Halite Brine in the Onondaga Trough near Syracuse, New York: Characterization and Simulation of Variable-Density Flow

By Richard M. Yager, William M. Kappel, and L. Niel Plummer

Prepared in cooperation with the Onondaga Lake Partnership and the Onondaga Environmental Institute

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Conversion Factors

Inch/Pound to SI

Multiply	By	To obtain
	Length	
foot (ft)	0.3048	meter (m)

SI to Inch/Pound

Multiply	By	To obtain
	Length	
kilometer (km)	0.6214	mile (mi)
meter (m)	1.094	yard (yd)
	Area	
hectare (ha)	2.471	acre
square kilometer (km^2)	247.1	acre
hectare (ha)	0.003861	square mile (mi^2)
square kilometer (km^2)	0.3861	square mile (mi^2)
	Volume	
liter (L)	33.82	ounce, fluid (fl. oz)
liter (L)	2.113	pint (pt)
liter (L)	1.057	quart (qt)
liter (L)	0.2642	gallon (gal)
cubic meter (m^3)	264.2	gallon (gal)
cubic meter (m^3)	0.0002642	million gallons (Mgal)
cubic meter (m^3)	35.31	cubic foot (ft^3)
	Flow rate	
meter per day (m/d)	3.281	foot per day (ft/d)
meter per year (m/yr)	3.281	foot per year ft/yr)
liter per second (L/s)	15.85	gallon per minute (gal/min)
	Mass	
megagram (Mg)	1.102	ton, short (2,000 lb)
megagram (Mg)	0.9842	ton, long (2,240 lb)
	Density	
kilogram per cubic meter (kg/m^3)	0.06242	pound per cubic foot (lb/ft^3)
gram per cubic centimeter (g/cm^3)	62.4220	pound per cubic foot (lb/ft^3)
	Hydraulic gradient	
meter per kilometer (m/km)	5.27983	foot per mile (ft/mi)

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

$$°F=(1.8\times°C)+32$$

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

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

Concentrations of chemical constituents in water are given either in grams per liter (g/L) or milligrams per liter (mg/L).

List of Abbreviations and Acronyms

^{2}H	Deuterium
^{18}O	Oxygen-18
^{11}B	Boron-11
^{13}C	Carbon-13
^{14}C	Carbon-14
BP	Before present
Br	Bromide
C	Carbon
Ca	Calcium
Cl	Chloride
CV	Coefficients of variation
DIC	Dissolved inorganic carbon
FD	Finite difference
Fe	Iron
K	Potassium
K_{basal}	Hydraulic conductivity of basal sand and gravel
K_{lac}	Hydraulic conductivity of lacustrine silt and sand confining layer
Mg	Magnesium
MWL	Meteoric water line
Na	Sodium
NETPATH	An interactive program for calculating NET geochemical reactions and radiocarbon dating along a flow PATH
NYSDEC	New York State Department of Environmental Conservation
pmc	Percent modern carbon
SEAWAT	A computer program for simulation of three-dimensional variable-density ground-water flow
SSE	Sum-of-squared errors
USGS	U.S. Geological Survey
NRP	National Research Program
S	Sulphur
TU	Tritium units
TVD	Total-variation-diminishing
V-PDB	Vienna Pee Dee Belemnite
V-SMOW	Vienna Standard Mean Ocean Water

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By Richard M. Yager, William M. Kappel, and L. Niel Plummer

Abstract

Halite brine (saturation ranging from 45 to 80 percent) lies within glacial-drift deposits that fill the Onondaga Trough, a 40-km long bedrock valley deepened by Pleistocene ice near Syracuse, N.Y. The most concentrated brine occupies the northern end of the trough, more than 15 kilometers (km) beyond the northern limit of halite beds in the Silurian Salina Group, the assumed source of salt. The chemical composition of the brine and its radiocarbon age estimated from geochemical modeling with NETPATH suggest that the brine formed through dissolution of halite by glacial melt water, and later mixed with saline bedrock water about 16,500 years ago.

Transient variable-density flow simulations were conducted with SEAWAT to assess current (2005) ground-water flow conditions within the glacial drift. A transient three-dimensional (3D) model using a grid spacing of 100 meters (m) and maximum layer spacing of 30 m was used to simulate a 215-year period from 1790 to 2005. The model was calibrated to observations of water levels, chloride concentrations, and discharges of water and chloride. The model produced an acceptable match to the measured data and provided a reasonable representation of the density distribution within the brine pool. The simulated mass of chloride in storage declined steadily during the 215-year period; however, the decline was mainly due to dispersion, which is probably overestimated because of the large layer spacing. Model results suggest that saline water from waste-disposal operations associated with a chemical plant has migrated beneath the western shore of Onondaga Lake.

Two-dimensional (2D) cross-sectional models of the aquifer system within the Onondaga Trough were prepared to test the plausibility of a hypothesis that the brine was derived from a relict source of halite that was dissolved by glacial melt water. The 2D models used parameter estimates obtained with the calibrated 3D model. Model results indicated the brine could have migrated from the bedded-halite subcrop area and remained in the glacial sediments at the northern end of trough for over 16,000 years, as suggested by radiocarbon dating. The 2D models also indicated that slow dissipation of brine occurs through a mixing zone formed by upward flow of freshwater over the southern end of the brine pool. The simulated depletion rate is controlled by the rate of mixing, which is limited by the specified grid resolution and the accuracy of the numerical method used to solve the advection-dispersion equation. A numerical solution obtained by using an implicit finite-difference method with upstream weighting and a 2D grid containing a column and layer spacing of 76 m and 3 m, respectively, provided an acceptable match to chloride concentration profiles measured at three locations within the Onondaga Trough.

Introduction

Halite brine lies within glacial-drift deposits that fill the Onondaga Trough, a bedrock valley near Syracuse, N.Y. (fig. 1). Brine springs that discharged at land surface from this valley-fill aquifer near the southern shore of Onondaga Lake became the Nation's most important salt source in the 19th century. The brine later formed the basis for a chemical industry that left a lasting environmental legacy in Onondaga Lake and the surrounding lakeshore. The U.S. Geological Survey (USGS), in cooperation with the Onondaga Lake Partnership and Onondaga Environmental Institute, has been studying the hydrogeology of the Onondaga Trough since 2002 to determine the movement and concentration of naturally occurring brine in the valley-fill aquifer.

Onondaga Lake has been identified as one of the Nation's most contaminated lakes as a result of discharges from industrial, sewage, and stormwater sources (Effler and Perkins, 1987). Although the remediation of polluted surface-water discharges is planned, the migration of poor quality (saline to brine) ground water toward the lake also may affect the quality of lake water and could impair the remediation plans. Anthropogenic saline contamination has been identified at a former industrial soda-ash production facility near the lakeshore. Saline water runoff from waste beds associated with soda ash production has affected the seasonal stratification of lake waters and is a primary concern to resource managers.

Brine originating from halite beds exposed in the Onondaga Trough also discharges through springs along the southern lakeshore; however, the relative contributions of natural and anthropogenic sources of salinity to lake water are unknown.

Effective cleanup of Onondaga Lake requires an understanding of how ground water flows through the valley-fill aquifer in the Onondaga Trough. A regional, three-dimensional ground-water-flow model provides a qualitative and quantitative description of the aquifer system and simulates changes that have occurred in the aquifer system as a result of anthropogenic development. Ground-water and mass budgets computed by the model provide estimates of the relative contributions of flow from areas contaminated by natural and anthropogenic sources. The computed distribution of hydraulic head and ground-water density provides a basis for further studies aimed at understanding the migration of brine into Onondaga Lake. This report details the development of variable-density flow models of the aquifer system in the Onondaga Trough, including (1) delineation of the bedrock valley that defines the glacial aquifer system, (2) mapping the thickness and extent of the aquifers within the glacial deposits, (3) analysis of the chemical quality of ground water within the aquifer system, and (4) the design and calibration of models used to simulate ground-water flow and estimate chloride mass discharges to surface waters. The models were used to simulate concentration and density distributions within the brine pool that resides in the glacial sediments, and to assess the validity of a hypothesis concerning the brine origin.

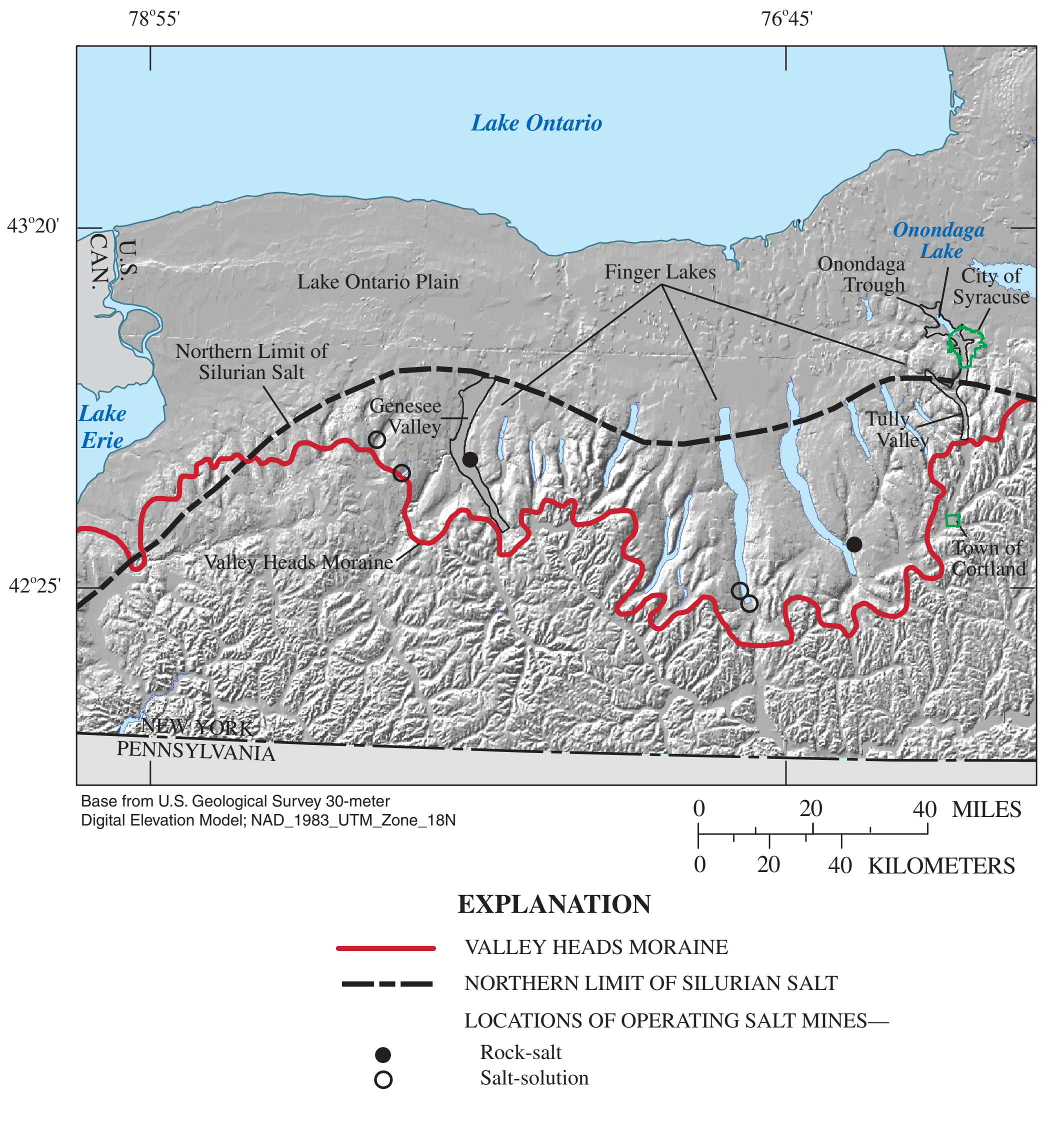

Figure 1. Geographic features in western New York, including northern limit of Silurian salt, Valley Heads Moraine, Finger Lakes, and location of Syracuse.

Hydrogeologic Setting

The brine is confined in a bedrock valley (Onondaga Trough), which is a pre-glacial river valley that was deepened and widened by ice during the Pleistocene Epoch. The trough extends from the north end of Onondaga Lake, 40 kilometers (km) south through the Tully Valley and connects to another bedrock valley that continues another 24 km south to the Town of Cortland (fig. 1). Downcutting by ice in the Onondaga Trough eroded the northern limit of halite beds within the upper Silurian Salina Group near its confluence with the West Branch Valley (fig. 2). This erosion probably exposed the halite beds to dissolution by meteoric waters, forming the brine that occurs in the northern end of the trough beneath Onondaga Lake.

Bedrock Geology

The Onondaga Trough is underlain by sedimentary rocks of Silurian and Devonian age that dip southward at about 9.5 meters per kilometer. The bedrock units strike east-west and extend across western New York and into southern Ontario. Most of the bedrock valley floor is underlain by shale of the Silurian Salina Group; these shales are overlain by Devonian carbonate rocks that outcrop south of Syracuse (fig. 2). The carbonate is overlain in turn by the Devonian shale and limestone that forms the surrounding uplands.

