.8	0.88	13.4	Anoxic	$Mn(IV)$-CH_4	3.0	5.4	4.1	0.0888	0.12
U3772	9/20/2011	1200	<0.2	0.006	6.2	24.0	0.83	1.3	Anoxic	$Fe(III)$-CH_4	4.5	4.3	0.70	0.446	0.66
U1645	9/21/2011	1200	0.4	0.023	0.054	22.1	0.77	6.1	Anoxic	$Mn(IV)$-CH_4	7.6	3.6	15	0.141	0.24
U1644	9/21/2011	1200	<0.2	0.80	16	23.4	0.84	2.5	Anoxic	$Mn(IV)$-CH_4	3.3	2.9	8.1	0.17	0.26

[1]Analyzed or estimated at the U.S. Geological Survey (USGS) Dissolved Gas Laboratory, Reston, Va.

[2]Analyzed at a USGS contract laboratory.

[3]Analyzed or estimated at the USGS CFC Laboratory, Reston, Va.

*Estimated based on mean annual temperature.

&Estimated based on sample temperature.

#Estimated based on average air temperature for November and December at Wawarsing, N.Y.

Table 4   33

springs, and wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster County,

SF_6 and CFCs have been corrected for excess air; SF_6, Sulfur hexafluoride; CFC, chlorofluorocarbon; bold text indicates most reasonable apparent age or recharge year; reducing; CH_4, methanogenic; mixed (Y/Z) indicates waters with different redox ranging from most oxidized (Y) to most reduced (Z); concentrations in milligrams per liter, temperature and pressure per liter; pCi, picocuries per liter]

SF_6 Apparent recharge year, piston flow[3]	SF_6 Apparent age, piston flow[3]	CFC-11 corrected concentration (pmol/kg)[3]	CFC-12 corrected concentration (pmol/kg)[3]	CFC-113 corrected concentration (pmol/kg)[3]	CFC-11 Apparent age piston flow (years)[3]	CFC-12 Apparent age piston flow (years)[3]	CFC-113 Apparent age piston flow (years)[3]	CFC-11 Apparent recharge year, piston flow[3]	CFC-12 Apparent recharge year, piston flow[3]	CFC-113 Apparent recharge year, piston flow[3]	Dissolved gas notes	Age tracer notes
--	--	5.05	3.87	0.645	27.0	C	**5.6**	1982.8	C	**2008.2**		CFC-12 contaminated; CFC-11 and -113 degraded
2003.0	**6.5**	5.25	3.28	0.464	23.15	**6.65**	21.25	1986.3	**2002.8**	1988		Early 2000s age
2000.5	**9.5**	1.08	1.75	0.154	41.12	**30.45**	30.29	1968.8	**1979.5**	1979.7	Presence of CH_4	Conflicting ages, CFCs could be degraded
1952.0	**57.5**	0.0857	0.0197	0	55.0	**62.7**	56.5	1954.5	**1946.8**	1953	High CH_4	Late 1940s–1950s age; tracers could be degraded
NP	NP	0.0905	0.0425	0	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain
NP	NP	0.284	0.584	0.0533	NP	NP	NP	NP	NP	NP	Excess air	Age uncertain. Probably a mixture of water ages
NP	NP	0.0875	0.0212	0.00583	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain. CFCs chromatograms appear degraded
NP	NP	0.0803	0.0167	0.0063	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain. CFCs could be slightly degraded
NP	NP	0.0925	0.0065	0.030	NP	NP	NP	NP	NP	NP	Excess air	Age uncertain. CFCs are degraded
NP	NP	0	0.429	0.075	NP	NP	NP	NP	NP	NP	Excess air	Age uncertain. CFC-11 degraded
1964.5	47.2	0.157	0.0501	0.0235	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain. CFCs are degraded
1978.3	33.5	0.311	0.243	0.0761	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain. CFCs are degraded
1970.3	41.5	0.286	0.15	0.0665	51.2	54.5	NP	1960.5	1957.2	NP	Trace CH_4	1970 age based on SF_6; CFC-113 and possibly CFC-11, -12 degraded
1970.8	41.0	0.131	0.0716	0.074	NP	NP	NP	NP	NP	NP	Excess air; presence of CH_4	Age uncertain. CFCs are degraded

Table 5.   Dissolved concentrations of trace elements and stable-isotope ratios in surface-water and groundwater samples from a lake, springs, County, New York, 2009–11.

[Analytes measured by the U.S. Geological Survey National Water Quality Laboratory unless otherwise noted; concentrations in micrograms per liter, (mg/L) unless Be, beryllium; B, boron; Cd, cadmium; Cr, chromium; Co, cobalt; Cu, copper; Fe, iron; Pb, lead; Li, lithium; Mn, manganese; Mo, molybdenum; Ni, nickel; N, nitrogen; isotope ratio of hydrogen-2 to hydrogen-1; $\delta^{18}O$, stable isotope ratio of oxygen-18 to oxygen-16, relative to Vienna Standard Mean Ocean Water standard; $\delta^{34}S$, stable ganic carbon relative to the Vienna Pee Dee Belemnite standard; SI, saturation index]

| Well identifier	Date	Sample time	Al	Ba	Be	Cd	Cr	Co	Cu	Fe	Pb	Li	Mn
U1626	12/15/2009	1500	E2.9	26	<0.01	E0.01	0.24	0.23	E0.96	290	<0.03	0.8	79
U1627	6/23/2009	1200	<4.0	29	<0.02	<0.02	E0.07	0.07	35.1	4	0.81	1.6	0.2
U1627	4/1/2010	0900	11.8	24	<0.01	<0.02	E0.11	0.05	E0.78	<6	<0.03	1.2	<0.3
U1637	8/31/2010	1400	190	140	0.014	0.029	0.34	0.3	<1.0	420	0.26	2.9	630
U1641	4/20/2010	1300	<17.0	83	<0.06	<0.10	<0.60	2.2	<5.0	92	<0.15	4.3	130
U1641	4/20/2010	1301	<17.0	84	<0.06	<0.10	<0.60	2.0	<5.0	91	<0.15	4.2	130
U1663	8/31/2010	1400	7.8	54	E0.01	0.04	<0.120	0.068	E0.92	2.3	<0.03	90	41
U1673	11/30/2011	1200	<2.2	240	<0.006	<0.02	<0.07	0.08	2.8	24	0.15	2.9	260
U1670	11/30/2011	1000	<2.2	180	<0.006	<0.02	<0.07	0.03	0.95	34	0.08	3	190
U1632	9/14/2009	1730	E3.6	13	<0.02	E0.01	0.19	0.08	<1.0	<4	<0.06	<1.0	16
U1633	9/15/2009	1200	<4.0	15	<0.02	0.03	0.33	0.04	<1.0	E2	<0.06	E0.7	18
U1667	9/15/2009	1400	20	14	E0.02	E0.02	0.21	0.07	<1.0	53	0.11	E0.7	19
U1668	7/1/2009	1300	15.9	14	<0.02	<0.02	<0.12	0.1	2.5	248	<0.06	E0.7	21
U1666	6/23/2009	1400	<4.0	25	<0.02	<0.02	<0.12	0.08	E0.77	<4	<0.06	1.8	<0.2
U1666	3/31/2010	1600	E1.9	23	<0.01	<0.02	E0.08	0.06	<1.0	<6	<0.03	2.3	<0.3
U1665	3/31/2010	1200	7.9	14	<0.01	E0.01	E0.10	0.03	<1.0	6	E0.02	<0.4	9.8
Lippman Lake effluent	6/24/2009	1330	--	--	--	--	--	--	--	--	--	--	--
Lippman Lake effluent	7/2/2009	1300	28	10	<0.02	E0.01	0.14	0.10	<1.0	317	0.16	E0.7	51
Lippman Lake effluent	9/1/2009	1230	--	--	--	--	--	--	--	--	--	--	--