The Syracuse Formation of the Salina Group consists of shale interbedded with halite and gypsum. These evaporite beds subcrop beneath the Onondaga Trough, thicken southward into the Appalachian Basin, and are contemporary

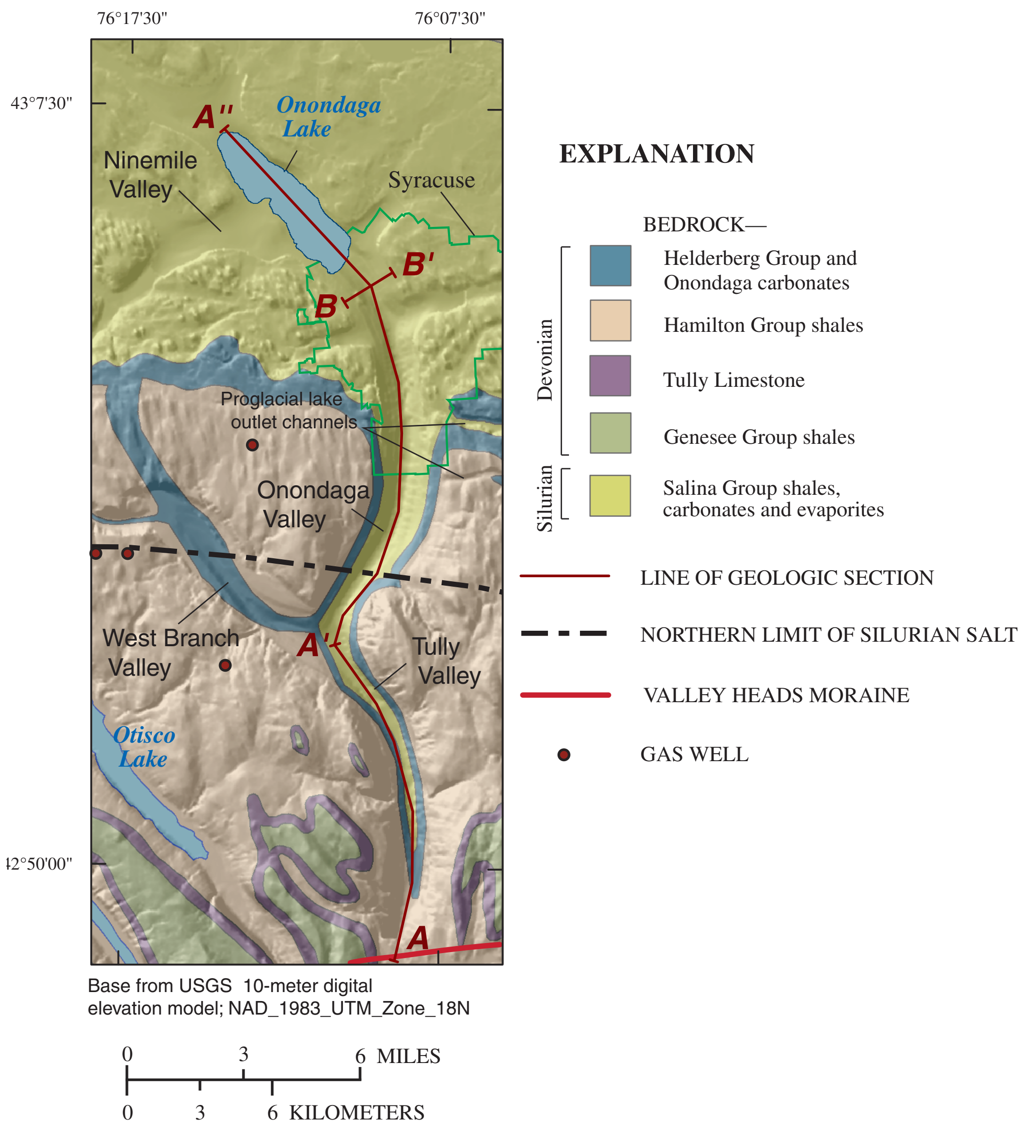

Figure 2. Bedrock geology in the vicinity of the Onondaga Trough. Shaded relief is bedrock surface within the trough and land surface outside the trough.

with evaporite beds in the Michigan Basin to the west (Rickard, 1969). Halite is present in four extensive beds with an aggregate thickness of about 45 m in the southern end of the Tully Valley, and over 150 m along the New York-Pennsylvania border. Halite currently (2005) is mined at several locations in western New York (fig. 1). Interpretation of geophysical logs from gas well boreholes (fig. 2) suggests that the halite beds pinch out about 19 km south of Syracuse, although isolated salt lenses probably occur within the Syracuse Formation north of this limit.

Glacial Sediments

The Onondaga Trough is partly filled with glacial drift deposited mostly during the last deglaciation. The trough was occupied by ice about 17,300 years before present (BP) when the Valley Heads Moraine was formed during the last major southward surge of the ice front (Mullins and others, 1996). The Valley Heads Moraine extends across central N.Y. (fig. 1) and marks the present drainage divide between streams that flow north to the St. Lawrence River and streams that flow south to the Susquehanna River. Most of the drift in the Onondaga Trough was deposited during the retreat of the ice from the moraine, which has been dated at 16,500 years BP (Mullins and others, 1996). Glacial deposition in the trough ceased with the final recession of the ice margin from the Onondaga Valley. This occurred about 14,300 years BP, and was marked by the formation of glacial Lake Iroquois that occupied the depression filled by the present-day Onondaga Lake. The drift thickness increases from north to south, ranging from 75 m thick beneath Onondaga Lake, about 120 m thick in the Tully Valley, and over 240 m thick beneath the Valley Heads Moraine (fig. 3).

The glacial drift in the trough is primarily composed of lacustrine sediments that were deposited in a series of proglacial lakes dammed by glacial ice to the north and by the uplands to the south. Coarse-grained sediment (sand and gravel) 3 to 30 m thick was deposited at the base of the ice where melt waters entered the lakes and formed subaqueous fans. Silty-clay lacustrine sediments, as much as 200 m thick, overlie these coarse-grained, ice-marginal sediments and

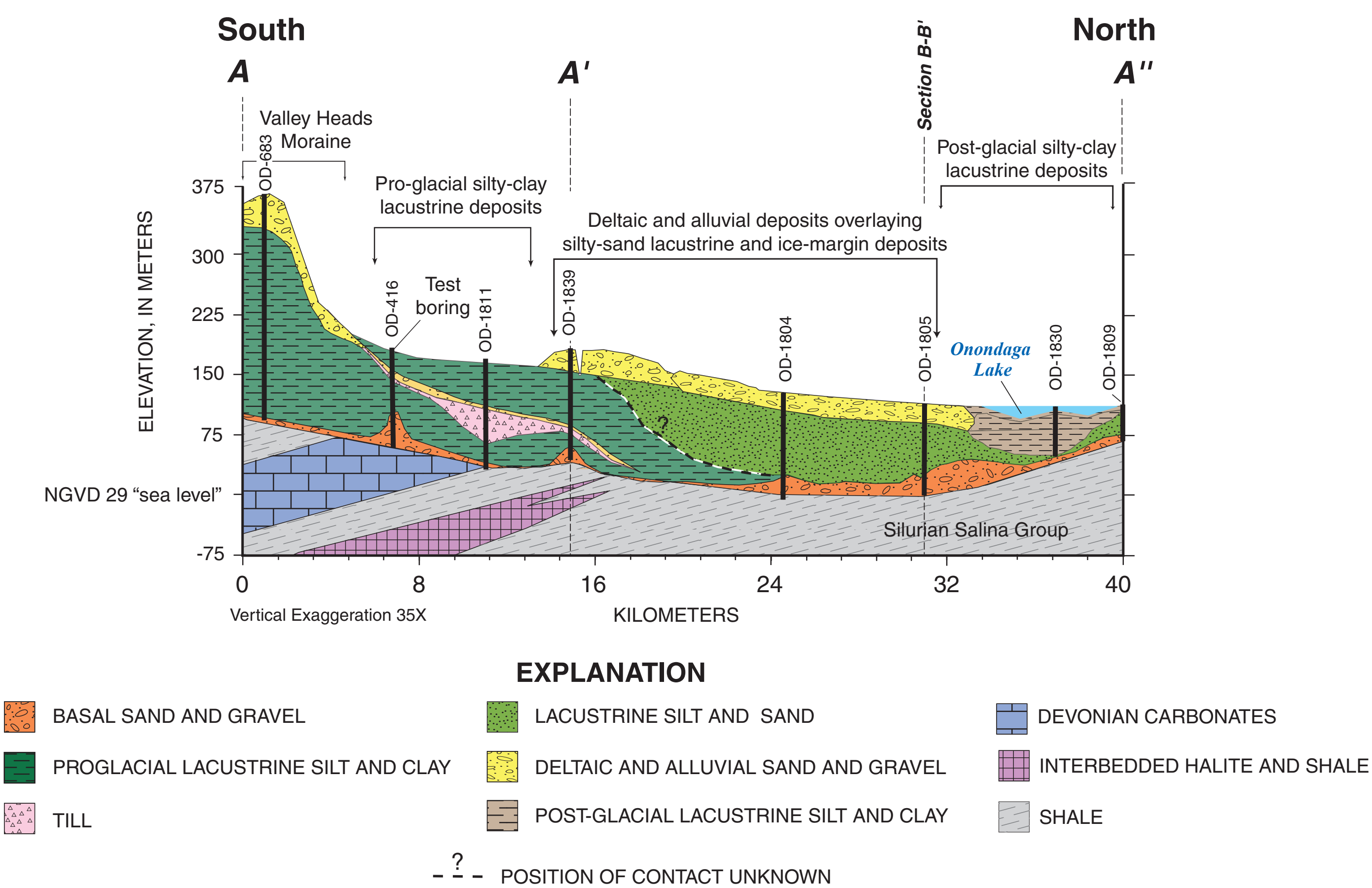

Figure 3. Generalized section A-A″ along Onondaga Trough showing glacial and bedrock stratigraphy. Section location shown on figure 2.

were deposited in a deep-water lake that occupied the Tully Valley. A till layer within the mid-section of glacial drift in the Tully Valley and at land surface on the Valley Heads Moraine suggests a readvance of the ice in the southern part of the Onondaga Trough (Kappel and Miller, 2003). Another depositional sequence of coarse-grained sediments overlain by fine-grained lacustrine sediments is repeated in the Tully Valley. Silty-sand lacustrine and deltaic sediments as much as 75 m thick were deposited in a younger and shallower lake that occupied the Onondaga Valley between the Tully Valley and Syracuse.

Lacustrine sediments in the West Branch and Onondaga Valleys are overlain by deltaic coarse-grained sediments as much as 30 m thick. A series of deltas were built out eastward from the West Branch Valley and northward into the Onondaga Trough. The top elevations of the deltas decrease northward and correspond to the series of outlet channels that were cut east of the trough by proglacial lake drainage (fig. 2; Hand, 1978). As the ice margin receded northward onto the Ontario Plain, the relatively shallow and long-lived Lake Iroquois formed in the lowland, including the depression now occupied by Onondaga Lake. A sequence of silty-clay lacustrine sediments, up to 40 m thick, was deposited beneath Onondaga Lake. The lacustrine sediments grade from silty clay to silty sand to the south and west of the lake and probably reflect an influx of coarser sediment from deltas that were built northward from the West Branch Valley and westward from the Ninemile Valley (fig. 2). Coarse-grained sediments, up to 15 m thick, overlie bedrock in the Ninemile Valley, the site of a large melt-water drainage channel. This coarse-grained deposit is overlain by silty sand up to 15 m thick that was deposited in Lake Iroquois. Another layer of coarse-grained sediment up to 10 m thick was deposited as alluvium by drainage from upland areas and overlies the silty sand in the Ninemile Valley.

The generalized depositional history described above formed the basis of a three-dimensional geologic model of the glacial drift (fig. 4). The sediment sequence in the Onondaga Trough is similar to that described by Mullins and others (1996) for several Finger Lake valleys in central New York delineated on the basis of water-borne seismic-reflection surveys. A similar geologic model described by Yager and others (2001) formed the framework for a ground-water flow model in the Genesee Valley, 160 km west of the Onondaga Trough (fig. 1). The geologic model for the Onondaga Trough was developed by using sections from Kappel and Miller (2005) that were based on logs of test borings drilled for construction projects and wells drilled for hydrogeologic studies conducted by the USGS and engineering firms. The geologic model is composed of six layers comprised of the nine units listed in table 1. The boundaries of these units were interpolated from available data to form continuous units consistent with the assumed depositional history.

Hydrology

The distribution of coarse-grained sediments has resulted in an aquifer system that consists of (1) a lower aquifer that is assumed to be hydraulically continuous throughout the Onondaga Trough and its two main tributaries, the West Branch and Ninemile Valleys; (2) a middle aquifer in the Tully Valley; and (3) upper aquifers in the West Branch, Onondaga and Ninemile valleys. These aquifers are separated by thick confining layers of lacustrine sediment. The lower aquifer corresponds to sand and gravel deposited at the base of the retreating ice in the Onondaga Trough and in melt-water channels in the West Branch and Ninemile Valleys. The middle aquifer overlies the Valley Heads Moraine and extends northward to the confluence of the West Branch Valley with the Onondaga Trough. The middle aquifer comprises the sand and gravel overlying till, which dips to the north (fig. 3). It is uncertain whether the middle aquifer is hydraulically connected to the lower aquifer near the confluence because deep borings have not been drilled at this location. The upper aquifers correspond to the deltaic sediments deposited in the West Branch and Onondaga Valleys and alluvial sediments deposited in the Ninemile Valley.