Lippman Lake effluent	9/16/2009	1300	34	19	<0.02	<0.02	E0.10	0.08	<1.0	34	<0.06	3.7	2.1
Lippman Lake effluent	10/13/2009	1515	--	--	--	--	--	--	--	--	--	--	--
Lippman Lake effluent	12/15/2009	1000	140	6	<0.01	<0.02	<0.12	0.12	<1.0	142	0.05	1.2	86
Lippman Lake effluent	4/1/2010	1200	58	7	<0.01	<0.02	E0.06	0.49	<1.0	58	E0.03	1.6	48
01366400	6/23/2009	0930	6.1	26	<0.02	<0.02	<0.12	E0.01	1.3	E4	<0.06	<1.0	1.7
01366400	9/1/2009	1030	26	29	0.02	E0.02	E0.08	0.02	18.1	6	0.34	E0.6	3.2
01366400	10/13/2009	1420	--	--	--	--	--	--	--	--	--	--	--
01366400	10/13/2009	1425	--	--	--	--	--	--	--	--	--	--	--
01366400	12/22/2009	1110	4.8	26	E0.01	<0.02	0.18	0.03	E0.94	E5	E0.02	0.4	1.5
01366400	4/1/2010	1000	17	30	E0.01	0.02	<0.12	0.02	E0.86	8	E0.02	0.5	5.2
U1625	6/24/2009	1100	<4.0	42	<0.02	<0.02	<0.12	0.02	10.7	<4	0.23	7.2	0.2
U1625	12/14/2009	1000	<3.4	130	<0.01	E0.01	<0.12	0.37	1.1	E5	0.44	20	13
U1625	4/7/2011	1900	11.2	24	<0.006	<0.016	0.11	0.068	1.1	54	0.028	4.4	7.6
U1629	6/24/2009	0800	<20.0	230	<0.10	<0.10	<0.60	<0.10	<5.0	146	<0.30	320	260
U1629	4/7/2011	1100	7.1	140	<0.006	<0.02	<0.06	0.17	<0.5	1,500	0.062	55	450
U1629	4/7/2011	0900	3.2	120	<0.006	0.016	0.11	0.1	<0.5	570	0.22	20	380
U1628	7/2/2009	1000	E3.5	32	<0.02	<0.02	E0.09	0.12	E0.69	17	E0.04	5.2	2.0
U1630	9/15/2009	1700	<4.0	49	<0.02	<0.02	<0.12	0.11	<1.0	260	<0.06	310	81
U1631	9/16/2009	1000	400	43	<0.02	0.02	<0.12	0.20	<1.0	230	<0.06	100	600
U1631	9/16/2009	1001	<4.0	44	<0.02	0.02	<0.12	0.19	<1.0	230	<0.06	101	660
U1631	12/14/2009	1630	<3.4	43	<0.01	0.35	<0.12	0.60	<1.0	370	<0.03	91	490
U1647	4/21/2010	1300	<34	97	<0.12	<0.20	<1.2	2.2	<10.0	40	<0.30	320	300
U7017	9/20/2011	1200	<1.7	240	0.009	<0.02	<0.06	<0.02	<0.5	1,800	0.032	120	150
U3772	9/20/2011	1200	1.8	1,120	<0.006	<0.02	0.077	<0.02	<0.5	91	<0.02	80	26
U1645	9/21/2011	1200	4.2	130	<0.006	<0.02	0.19	0.03	<0.5	630	<.01	29	150
U1644	9/21/2011	1200	6.6	480	0.008	<0.02	<0.06	<0.02	<0.5	94	<0.015	730	330

[1]Analyzed at the U.S. Geological Survey (USGS) Isotope Laboratory, Menlo Park, Calif.

[2]Analyzed at the USGS Reston Stable Isotope Laboratory, Reston, Va.