Most of the ground water in the aquifer system flows through the upper aquifers, which are unconfined and receive recharge through infiltration of precipitation on the valley floor and runoff from surrounding upland areas. Ground water from the upper aquifers discharges to the principal streams draining the valleys—West Branch Onondaga (referred to as West Branch herein), Onondaga and Ninemile Creeks (fig. 5). Large aquifers do not occur in the uppermost sediments of the Tully Valley where surficial coarse-grained sediments are limited to small alluvial fans deposited by tributary streams. Recharge reaches the middle aquifer in areas where it is exposed on the Valley Heads Moraine and perhaps locally through alluvial fans emanating from two large tributary valleys, Rattlesnake Gulf and Rainbow Creek (Kappel and others, 1996). Artesian pressure in the middle aquifer in the Tully Valley causes ground water to discharge through breaches in the overlying confining layer to springs along the scarps of past landslides, and within a 4-hectare (ha) area where numerous mudboils discharge water and sediment, causing land subsidence (fig. 5; Kappel and others, 1996). Recharge to the lower aquifer is limited to infiltration of runoff along the walls of the bedrock valley and from leakage from the upper and middle aquifers. Ground water discharges from the lower aquifer through upward flow to Onondaga and Ninemile Creeks, which are the major tributaries to Onondaga Lake.

Little information is available concerning ground-water flow through the bedrock surrounding the Onondaga Trough. The rocks are relatively undisturbed, so ground water probably flows through a network of bedding plane fractures and joints similar to fracture networks in other bedrock terranes in western New York (Yager, 1996). Carbonates underlie the uplands adjacent to the Lake Ontario Plain and probably intercept most of the ground-water recharge in these areas.

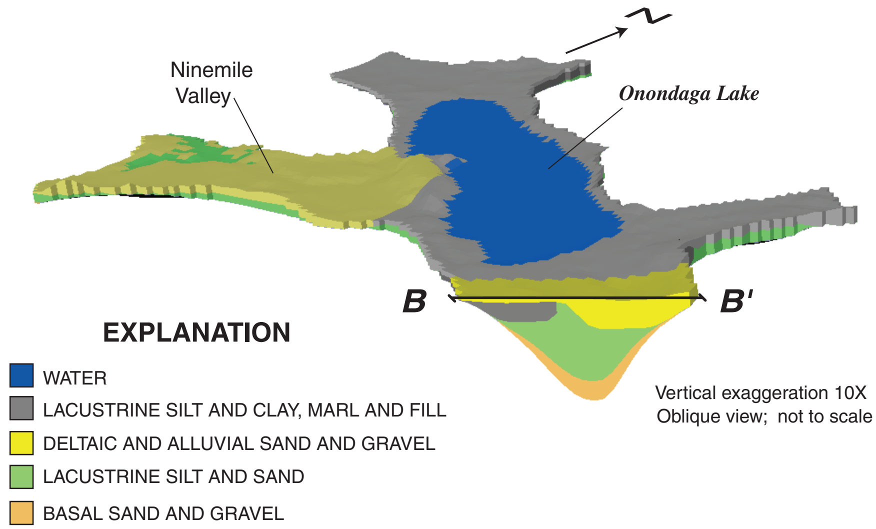

Figure 4. Perspective view of geologic model of Onondaga Trough showing generalized section B-B′ south of Onondaga Lake. Section location shown on figure 2.

Table 1. Lithologies represented in three-dimensional geologic and flow models of Onondaga Trough.

Layer		Units	Location
Geologic model	Flow model		
1	1	Water	Onondaga Lake
1	2 to 4	Marl & fill	Surrounding Onondaga Lake
1	2 to 4	Alluvial sand & gravel	Ninemile Valley
1	2 to 4	Deltaic sand & gravel	West Branch and Onondaga Valleys
2	2 to 4	Lacustrine clay & silt	Beneath Onondaga Lake
3	5 to 7	Lacustrine silt & sand	Ninemile and Onondaga Valleys
3	5 to 76	Lacustrine clay & silt	Tully Valley
4	8	Mid-section sand & gravel	Tully Valley
5	9	Lacustrine clay & silt	Tully Valley
6	10 and 11	Basal sand & gravel	All valleys
6	10 and 11	Bedrock	All valleys

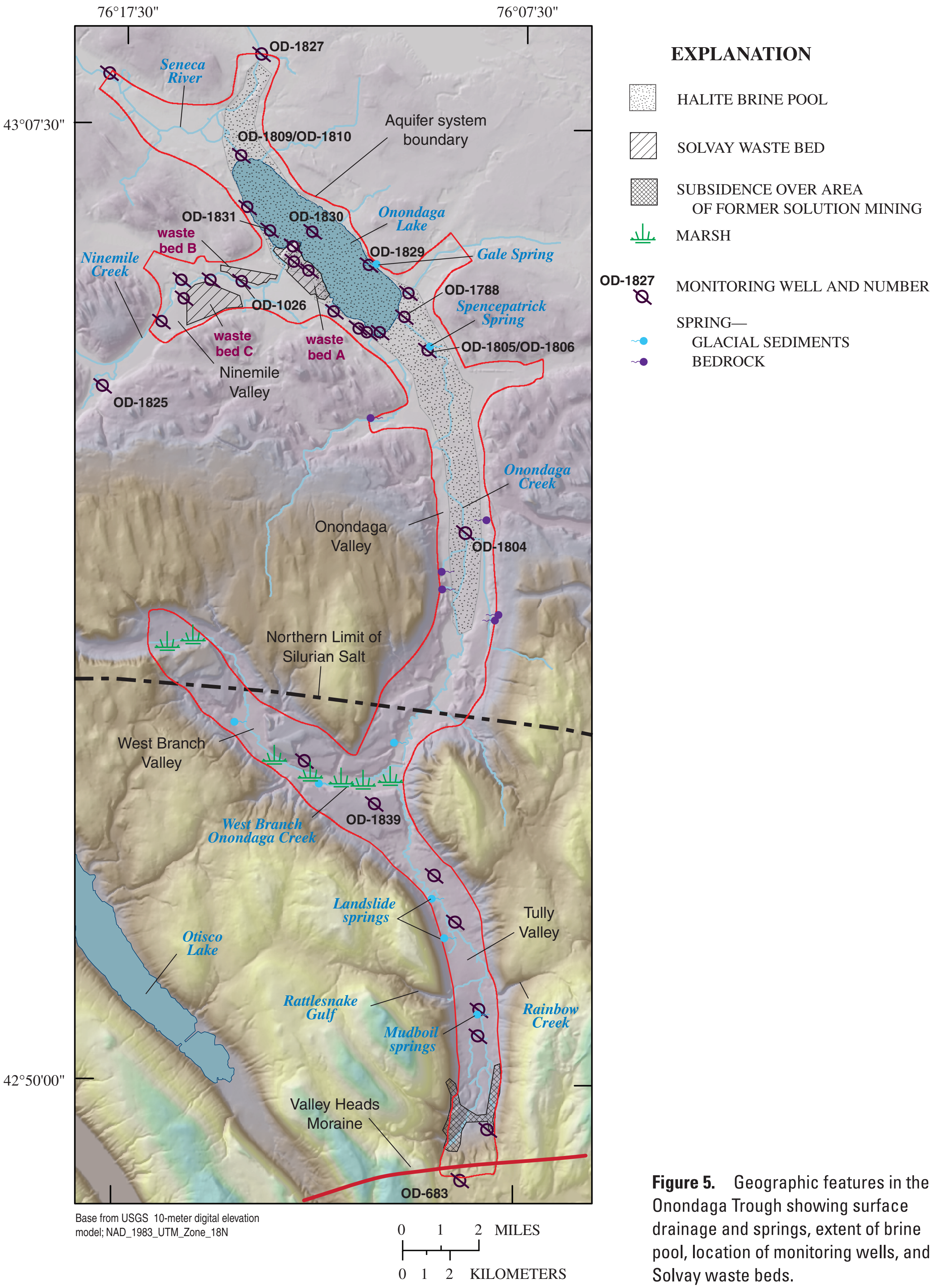

Figure 5. Geographic features in the Onondaga Trough showing surface drainage and springs, extent of brine pool, location of monitoring wells, and Solvay waste beds.

A number of springs have been mapped in the Onondaga Valley where carbonate bedrock outcrops along the valley walls (fig. 5). Ground water could enter the lower aquifer through bedrock bedding planes that intersect the Onondaga Trough, but the rate of flow is probably low throughout most of the trough. The flow of ground water from the bedrock could be substantial, however, in the southern part of the Tully Valley where subsidence over former areas of solution mining of halite has enhanced hydraulic connections between the bedrock and overlying aquifers (fig. 5). Tritium in saline water sampled from bedrock fractures beneath the mudboil area indicates that recent water introduced through solution mining is now moving updip through the bedrock toward the lower aquifer (Kappel and others, 1996). The representation of this hydraulic connection between the aquifer system and the bedrock is outside the scope of the modeling described in this report, however, and flow between bedrock and the aquifer system is assumed to be negligible.

Occurrence of Brine and Saline Water and History of Brine Production

Halite brine occurs in glacial-drift sediments at the northern end of the Onondaga Trough, covering an area of about 26 square kilometers (km^2) and extending 10 km south of Onondaga Lake (fig. 5). The brine pool occupies the lowest part of the trough and is confined beneath Onondaga Lake by silty-clay lacustrine sediments. The brine pool prevents fresh water from discharging directly to Onondaga Lake from the south through the Onondaga Trough and from the west through the Ninemile Valley. Instead, the flow of fresh water is probably directed upward in these areas along the interface between brine and fresher water. Some brine probably mixes with fresh water along this interface and then discharges to Onondaga and Ninemile Creeks. Saline water also could enter the lower aquifer from bedrock fracture zones that intercept the Onondaga Trough, but the rate of discharge is unknown.

Halite brine that discharged from springs around the southern end of Onondaga Lake was collected and boiled down to produce salt by European settlers in the 18th century. Solar evaporation of the brine was introduced in the 1800s when wells were constructed to pump more concentrated brine from the confined aquifer beneath Onondaga Lake (fig. 6). Upon completion of the Erie Canal in 1825, the salt works became the most important source of salt in the United States (Kurlansky, 2003). More than 10 million megagrams (Mg or metric ton) of salt were produced from 1797 through 1917, primarily from brine wells (Phalen, 1919). During this period, salt concentrations of brine pumped from the deepest wells declined from more than 75 percent to less than 60 percent saturated brine (or from 200 to 170 g/L dissolved solids) (Kappel, 2000).

The salt industry in Syracuse was rejuvenated in 1888 when a chemical plant was constructed along the western shore of Onondaga Lake and used the Solvay Process (Effler, 1996) to manufacture sodium carbonate or soda ash (Na_2CO_3) from the halite and limestone within the local bedrock. To supply this industry, new wells were drilled at the southern end of the Tully Valley 24 km south of Syracuse (fig. 5) to replace the brine wells near Onondaga Lake where brine concentrations were decreasing. The Tully Valley well fields penetrated halite deposits at depths of more than 370 m below land surface (Kappel, 2000). Brine was produced by injecting local sources of freshwater to dissolve halite, and then pumping the resulting brine to Syracuse. Brine withdrawals from these well fields from 1890 through 1986 resulted in the removal of about 87 million Mg of salt (C&S Engineers, Inc. and H&A of New York, 1992).

Waste materials from the Solvay Process, including calcium chloride ($CaCl_2$), calcium sulfate ($CaSO_4$), and unreacted calcium carbonate ($CaCO_3$) and halite (NaCl), were deposited in extensive waste beds covering more than 8.1 km^2 around the western shore of Onondaga Lake (fig. 5). Waste slurry was pumped into the beds and some of the impounded water evaporated; the remainder of the waste slurry overflowed and drained to Onondaga Lake or infiltrated into the underlying sediments. The height of some waste beds reached over 20 m after repeated filling; the total volume of solid waste generated before the plant closed in 1986 is estimated to be 6.2×10^7 cubic meters (m^3) (Blasland, Bouck & Lee, 1988). Saline water from the disposal of Solvay waste underlies the waste beds in the Ninemile Valley west of the lake.

The runoff of saline water from these waste beds caused hypersaline conditions in Onondaga Lake by the middle of the 20th century, resulting in chemical stratification of lake water and failure of spring turnover during a number of years (Effler and Perkins, 1987). Following closure of the plant, the salinity of the lake water decreased significantly, with chloride concentrations falling from 2,000 milligrams per liter (mg/L) in 1980 to 500 mg/L by 2005. Continual remedial activities collect and treat leachate from the waste beds, and thereby limit discharge of saline water, which accounts for about 30 percent of the total chloride loading to the lake (Onondaga County Department of Water Environment Protection, 2002).