Table 5   35

and wells in the Wawarsing study area, and for the Rondout Reservoir at the influent to the Rondout–West Branch Tunnel in Lackawack, Ulster

otherwise noted; --, not measured; NA, not applicable; <, less than; E, estimated value below minimum reporting level; Al, aluminum; Sb, antimony; As, arsenic; Ba, barium; Se, selenium; Ag, silver; Sr, strontium; Tl, thallium; U, uranium; V, vanadium; Zn, zinc; $^{87}Sr/^{86}Sr$, stable isotope ratio of strontium-87 to strontium-86; d, delta; δ^2H, stable isotope ratio of sulfur-34 to sulfur-32 of sulfate relative to the Vienna Canyon Diablo Troilite standard; $\delta^{13}C$ of DIC, stable isotope ratio of C-13 to C-12 of dissolved inor-

Mb	Ni	Ag	Sr	Tl	V	Zn	Sb	As	B	Se	U	δ^2H in water (per mil)	$\delta^{18}O$ in water (per mil)	$\delta^{34}S$ of SO_4^{2-} (per mil)	$\delta^{13}C$ of DIC (per mil)	$^{87}Sr/^{86}Sr$ (per mil)[1]
M	0.89	<0.010	52	E0.01	<0.16	E1.4	E0.03	0.13	6	0.06	0.01	-52.9	-8.44	9.36	-22.1	0.71214
0.3	0.48	<0.008	160	<0.04	0.24	3.2	0.10	0.37	15	0.40	0.76	-51.3	-8.15	-2.95	-16.6	0.71139
0.2	0.34	M	130	<0.02	0.22	<2.8	0.08	0.27	11	0.35	0.86	-71.0	-10.7	-3.72	-16.7	0.71136
6.6	0.97	<0.01	1,400	<0.02	0.35	E2.2	0.27	2.5	10	E0.036	1.2	-59.0	-9.24	-1.95	-14.0	0.70909
1.0	1.7	<0.1	1,220	<0.10	<0.80	<14	E0.23	2.1	E9	<0.20	0.29	-58.4	-9.23	0.34	-11.0	0.70916
1.1	1.5	<0.1	1,200	<0.10	<0.80	<14	E0.25	2.0	E9	<0.20	0.27	--	--	0.48	-11.3	0.70913
7.5	0.28	<0.01	340	<0.02	<0.16	<2.8	0.5	1.6	280	E0.026	0.092	-61.9	-9.34	8.8	-14.0	0.71164
0.48	0.30	<0.005	130	<0.01	<0.080	8.3	<0.03	5.9	6	<0.030	0.20	-55.2	-8.97	0.61		0.7108
0.68	0.26	<0.005	120	<0.01	<0.080	6.2	<0.03	6.4	6	<0.030	0.30	-55.7	-8.97	-5.08		0.71069
M	0.33	<0.008	35	<0.04	E0.09	2,000	<0.04	0.17	5	0.09	E0.01	-56.2	-8.89	2.23	--	0.71227
M	0.42	<0.008	22	<0.04	<0.16	5,300	<0.04	0.17	7	E0.05	<0.01	-55.7	-8.96	3.09	--	0.71176
M	0.64	<0.008	23	<0.04	E0.15	E2.0	<0.04	0.26	6	0.07	E0.00	-54.9	-8.82	3.36	--	0.71196
0.1	0.22	<0.008	55	<0.04	1.4	<2.0	E0.02	0.37	E3	E0.06	0.03	-54.0	-8.71	3.72	--	0.71223
0.1	0.47	<0.008	130	<0.04	E0.10	<2.0	0.09	0.33	19	0.3	0.46	-50.4	-8.01	-6.84	-17.7	0.71552
0.2	0.38	<0.010	150	<0.02	E0.09	<2.8	0.07	0.24	13	0.25	0.91	-68.5	-10.4	-6.97	-15.5	0.71148
M	0.37	<0.010	19	<0.02	E0.09	<2.8	0.07	0.18	9	0.06	E0.01	-67.9	-10.5	2.79	-23.5	0.71352
--	--	--	--	--	--	--	--	--	--	--	--	-49.0	-7.95	--	--	--