Measured brine densities in the brine pool currently range from 1.09 to 1.16 grams per cubic centimeter (g/cm^3), corresponding to salt saturations of 45 to 80 percent. Salt saturation is highest beneath Onondaga Lake and generally increases with depth (fig. 7). Brine saturation decreases towards the bottom of the glacial sediments at the southern end of Onondaga Lake, however, possibly reflecting the removal of brine through pumping in the 19th century. The mass of halite in the current brine pool is estimated as 45 million Mg, and the mass produced by pumping from the Onondaga Trough in the 19th century was about 10 million Mg. The total mass of halite present in 1800 would, therefore, have been 55 million Mg, which is equivalent to a 4-km slab of salt 5-m thick extending across the width of the trough (about 1,300 m).

The natural salt springs that occurred in the 18th century are now buried by fill materials and have ceased to flow at

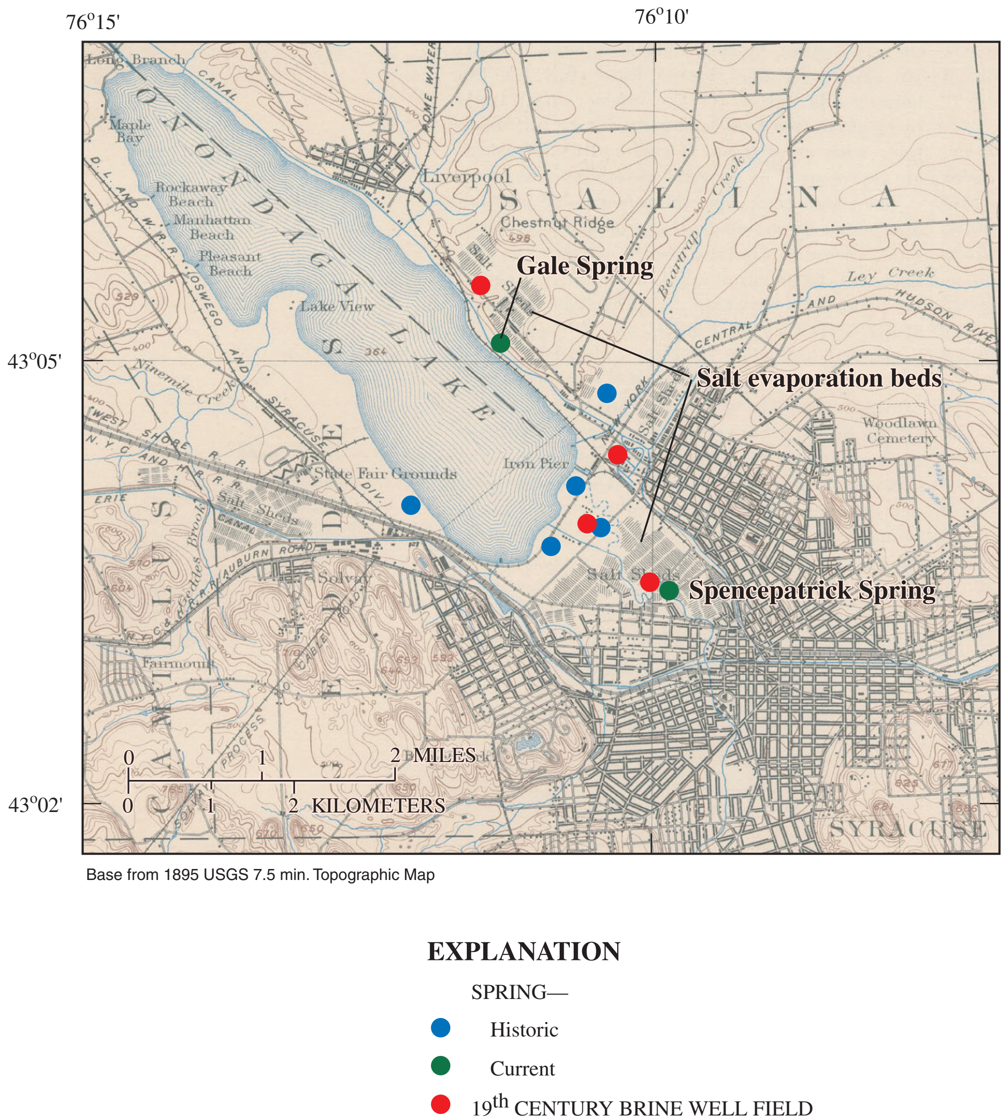

Figure 6. Syracuse and Onondaga Lake, showing current and historic locations of natural brine springs and brine production well fields.

land surface. Brine currently discharges from Spencepatrick Spring in Onondaga Creek about 1.5 km south of Onondaga Lake and from Gale Spring along the eastern shore of the lake (fig. 6). Spencepatrick Spring is larger than Gale Spring and currently flows at 28 liters per second (L/s) and discharges about 90,000 Mg of NaCl annually to Onondaga Lake. This discharge rate would have depleted the brine pool in about 600 years, so the spring likely began discharging relatively recently. Both of the springs could be sites of abandoned wells because they are in areas where brine wells were drilled in the 19th century. Brine and saline water also discharge directly to Onondaga Lake, but the rate of flow is limited by silty-clay lacustrine sediments that underlie the lake. The mass of halite discharged annually by ground water to Onondaga Lake was estimated to be 5,300 Mg by Effler and others (1990). Brine also could discharge to the Seneca River north of the lake (fig. 5), but little information is available in this area.

Geochemistry and Origin of Brine and Saline Water

Samples of ground water were collected for this study by the USGS from 31 wells and 12 springs in the Onondaga Trough and tributary valleys. Samples were analyzed for: (1) major and minor ions by a USGS National Research Program (NRP) laboratory (Reston, Va.); (2) stable isotopes of hydrogen and oxygen (^{2}H and ^{18}O, respectively) by the USGS Stable Isotope Laboratory (Reston, Va.); (3) dissolved gases by the USGS Dissolved Gas Laboratory (Reston, Va.); and (4) a

Aerial view looking east toward Onondaga Lake and City of Syracuse with Solvay Process waste beds in the foreground. Photograph by William Hecht.

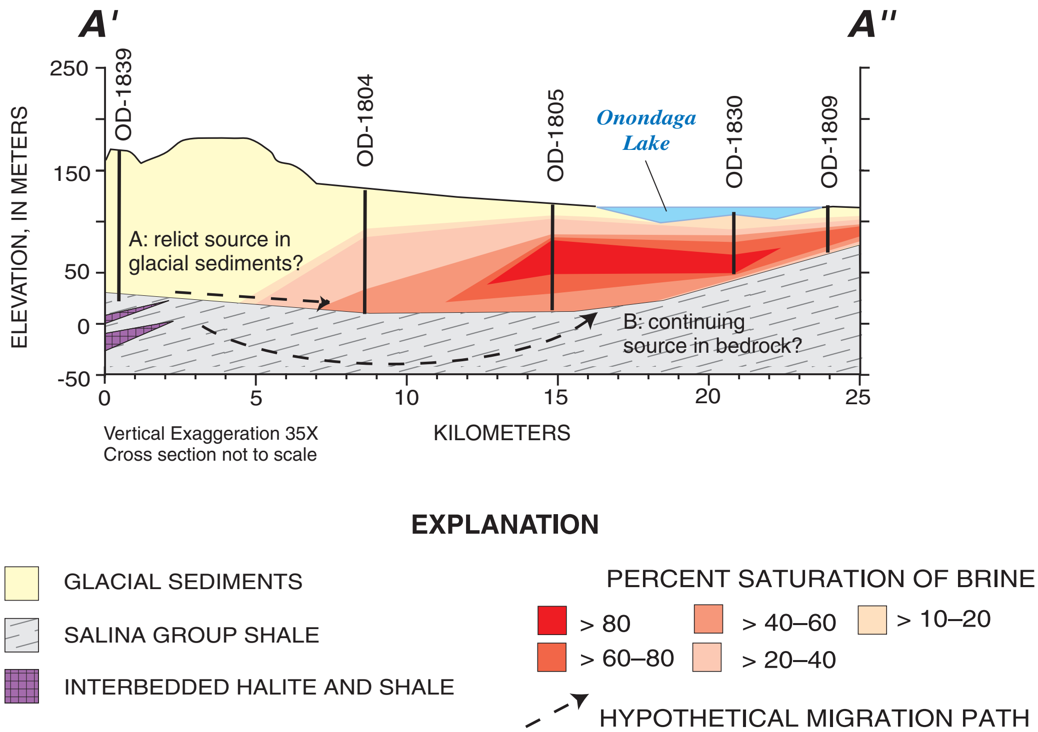

Figure 7. Generalized section A′-A″ showing percent saturation of brine at the northern end of the Onondaga Trough. Section location shown on figure 2.

stable boron isotope (^{11}B) by another USGS NRP laboratory (Menlo Park, Calif.). Samples of dissolved inorganic carbon were analyzed for stable and radioactive isotopes of carbon: ^{13}C was analyzed by the University of Waterloo Environmental Isotope Laboratory, Canada and ^{14}C was analyzed by Rafter Radiocarbon Laboratory, New Zealand and by the Laboratory of Isotope Geochemistry at the University of Arizona. A list of analytical results for the samples discussed in the text is presented in table 2 and the dissolved gas analyses are summarized in the appendix. The full table of analytical results for water samples is presented online at http://pubs.usgs.gov/sir/2007/5058.

Major and Minor Ions

Although sodium and chloride are the principal constituents of the halite brine (for example, well OD-1805, fig. 8), significant concentrations of potassium, calcium, magnesium and sulfate also are present in excess of that in brine prepared by dissolving halite samples in deionized water. The halite brine also contains bromide (40 to 120 mg/L), iron (1 to 14 mg/L), and boron (1 to 5 mg/L). The halite brine differs from saline bedrock waters sampled in the Onondaga Trough (for example, well OD-1827, fig. 8) in both ionic composition and the relative proportions of chloride and bromide. Saline bedrock waters are similar to Appalachian Basin brines typically present in western New York (New York State Department of Environmental Conservation, 1988) and contain higher concentrations of cations (except sodium) and bromide, and lower concentrations of sulfate than the brine prepared from bedded halite. Bedrock waters in the Onondaga Trough generally have chloride to bromide (Cl:Br) ratios (120:1) that are similar to Appalachian Basin brines (fig. 9A). Three bedrock wells along the shore of Onondaga Lake have large Cl:Br ratios (1300:1) that probably are typical of halite brine. The saline water discharged from the Solvay Process plant in the Ninemile Valley contained primarily sodium and chloride, but the proportion of calcium in the waste slurry was much larger than that of the halite brine due to the addition of limestone ($CaCO_3$) and removal of sodium carbonate (Na_2CO_3). Waters affected by contamination with Solvay waste are readily apparent on plots of calcium and magnesium and have calcium to magnesium (Ca:Mg) ratios of about 40:1 (fig. 9B). Most wells sampled by the USGS for this study were outside the waste-bed areas and have Ca:Mg ratios of less than 10:1. Well OD-1831, which is screened in the lower aquifer and located along the west shore of Onondaga Lake (fig. 5) is an exception. The saline water sampled in this well (saturation 30 percent) has a large Ca:Mg ratio (60:1) characteristic of Solvay waste water, and probably reflects migration of the waste northward along the western lake shore.

Table 2. Chemical and isotope composition of brine and ground water, Onondaga Trough, used in geochemical modeling.

[mS/cm, millisiemens per centimeter; g/cm³, grams per cubic centimeter; Ca, calcium; g/L, grams per liter; Mg, magnesium; mg/L, milligrams per liter; Na, sodium; K, potassium; Cl, chloride; SO_4^{2-}, sulfate; HCO_3^-, bicarbonate; Fe, iron; Br, bromide; δ^2H, del deuterium; ‰ , per mil; V-SMOW, Vienna Standard Mean Ocean Water; $\delta^{18}O$, del oxygen-18; ^3H, tritium; pCi/L, picoCuries per liter; B, boron; $\delta^{11}B$, del boron-11; ^{14}C, carbon-14; pmc, percent modern carbon; $\delta^{13}C$, del carbon-13; V-PDB, Vienna Pee Dee Belemnite; --, not analyzed]

County well number	pH	Specific conductance (mS/cm)	Density (g/cm³)	Saturation percent	Ca (g/L)	Mg (mg/L)	Na (g/L)	K (mg/L)	Cl (g/L)	SO_4^{2-} (g/L)	HCO_3^- (mg/L)
OD-683	7.9	0.5	0.9980	0	0.035	14	0.043	1	0.028	0.067	160
OD-1026	6.3	171	1.0775	41	18.	300	20.	200	66.2	.73	67
OD-1804	6.7	167	1.0978	51	1.28	200	49.4	200	74.	4.24	160
OD-1805	6.9	210	1.1307	65	1.81	350	66.3	340	102	3.26	92
OD-1806	6.8	159	1.0870	43	1.74	230	41.4	180	69	4.52	140
OD-1825	7.5	3	1.0017	2	0.58	77	1.	130	1.12	2.30	170
OD-1827	7.3	94.8	1.0456	25	9.9	2,100	12.	1,600	41.1	1.3	29
OD-1831	6.6	111	1.0546	30	9.9	170	19.	320	46.4	1.1	43
OD-1852[a]	7.6	4.6	1.00	0	0.64	30	0.55	17	1.5	0.18	210

County well number	Fe (mg/L)	Br (mg/L)	δ^2H ‰ V-SMOW[b]	$\delta^{18}O$ ‰ V-SMOW[b]	^3H pCi/L	B (mg/L)	$\delta^{11}B$ ‰	^{14}C[c] pmc	$\delta^{13}C$[c] ‰ V-PDB
OD-683	.5	0.5	-74.34	-10.71	0	1.9	4.25	50[d]	-12[d]
OD-1026	38.2	150	-65.58	-9.32	-0.2	1.3	34.47	15.8	-7.98
OD-1804	13.3	47	-76.74	-11.41	2.6	5.1	19.98	15.5	-7.52
OD-1805	13.5	86	-76.75	-11.3	-0.3	1.6	20.98	5.1	-13.5
OD-1806	6.8	45	-76.70	-11.46	2.6	5	15.98	13.4	-8.64
OD-1825	1.8	8.2	-69.92	-10.36	9.6	0.7	33.97	29.7	-8.69
OD-1827	30.1	510	-90.12	-12.4	1.6	2.9	44.21	4.0	-11.5
OD-1831	5.5	360	-67.01	-9.89	1.6	2.5	37.71	93.8	-18.07
OD-1852	.02	--	--	--	--	--	--	--	--

[a] Murphy (1978; table B-1).

[b] Corrected for electrolyte-water interaction resulting from the high concentrations of NaCl using the experimental calibrations of Horita and others (1993).

[c] Dissolved inorganic carbon.

[d] Estimated assuming closed-system evolution.

Isotopic Composition

Hydrogen and Oxygen

Most samples of halite brine have isotopic compositions of hydrogen (δD) and oxygen ($\delta^{18}O$) that plot along the local meteoric water line (MWL) (Burnett and others, 2004). The δD values have been corrected for electrolyte-water interaction resulting from the high concentrations of NaCl using the experimental calibrations of Horita and others (1993); no corrections were made for $\delta^{18}O$ measurements because such corrections are negligible for NaCl (Taube, 1954). The mean isotopic values are -76.6‰ δD and -11.3‰ $\delta^{18}O$ (fig. 10A). These values are slightly lighter (more negative or depleted) than those typically present in recent recharge in western New York, suggesting that the water infiltrated to the aquifer when the average temperature was cooler than at present (2005). Saline bedrock waters contain even more depleted isotopic values, indicating recharge under still colder conditions.

The two saline-water samples from the lower aquifer affected by contamination with Solvay waste have heavier (less negative or enriched) isotopic values that plot below the local MWL, suggesting enrichment as a result of evaporation. The waste slurry discharged from the Solvay Process plant was probably enriched in δD and $\delta^{18}O$ because the production of sodium carbonate required heat (approximately 300°C) that evaporated some of the water (for example, well OD-1026). The isotopic values of water from well OD-1831 (on the western shore of Onondaga Lake) plot along a mixing line that connects the isotopic composition of halite brine with that of well OD-1026 (fig. 10A), suggesting that about 40 percent of the water in OD-1831 is derived from Solvay waste water.

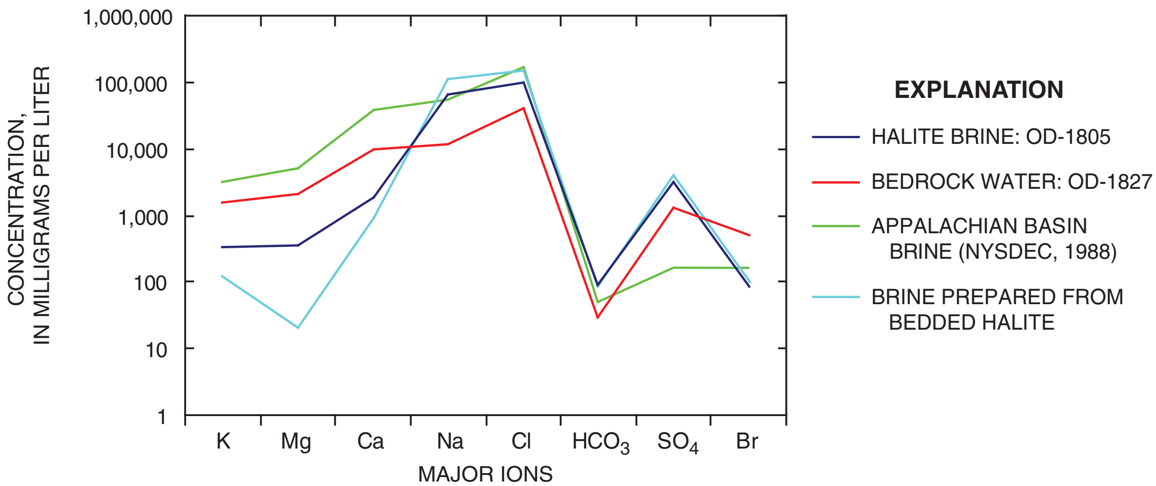

Figure 8. Concentrations of major ions in halite brine from a representative well in the Onondaga Trough (well OD-1805), in saline bedrock water (well OD-1827), in Appalachian Basin brine (New York State Department of Environmental Conservation, 1988, table 15.4), and in bedded halite.

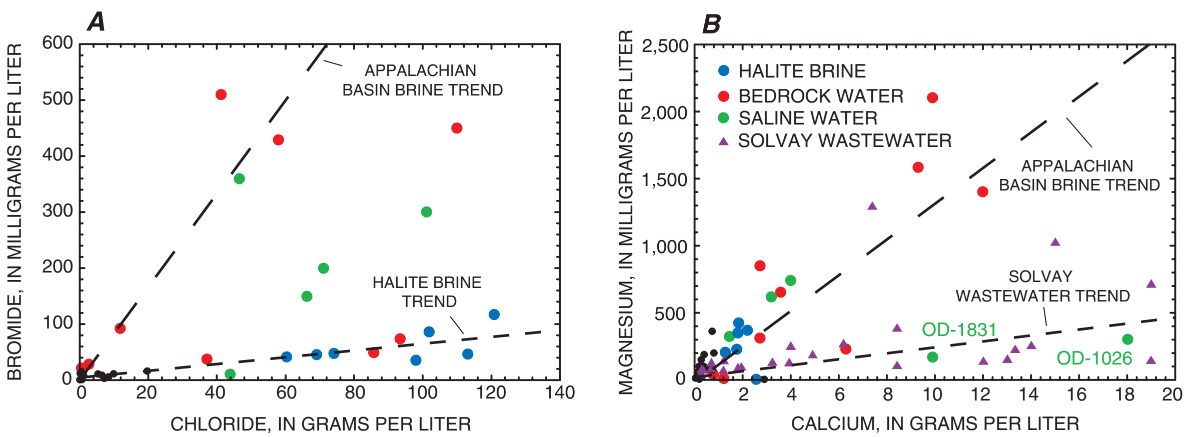

Figure 9. Relation between (*A*) chloride and bromide and (*B*) calcium and magnesium in ground water in the Onondaga Trough.

Boron

Halite brine samples generally have $\delta^{11}B$ values that are less than 22‰, while the $\delta^{11}B$ values of bedrock waters are larger and close to values typical of marine waters (39‰) (Spivack and others, 1987) (fig. 10B). Brine samples from wells OD-1809 and OD-1810 near the outlet of Onondaga Lake have values between these two limits. Salt solutions created by dissolving samples of halite from the Salina Group shale with deionized water have very little boron and $\delta^{11}B$ values that are near zero, which indicates that the boron in the brine was not derived from salt. Solutions created by leaching powdered samples of Salina Group shale with deionized water yield $\delta^{11}B$ values (10 to 28‰) that overlap the range of values in halite brines (fig. 10B). This evidence suggests that boron in the brine originated from desorption from glacial sediments, which are largely derived from the local shales. The process of sorption and desorption of boron from these sediments would explain the fractionation of the $\delta^{11}B$ from the values over 40‰ found in bedrock waters, compared to less than 22‰ found in the halite brine (Oi and others, 1989).

Carbon

The halite brine samples contain relatively low concentrations of dissolved inorganic carbon (DIC), ranging from 0.5 to about 2.5 millimoles per liter (mmol/L) with log CO_2 partial pressures of $10^{-3.4}$ to $10^{-2.2}$ atmospheres. The halite brines are near calcite saturation (the average calcite

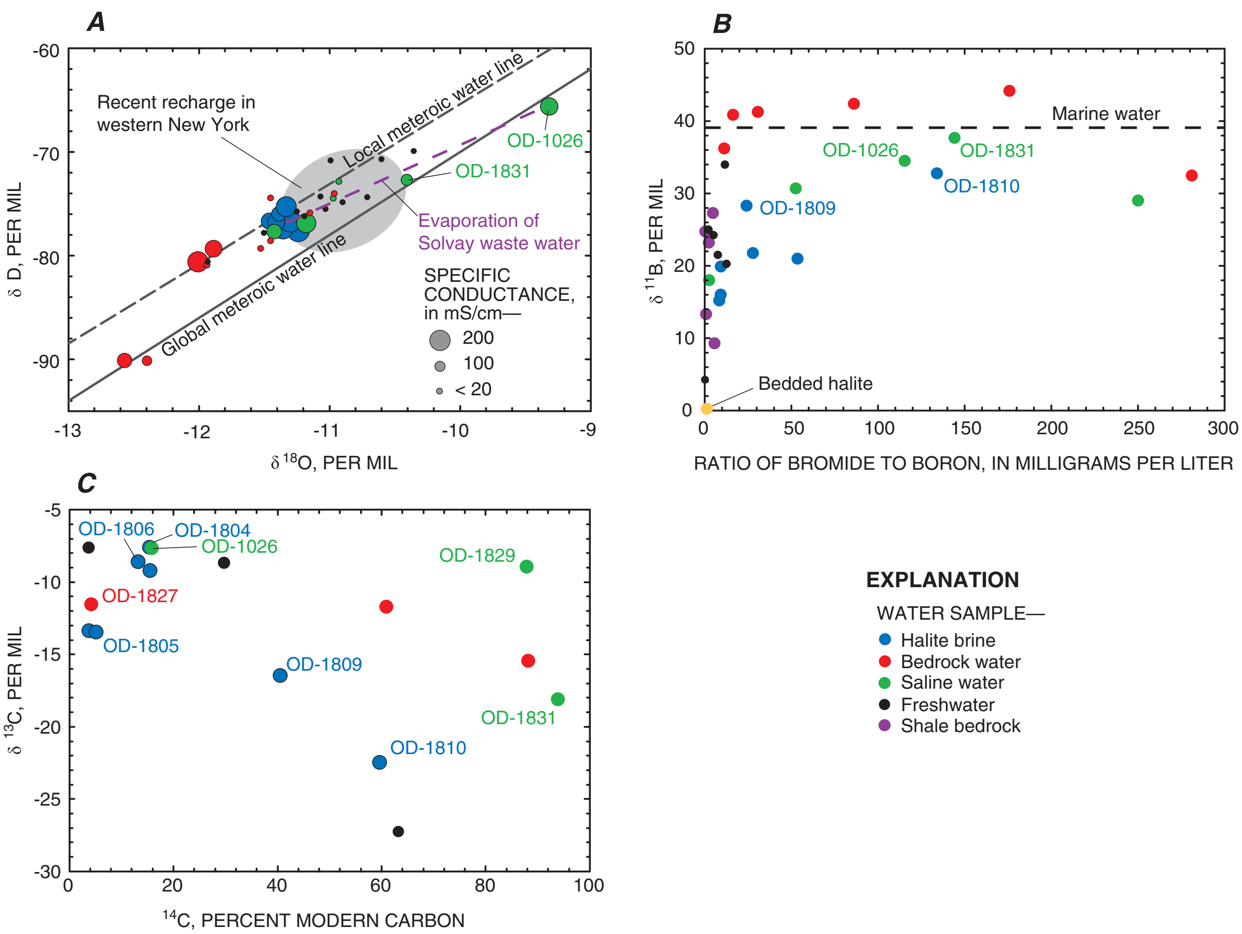

Figure 10. Isotopic concentrations of brine and saline waters in the Onondaga Valley: (*A*) deuterium and oxygen-18, (*B*) boron-11 and bromide to boron ratio, and (*C*) carbon-13 and carbon-14.

saturation index is -0.05±0.32). The ^{14}C activities of DIC in the halite brines generally range from 4 to 15 percent modern carbon (pmc), with the exception of samples from wells near Onondaga Lake. Saline waters from wells OD-1809 and OD-1810 near the Onondaga Lake outlet have values of 40 and 60 pmc, respectively (fig. 10C), while waters from wells OD-1829 and OD-1831 on the eastern and western lake shores, respectively, have values greater than 85 pmc. The ^{14}C values of bedrock waters range from 4 to 90 pmc.