M	0.36	<0.008	28	<0.04	0.26	2.0	E0.02	0.53	4	0.10	0.01	-47.8	-7.60	1.76	-8.17	0.71209
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0.5	0.77	<0.008	120	<0.04	E0.13	<2.0	0.13	2.3	17	0.08	0.32	-40.1	-5.99	-3.17	--	0.71125
--	--	--	--	--	--	--	--	--	--	--	--	-40.2	-6.00	--	--	--
M	0.52	<0.010	44	<0.02	<0.16	<2.8	E0.03	0.21	6	E0.03	0.02	-56.7	-8.98	3.71	-18.2	0.71259
M	0.43	<0.010	47	<0.02	<0.16	<2.8	0.06	0.34	9	0.05	0.04	-67.2	-10.3	1.15	-13.1	0.7119
M	0.34	<0.008	16	<0.04	<0.16	2.3	E0.03	0.18	5	<0.06	0.01	-58.4	-9.14	3.36		0.71416
M	0.45	M	16	<0.04	<0.16	5.1	0.05	0.27	4	E0.05	0.02	-55.3	-8.76	4.16	-13.8	0.71392
--	--	--	--	--	--	--	--	--	--	--	--	-55.9	-8.77	--	--	--
--	--	--	--	--	--	--	--	--	--	--	--	-56.0	-8.70	--	--	--
M	0.48	<0.010	19	<0.02	<0.16	E1.6	E0.04	0.28	4	0.04	0.01	-55.7	-8.64	4.26	-13.9	0.71419
M	0.34	<0.010	17	<0.02	<0.16	E2.1	E0.03	0.18	4	E0.03	0.02	-62.7	-9.58	4.16	-12.9	0.71424
0.5	0.37	<0.008	150	<0.04	<0.16	E1.8	0.05	0.18	11	0.10	0.33	-57.9	-9.08	-8.44	-12.7	0.71416
1.1	3.3	<0.010	1,000	<0.02	E0.11	3.7	0.12	0.25	44	0.16	2.00	-54.5	-8.61	-11.5	-15.1	0.712
0.52	2.3	<0.005	90	<0.01	<0.08	1.6	0.063	0.2	6.9	0.091	0.09	-63.4	-9.75	--	--	0.71198
0.6	<0.60	<0.040	590	<0.20	<0.80	<10.0	<0.20	<0.30	65	E0.24	0.04	-56.2	-8.99	0.99	-13.1	0.71158
1.0	8.4	<0.005	280	<0.01	<0.80	2.1	<0.027	0.027	22	<0.03	0.16	-55.9	-8.86	--	--	0.71129
1.0	4.4	<0.005	230	<0.01	<0.80	62	<0.027	0.057	18	<0.03	0.22	-55.9	-8.86	--	--	0.71151
1.1	0.81	<0.008	380	<0.04	1.6	<2.0	0.06	0.97	21	0.47	0.77	-61.8	-9.70	25.4	-9.68	0.70983
2.9	0.57	M	--	<0.04	<0.16	2.1	<0.04	1.4	284	<0.06	0.12	-67.8	-10.3	28.6	--	0.70919
9.9	1.4	M	17,700	<0.04	E0.12	<2.0	<0.04	3.9	97	E0.03	0.58	-64.4	-10.1	25.3	--	0.70901
10.9	1.3	M	17,800	<0.04	E0.12	<2.0	<0.04	4.0	112	<0.06	0.64	-64.6	-10.0	25.3	--	0.70900
11.8	3.9	M	19,800	<0.02	0.34	<2.8	<0.05	6.1	92	<0.04	0.56	-64.9	-9.98	25.7	-12.0	0.70902
3.2	2.5	<0.1	13,800	<0.20	1.9	<28.0	<0.54	8.3	269	<0.40	0.48	-64.8	-10.1	31.6	-16.6	0.70947
0.12	<0.09	<0.005	180	<0.010	<0.080	3.4	<0.027	1.2	190	<0.030	0.006	-60.8	-9.52	--	-11	0.71277
0.16	<0.09	<0.005	580	<0.01	<0.080	1.8	<0.03	0.67	150	<0.030	0.03	-59.0	-9.26	--	-17.3	0.71367
1.5	0.33	<0.005	850	<0.01	<0.080	2.9	<0.03	10	43	<0.030	0.34	-58.2	-8.97	-9.66	-14.3	0.71136
2.0	0.15	<0.005	2,170	<0.01	0.10	<1.4	<0.03	5.3	290	<0.030	0.11	-63.8	-9.77	-1.88	-17.5	0.71195

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