Waters with ^{14}C values less than 15 pmc could be as old as 15,000 to 25,000 years. The DIC in these samples have $\delta^{13}C$ values of -8 to -15‰, which could result from dissolution of marine carbonate rocks ($\delta^{13}C$ ~ 0‰) with soil CO_2 derived from organic carbon ($\delta^{13}C$ ~ -25‰) in a closed system (Clark and Fritz, 1997). The addition of "dead" carbon from dissolution of carbonate rocks containing negligible amounts of ^{14}C dilutes the ^{14}C content, resulting in unadjusted radiocarbon ages that appear to be older than the actual age. Waters with ^{14}C activities greater than 85 pmc probably are recent meteoric waters, though tritium contents were at the detection limit of <0.7 tritium units (TU), indicating the waters were more than 50 years old. The $\delta^{13}C$ values of these samples are generally lighter than -15‰, suggesting that more of the carbon could be derived through oxidation of organic matter ($\delta^{13}C$ ~ -25‰). The age of the DIC in the halite brine was estimated through geochemical calculations by using NETPATH, as described later.

Origin and Age of Brine

The halite brine in the Onondaga Trough probably formed through dissolution of halite and gypsum beds that were exposed in the Syracuse Formation through erosion by glacial ice. The geochemical composition of the brine differs markedly from that of saline bedrock waters obtained from wells adjacent to the trough in that: (1) the Cl:Br ratio of brine samples is much larger (fig. 9A), (2) the δD and $\delta^{18}O$ values are heavier (fig. 10A), and (3) the $\delta^{11}B$ values are lower (fig. 10B) than those of the saline bedrock waters. This evidence suggests that the halite brine was not derived directly from saline water in the local bedrock. The presence of potassium and magnesium and other minor ions in the brine, however, suggests that bedrock waters probably mixed with the brine, as these elements are not present in the halite beds in the Syracuse Formation.

Geochemical Modeling

The computer program NETPATH (Plummer and others, 1994) was used to determine whether mixtures of representative waters and accompanying water-rock reactions could account for the observed geochemical composition of the halite brine. Two end-member waters were considered in the mixing scenarios: (1) freshwater derived from glacial melt water and (2) saline water derived from the bedrock. The freshwater was represented by the sample from well OD-683, which is screened in the lower aquifer beneath the Valley Heads Moraine and contains the most dilute water sampled in the study area (wells are located on fig. 5). Saline bedrock water was represented by the sample that appears to contain the oldest ground water, based on the measured ^{14}C value of 4 pmc from well OD-1827 located north of Onondaga Lake (fig. 10C; table 2).

Modeling Approach

The aqueous speciation calculation indicated that charge imbalances were typically less than 2 percent in the most saline waters. Though small, charge imbalances of even several percent can lead to large uncertainties in calculated mass transfer in geochemical mass-balance calculations involving highly saline fluids. Most affected are the calculated mass transfers of “neutral” phases, such as organic matter or CO_2 that are not formed by combination of positive and negative charges. Therefore, the charge-balance algorithm of NETPATH was invoked to adjust the compositions of all initial and final waters prior to making the mass-transfer calculations.

Mixtures of waters were assumed to react with the principal carbonate minerals (calcite and dolomite) and evaporite minerals (halite and gypsum) present in the study area. Additional reactions considered the possibility of (1) iron reduction (from goethite), (2) sulfate reduction accompanying the oxidation of organic carbon, (3) precipitation of iron sulfide, (4) cation exchange (involving Ca^{2+} and Mg^{2+} for Na^+) on surfaces of clay minerals, and (5) exsolution of a CO_2-CH_4 gas mixture containing 5% CH_4 (as indicated by analyses of gas bubbles sampled from the Spencepatrick Spring, OD-1819). The models were constrained by measured concentrations (adjusted for charge imbalance) of the elements Ca, Mg, Na, K, Cl, S, C, Fe, and Br; and an electron balance constraint (conservation of electrons in redox reactions) was included. Carbon containing ^{14}C was assumed to originate from soil CO_2 and organic matter present in valley sediments during the final recession of the ice margin about 16,500 years BP. Because ^{13}C and ^{14}C analyses are not available for these materials, a range of potential values (-22 to -25 per mil and 50 to 100 pmc, respectively) was considered for both of these carbon sources. Inorganic carbon sources (calcite and dolomite) were assumed to have $\delta^{13}C$ and ^{14}C activities of 0 per mil and 0 pmc, respectively.

Reaction Models

One reaction model satisfied all the constraints and predicted the observed $\delta^{13}C$ of DIC in brine in well OD-1805, which is screened in the lower aquifer at the southern end of Onondaga Lake. The reaction model indicated a mixture of freshwater (83 percent) and saline bedrock water (17 percent), and dissolution of 2.8 moles per kilogram of water (mol/kg_{water}) of halite, 0.033 mol/kg_{water} of gypsum, and 0.029 mol/kg_{water} of cation exchange (Ca^{2+} for Na^+). The rest of the mineral mass transfers were comparatively small (< 0.001 mol/kg_{water}). The computed age of DIC in water from OD-1805, following adjustment for the modeled geochemical reactions, was 16,700 years. The computed age is sensitive to the initial ^{14}C content specified for OD-683, which is unknown, but assumed to be about 50 pmc, a value consistent with geochemical evolution in a system closed to CO_2 gas exchange. Closed-system evolution is commonly observed in humid areas with relatively high recharge rates where infiltration to the water table is rapid, followed by subsequent closed-system evolution in saturated zones that contain carbonate rocks (Deines and others, 1974). At calcite saturation, the bicarbonate content of the resulting ground water in the recharge area contains about half of its carbon from soil gas CO_2 (100 pmc) and about half of its carbon from old carbonate rocks (0 pmc). In arid regions where the recharge rates can be low, approach to open-system evolution is more common resulting in initial ^{14}C activities near 100 pmc. Increasing the ^{14}C value from 50 to 100 pmc increased the computed age to over 22,000 years. Although open-system conditions are unlikely to apply to recharge in the glacial drift system of the Onondaga Lake region, partially open systems may prevail and the adjusted radiocarbon age of DIC in water from well OD-1805 could be greater than 16,700 years. Another brine sample from well OD-1788, located within 1 km of OD-1805, contained ^{13}C and ^{14}C values of DIC similar to those from well OD-1805, suggesting a comparable age for this sample. Although the mineral saturation indices and compositions of these two brine samples are similar, a valid reaction model for OD-1788 was not found, owing to compositional variations resulting from uncertainty in the charge imbalance calculation.

The same reaction model as that presented above for water from well OD-1805, with only minor modifications, also reproduced the observed chemical concentrations and $\delta^{13}C$ of DIC in more dilute brines at wells OD-1804 and OD-1806. Both of these wells are along the periphery of the brine pool where freshwater from the south (upgradient) flows upward and over the brine and discharges to Onondaga Creek. Well OD-1804 is screened in the lower aquifer at the southern end of the brine pool, and well OD-1806 is screened in coarse-grained sediments about 60 m above well OD-1805. The specified ^{14}C content of OD-683 was increased to 100 pmc in these reaction models to reflect additional freshwater from a recent source in the mixing model, and the ion exchange reaction (Ca^{2+} for Na^{+}) was modified to include Mg^{2+} to account for the enriched $\delta^{13}C$ (-7.5) observed at OD-1804. Both reaction models indicated a mixture of 91 percent freshwater and 9 percent saline bedrock water, and the occurrence of the dedolomitization reaction (dissolution of dolomite and gypsum accompanied by precipitation of calcite) as the predominant water-rock reaction. The adjusted radiocarbon ages of the DIC in water from wells OD-1804 and OD-1806 calculated from the geochemical models was 2,000 and 2,400 years, respectively. Although the modeled and measured $\delta^{13}C$ were in close agreement at well OD-1804, the calculated $\delta^{13}C$ was enriched by 4 per mil in DIC at well OD-1806 compared to the measured value (-8.6‰). This difference could have resulted from uncertainties related to the adjustment of charge imbalances in water compositions, or other uncertainties in the model. The calcite precipitation predicted by both of these models is consistent with observations of calcite rinds that encrust sand and gravel in core material from shallow depths (~20 m) at the southern end of the brine pool. The younger computed ages probably reflect mixing of the brine with recent meteoric recharge.

A separate reaction model was prepared to investigate the origin of the chemical composition of saline water in well OD-1026, which is screened in the lower aquifer beneath the Solvay waste beds in the Ninemile Valley. This model represented dissolution of waste materials (sodium carbonate and calcium chloride) by freshwater taken from Onondaga Lake (OD-1852) and discharged by the chemical plant. This wastewater was then mixed with ground water in the lower aquifer (OD-1825) and saline bedrock water (OD-1827). A mixture of 60 percent lake water, 11 percent fresh ground water and 29 percent saline bedrock water satisfied all the constraints and predicted the observed $\delta^{13}C$ of DIC in brine in well OD-1026. In addition to dissolution of sodium carbonate and calcium chloride, the reaction model predicted precipitation of calcite and ion exchange (Na^{+} for K^{+}). Although most reactions modeled in the mass-balance calculations were reasonable, the model also predicted precipitation of a small amount of dolomite, which is unlikely during the relatively young timescale of the waste beds. This prediction was related to uncertainty in the adjustment of water analyses for charge imbalances, or perhaps different reactions and(or) additional water sources could be considered. The computed age for the resulting mixture was about 600 years and, within the uncertainty of the calculations, could easily be modern, although older than 1950 because tritium was not detected (< 0.7 TU).

Alternative Hypotheses for Brine Formation

The NETPATH calculations indicate that the halite brine could have formed during deglaciation of the Onondaga Trough (16,500 to 14,300 years BP) if freshwater (derived from glacial melt water) mixed with saline water (derived from the bedrock) and reacted predominantly with halite, gypsum, and Ca^{2+} for Na^{+} cation exchange. The radiocarbon age of the brine pool (16,700 years) and its position at the northern end of the Onondaga Trough suggest that the brine formed during deglaciation and then moved northward through the lower aquifer to its current position beneath Onondaga Lake. If the brine pool were sustained through contemporary dissolution of salt beds in the Syracuse Formation by recent meteoric recharge, a plume of brine would emanate northward from the subcrop area 15 km south of the lake, and salt saturations would decrease from south to north, which is opposite to the observed pattern. In addition, the age of the brine pool would likely be younger than that calculated by NETPATH. An alternative explanation for the brine pool's position is that the brine in the lower aquifer is replenished by the upward flow of old brine from Salina Group shales beneath the Onondaga Trough (fig. 7). In this scenario, the brine pool resides in the bedrock, and its upward flow causes salinity in the lower aquifer to increase along a flow path from the Tully Valley towards Onondaga Lake.

The difference between these two alternative hypotheses is significant. Under the first hypothesis, the brine originated from a relict source of salt and is slowly being depleted. Under the second hypothesis, a contemporary source of salt could sustain the brine pool indefinitely. Unfortunately, no information is available on the quality of the bedrock water directly beneath the Onondaga Trough between the delineated brine pool and the halite beds to the south to either confirm or deny the second hypothesis. Although the geochemical mixing model supports the first hypothesis that the halite brine is derived from glacial melt water and not recent meteoric recharge, melt water could still reside in the bedrock beneath the trough. The question of whether the halite brine could have originated from dissolution of a relict source of salt, migrated from the halite subcrop area, and persisted for over 16,000 years is the subject of two-dimensional, variable-density flow simulations described later in this report.

Three-Dimensional Variable-Density Flow Model

A variable-density, transient ground-water-flow model of the glacial aquifer system in the Onondaga Trough was constructed using SEAWAT-2000 (Langevin and others, 2003), a computer program that combines a modified version of MODFLOW-2000 (Harbaugh and others, 2000) with MT3DMS (Zheng and Wang, 1998). The three-dimensional (3D) model was calibrated to changing aquifer conditions over a 215-year period from 1790 to 2005. The grid resolution of the 3D model was selected to limit computational time and allow calibration of model parameters, but was not sufficiently detailed to accurately represent the flow dynamics in the vicinity of the brine pool over extended periods of time. A higher resolution, two-dimensional (2D) cross-sectional model aligned along the longitudinal axis of the Onondaga Trough was also developed to simulate the origin and fate of the brine over a 17,000-year period, using the parameter estimates obtained with the 3D model. The 2D model is described in a later section.

SEAWAT-2000 was chosen over other available computer programs because a wide range of boundary conditions could be specified and changed during the transient simulations. The SEAWAT program solves the variable-density flow equation by formulating the matrix equations in terms of fluid mass and assuming that the fluid density is solely a linear function of solute concentration (Guo and Langevin, 2002). The flow and transport equations can be coupled either explicitly, in which case the equations are solved sequentially, or implicitly, in which case the equations are solved iteratively until the maximum difference in fluid density is reduced to a specified level. The effect of variable fluid viscosity on flow was not considered in these simulations because the temperature range in this shallow aquifer system is small. Langevin and Guo (2006) showed that accounting for variable viscosity had a negligible effect in their SEAWAT simulation of the salt-pool problem. Langevin and Guo (2006) showed that accounting for variable viscosity had a negligible effect in their SEAWAT simulation of the salt-pool problem (Oswald & Kinzelbach, 2004), a laboratory experiment in which a three-dimensional mixing zone was formed between saline water with a 10% mass fraction and an overlying layer of slow-moving freshwater.

Numerical Solution

The solution of the advection-dispersion equation that forms the basis of the transport simulation is difficult, and several numerical methods are provided for this purpose in MT3DMS (Zheng and Wang, 1998). The selection of a numerical method involves a compromise between the time required for the solution and the accuracy attained. One major concern is that numerical dispersion resulting from the solution technique can affect simulated concentrations by artificially spreading and smoothing sharp concentration fronts. Numerical dispersion can be reduced by refining the spatial and temporal discretization specified in the model, or by selecting a solution technique that is free from numerical dispersion (Zheng and Bennett, 2002). Both of these methods require more computational effort and longer simulation times than less accurate methods with larger amounts of numerical dispersion.

In the variable-density flow model described herein, the flow and transport equations were explicitly coupled using a one timestep lag and solved alternately until the maximum difference in fluid density was less than 10^{-6} kg/m^3, which provided a mass-balance error less than 0.01 percent. An implicit finite-difference (FD) method with upsteam weighting was used to solve the advection equation. The selection of the FD method allowed the use of relatively large time steps (up to 750 days) in the 215-year simulation specified in the 3D models and resulted in run times of less than 1 hour on a 3.2-GHz Pentium D processor. Application of the FD method caused spreading of the simulated brine pool. This resulted in simulated concentration distributions in which the width of the mixing zone between brine and surrounding fresher waters was determined by numerical dispersion. The potential effect of numerical dispersion on model results was explored in alternative simulations discussed later in this report.

Model Design

The design of the 3D variable-density flow model was based on the 3D geologic model presented earlier. The model domain encompasses 120 km^2 and is divided into a uniformly spaced grid of 100 m with 369 rows and 136 columns. The 11 flow-model layers contain a total of 111,171 active cells. The flow-model layers generally correspond to the six layers represented in the geologic model (table 1), but three of the geologic model layers were subdivided to better represent flow through the surficial sediments (geologic layer 1), the silty-sand confining layer (geologic layer 3) and the basal sand and gravel layer (geologic layer 6). In addition, flow-model layer 1 only represents Onondaga Lake, while flow-model layers 2 to 4 represent both the surficial sediments (geologic layer 1) and the silty-clay lacustrine sediments beneath the lake (geologic layer 2). The bedrock along the walls of the Onondaga Trough is represented in flow layers 10 and 11 in areas where the basal sand and gravel is absent to allow hydraulic connection between the lower aquifer and upper units along the valley walls. Several alternative models developed to investigate the sensitivity of model results to changes in specified parameters were based on this same design (table 3). In model 3D-E, the grid and layer spacing were reduced by one-half to reduce numerical dispersion.

The model simulation was divided into two periods: (1) a 30-year simulation with steady-state flow and transient transport that represents natural conditions from 1790 to 1820; and (2) a 185-year simulation with transient flow and transport

Table 3. Alternative three-dimensional variable-density flow models of Onondaga Trough.

[Shading denotes change from calibrated model 3D-A; m/d, meters per day; FD, implicit finite difference; TVD, total variation diminishing]

Model	Grid spacing, in meters: Row/column	Grid spacing, in meters: Layer	Solvay waste application rate[a]	Hydraulic conductivity of silty-sand confining layer, m/d	Numerical method
3D-A	100	1 to 30	15	.3	FD
3D-B	100	1 to 30	25	.3	FD
3D-C	100	1 to 30	100	.3	FD
3D-D	100	1 to 30	15	.03	FD
3D-E	50	0.5 to 15	15	.3	FD
3D-F	100	1 to 30	15	.3	TVD

[a] Percent of total waste chloride volume produced.

that represents brine pumping from 1820 to 1920, disposal of Solvay waste from 1920 to 1985, and closure of the waste disposal areas from 1985 to 2005. Hydraulic heads and solute concentrations computed by the 30-year simulation served as initial conditions for the transient simulation. Chloride was selected as the migrating solute in the transport simulation because the relation between chloride and density in brine samples is relatively linear (fig. 11). The initial chloride distribution C in the brine pool in the steady-state simulation was computed as a linear function of increasing concentration with depth:

$$C = Min + (Max - Min) * Depth / Threshold ; Depth < Threshold \quad (1)$$
$$C = Max ; Depth \geq Threshold ,$$

where

Min and *Max* are the minimum and maximum chloride concentrations, respectively (2,000 and 170,000 mg/L);

Depth is meters below land surface;

and

Threshold is the depth below which the brine is saturated. The threshold depth was estimated through model calibration, which is described later.

Boundaries were specified in the model to represent inflows from underflow and recharge, and outflows to surface water and pumped wells (table 4). Constant head and flux boundaries were specified to represent underflow to valleys tributary to the Onondaga Trough and discharges to Onondaga Lake. The bottom boundary of the model was specified as no-flow because no information is available concerning the rate of potential inflow from fracture zones in the bedrock to the glacial sediments. Discharges to perennial streams and springs were generally represented by drains (head-dependent boundaries that only allowed outflow), although discharge to a large wetland in the West Branch Valley was represented by evapotranspiration (negative recharge). Boundary conditions remained fixed throughout the two simulation periods, with the exception of: the elevations of Onondaga Lake and the Seneca River which were raised from 110 to 110.6 m in 1920; the depth of the Seneca River, which was filled by as much as 5 m in 1920; and pumping from brine wells from 1820 through 1920.

Recharge was specified to surficial sediments in the West Branch, Onondaga, and Ninemile Valleys. Recharge rates were estimated for both rural and urban areas. Although infiltration of precipitation in urban areas is limited by impervious surfaces, conveyance losses from water-distribution networks are significant and constitute a source of recharge. Runoff from upland areas was represented by arbitrarily doubling the recharge rate in model cells that bordered the valley walls in the West Branch and Onondaga Valleys. Recharge to the middle aquifer in the Tully Valley was specified where the mid-section sand and gravel occurs at land surface at the Valley Heads Moraine. Wastewater infiltrating from the Solvay disposal areas in the Ninemile Valley was represented by recharge of saturated brine (170,000 mg/L Cl) in waste bed A from 1920 to 1945, and in waste beds B and C from 1945 to 1985 (fig. 5). The recharge rate associated with Solvay waste disposal (33 centimeters per year [cm/yr]) was arbitrarily specified as about 15 percent of the average water application rate from 1925 to 1985 in waste beds A, B, and C.

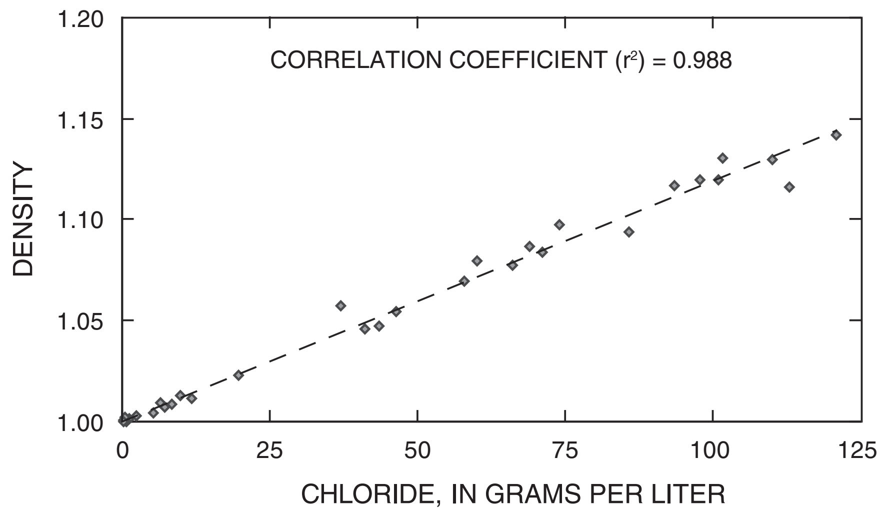

Figure 11. Relation between chloride and density in halite brine samples.

Model Calibration

The variable-density flow model 3D-A was calibrated by adjusting values of hydraulic properties to match 95 measurements of several kinds of data: water levels (37), ground-water discharges (6), chloride concentrations (47), and mass flows (5). A total of 15 parameter values were specified in the model (table 5), 8 of which were estimated through nonlinear regression using UCODE (Poeter and Hill, 1998), a computer program that uses weighted least squares to minimize model residuals (difference between observed and simulated data). Model sensitivities corresponding to the remaining parameters were too small to allow estimation by regression, and were based on a flow model previously developed for the Solvay area west of Onondaga Lake (Parsons, 2004) or were taken from the literature. Weights assigned to most observations included in the regression were chosen to account for the different units associated with the measurements and adjusted such that the observations were weighted equally. Water-level measurements made in 18 wells containing high-salinity water were adjusted to reflect the density of the water column in the well casing, which may not be uniform with depth. Water-level observations for these wells were calculated by measuring the water density and bottom-hole pressure, and then computing the water-column length required to offset the bottom-hole pressure using water with the measured density. Pressure data were not available for 6 other wells containing high-salinity water, so the regression weights corresponding to these water-level observations were reduced by 50 percent.

Coefficients of variation (CV) for six of the eight estimated parameters were less than 25 percent, indicating that the regression was sensitive to these parameters and that the values were well-estimated. The estimated values of the recharge parameters had CVs ranging from 27 to 59 percent and are more uncertain than the estimated values of the other six parameters. The estimated value of hydraulic conductivity of the basal sand and gravel (72 meters per day [m/d]) is within the range of values estimated from aquifer tests (O'Brien & Gere, 2002) (30 to 330 m/d). The estimated rural recharge rate (42 cm/yr) is slightly less than the value of 53 cm/yr estimated by Miller and others (1998) for a glacial-drift aquifer in Cortland County, 50 km south of Onondaga Lake.

Model Fit

The error associated with model 3D-A for the four types of observations is depicted in a series of residual plots (fig. 12). A comparison of simulated and observed values (fig. 12A) indicates that the largest errors are associated with concentration values, although model results contain little bias (approximately equal numbers of over- and under-predicted values). Note that log values are shown on this plot because of the large range in values presented. The weighted residuals shown in figures 12B–12D all have units of head in meters to facilitate comparisons between the different types of observations.

Water-level residuals (fig. 12B) are as much as 6 m at higher elevations in the southern part of the Onondaga Trough (4 percent of the 150-m range in head), but are less than 3 m at lower elevations near Onondaga Lake. The water levels produced by SEAWAT incorporate the effects of density and are comparable to values that would be measured in the field, assuming a uniform-density water column. Inspection of

Table 4. Boundary conditions specified in three-dimensional variable-density flow models.

[CH, constant head; CF, constant flux; Drn, drain; Ghb, head-dependent flow; Rch, recharge; m, meters; m^3/d, cubic meters per day; cm/yr, centimeters per year]

Boundary	Type	Model layer	Elevation or flow rate
Onondaga Lake	CH	1	110.6 m[a]
Underflow			
Tully Valley	CH	11	342.9 m
West Branch Valley	CH	11	190.5 m
Ninemile Valley	CF	11	255 m^3/d
Ley Creek Valley	CH	7	115.8 m
Springs			
Mudboils	Drn	8 and 10	170.1 m
Landslides	Drn	8	166.7 and 153.9 m
Streams			
West Branch Onondaga Creek	Drn	4	Varies
Onondaga Creek	Drn	4	Varies
Ninemile Creek	Drn	4 and 5	Varies
Seneca River	Ghb	3[b]	110.6 m[a]
Wetland			
Upper West Branch Valley	CH	2	198 m
Lower West Branch Valley	Rch	5	-63 cm/yr[c]
Brine wells	CF	11	1,320 m^3/d[d]
Recharge, cm/yr			
Rural areas	Rch	2	42
Urban areas	Rch	2	11
Moraine	Rch	8	22
Solvay waste	Rch	2	33[e]

[a]Elevation specified as 110 m from 1790 to 1920.

[b]Boundary specified in layer 5 from 1790 to 1920.

[c]Evapotranspiration rate.

[d]Average rate specified from 1790 to 1920.

[e]Specified from 1920 to 1985.

Table 5. Parameter values specified and estimated in model 3D-A.

[Shaded values in bold estimated by regression. m/d, meters per day; cm/yr, centimeters per year]

Parameter	Value	Coefficient of variation, percent
Hydraulic conductivity[a], m/d		
Water	300	
Marl and fill	9×10^{-4}	
Alluvial sand and gravel	**2.1**	22
Deltaic sand and gravel	**5.2**	6
Lacustrine clay and silt	9×10^{-5}	
Lacustrine silt and sand	.3	
Mid-section sand and gravel	**50**	9
Basal sand and gravel	**72**	2
Bedrock	.3	
Recharge, cm/yr		
Urban	**11**	76
Rural	**42**	11
Moraine	**22**	48
Solvay waste	33	
Transport properties		
Porosity[b]	.3	
Threshold for saturated Cl, m	**70**	2

[a]Isotropic values assumed.

[b]All sediments.

the largest residuals of concentrations (fig. 12C and fig. 13) reveals that concentrations are over-predicted in the central and deep parts of the brine pool, and concentrations are under-predicted at shallow depths (up to 40 m) in the vicinity of the Spencepatrick Spring south of Onondaga Lake and beneath some of the Solvay waste beds. The depositional history and resulting glacial stratigraphy in these areas are probably more complex than was assumed in the construction of the geologic model.

Residuals of ground-water discharge and chloride mass flows also indicate little bias in the model results (fig. 12D). Ground-water discharges to the mudboil and landslide springs in the Tully Valley are over-predicted by as much as 70 percent, while discharges to Ninemile Creek and Spencepatrick Spring are under-predicted by about 60 percent (table 6A). The uncertainty in actual average ground-water discharge at these locations is relatively large, however, because the estimates are based on few measurements.

Simulated chloride mass flows to Onondaga Creek and Onondaga Lake are both predicted accurately, as is the total mass of chloride pumped from brine wells during the period from 1820 to 1920. Chloride mass flows to Ninemile Creek are over-predicted by more than 30 percent, while chloride mass flows discharged through Spencepatrick Spring are under-predicted by 70 percent. The latter error results from under-prediction of both the rate of simulated ground-water discharge through Spencepatrick Spring, and simulated chloride concentrations at the shallow depths south of Onondaga Lake.

Simulated heads along a longitudinal profile A-A” through the Onondaga Trough are in good agreement with measured water levels in wells (fig. 14). Simulated heads are as much as 18 m above land surface in the Tully Valley where the combination of the thick confining layer at land surface together with a steep topographic gradient creates artesian conditions. Simulated heads increased to 60 m above land surface in a separate hypothetical simulation that neglected ground-water discharge through springs in the Tully Valley. These results suggest that the mudboils and landslide springs in the valley release pressure generated in the underlying aquifers.

The agreement between observed and simulated chloride concentrations is depicted in a series of profiles showing variations of concentration with depth at three locations at the end of the 215-year simulation (figs. 15A–C). The observed values were obtained from pore-water samples extracted from sediment cores collected during the drilling of boreholes at these locations. Simulated chloride concentrations at OD-1830 drilled beneath Onondaga Lake are in good agreement with observed concentrations, which have relatively little scatter. The simulated concentrations at the end of the simulation are nearly equal to the initial concentrations, indicating little movement of chloride at this location.

The difference between observed and simulated chloride concentrations is greater at the two locations south of Onondaga Lake. Concentrations are under-predicted at OD-1805 (particularly at shallow depths) and over-predicted at OD-1804. Wide scatter in the observed chloride concentrations at both locations could reflect mixing of the brine with saline bedrock water as a result of brine pumping in the 19th century. The simulated chloride concentrations are less than the initial concentrations at both locations, indicating that the brine was diluted during the 215-year simulation in response to pumping and mixing with freshwater.

The only historical data available on chloride concentrations were reported for brine wells drilled in 1842 south of Onondaga Lake in the vicinity of OD-1805

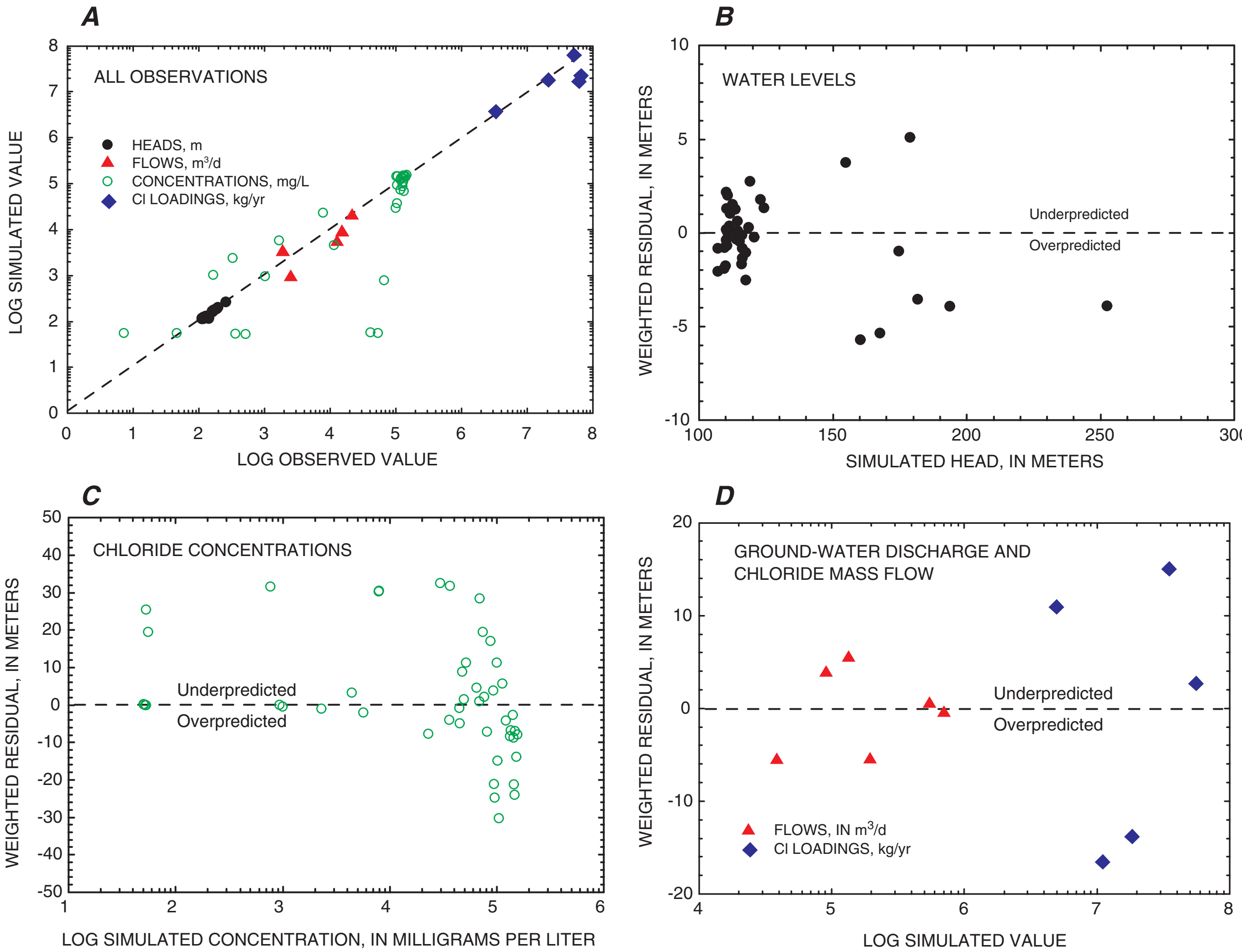

Figure 12. Residual plots showing relations between observed and simulated values, and weighted residuals: (*A*) all observations, (*B*) water levels, (*C*) chloride concentrations, and (*D*) ground-water discharge and chloride mass flows.

(fig. 15D). The sharp decline in chloride concentration from 1842 to 1858 indicates the effect of brine pumping, but chloride concentrations appear to have continued to decline up to the most recent sampling in 2005. No additional data are available prior to the cessation of pumping in 1920, but declining chloride concentrations after 1858 likely result from brine withdrawals because more than 50 percent of the brine production occurred between 1850 and 1920. The simulated concentrations at this location are over-predicted, and indicate a slight decline in chloride over the 163-year period.

Simulated Aquifer Conditions

The simulated water budget indicates that nearly all the ground water in the aquifer system within the Onondaga Trough is derived through recharge from precipitation (table 7). Onondaga Creek (49 percent) and the West Branch Valley (29 percent) account for most of the ground-water discharges. The remainder discharges to Ninemile Creek and springs. Less than one percent discharges to Onondaga Lake and the Seneca River.

Representation of the Brine Pool

Ground water in the lower aquifer flows northward through the Onondaga Trough towards Onondaga Lake. Flow from the Tully and West Branch Valleys converge near well OD-1839 (fig. 5) where the ground water is relatively fresh with a density near 1.0 g/cm^3 and a chloride concentration of 0.6 g/L. The freshwater encounters the brine pool in the vicinity of well OD-1804 where the ground-water density is 1.01 g/cm^3 with a chloride concentration of over 70 g/L (fig. 13). Freshwater at this location is diverted around the brine pool where ground water flows upward over the brine-filled trough. This movement creates a mixing zone where some of the mass of the brine is entrained in the upward flow and eventually lost to the aquifer system as it discharges to Onondaga Creek.

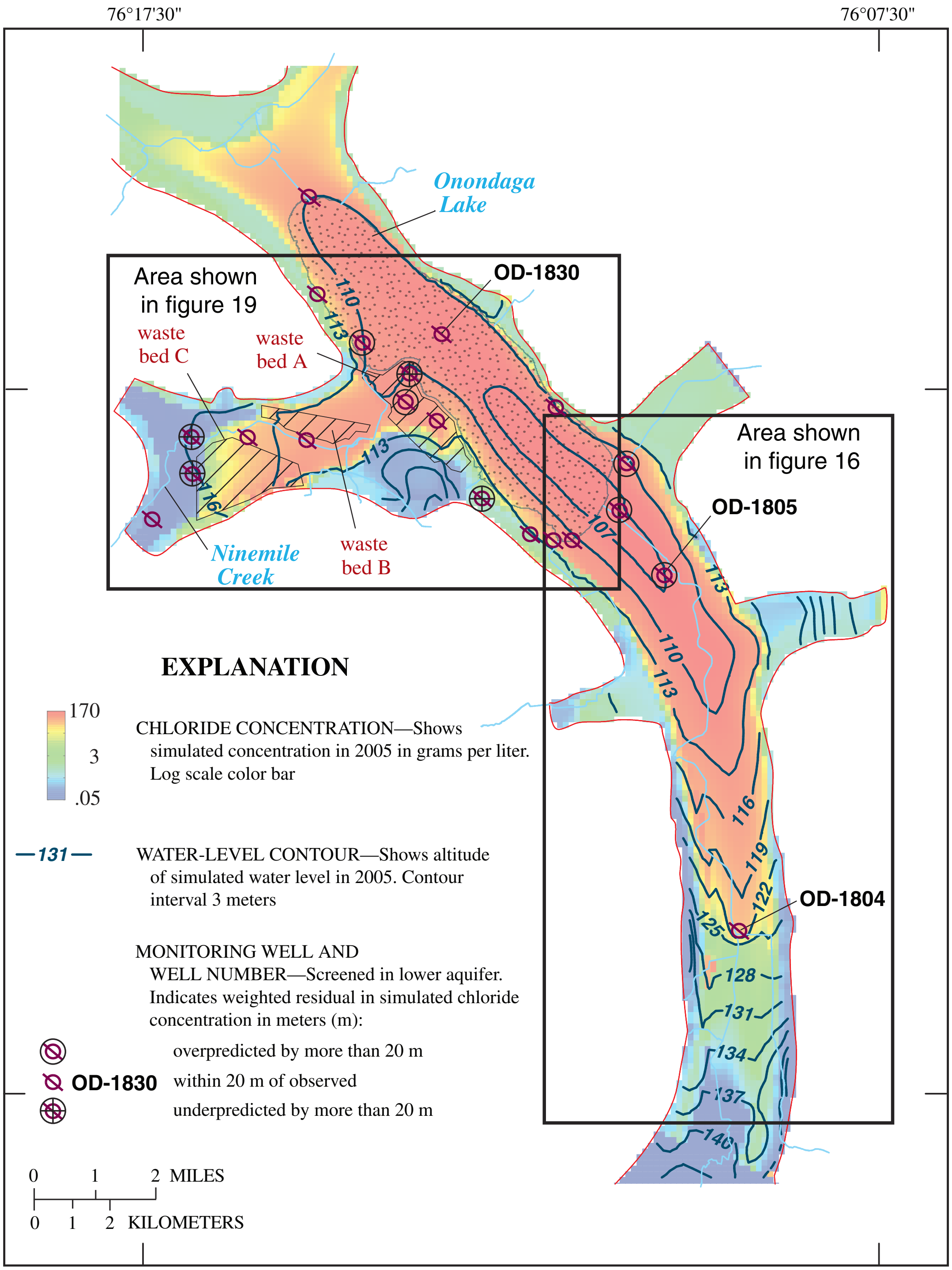

Figure 13. Water levels and chloride concentrations simulated for current conditions in the lower aquifer.

Table 6. Observed and simulated values of ground-water discharge and chloride mass flows in model 3D-A.

[m^3/d, cubic meters per day; Mg/yr, megagrams per year]

Observation	Observed	Simulated
Ground-water discharge, m^3/d		
Onondaga Creek:		
Upstream	20,700	19,600
Downstream	14,700	9,000
Ninemile Creek	12,200	5,200
Spencepatrick Spring	2,400	900
Mudboil springs	1,800	3,100
Landslide springs	2,400	3,800
Chloride mass flows, Mg/yr		
Pumped brine[a]	48,000	43,000
Onondaga Lake	3.2	3.4
Onondaga Creek	20	17
Ninemile Creek	49	64
Spencepatrick Spring	59	16

[a]Average rate from 1790 to 1920.

The simulated pattern of ground-water flow around the southern end of the brine pool is depicted in figure 16, which shows chloride-concentration distributions under current conditions (2005) in the lower aquifer and overlying confining layer, together with the rate and direction of ground-water flow. The velocity of freshwater flowing northward through the lower aquifer decreases abruptly when it encounters the brine pool. Water flows around the edges of the pool, diluting the brine as mass is dissipated through dispersion. Velocities are much lower throughout most of the overlying confining layer, and upward flow is concentrated in a few areas around the periphery of the pool where the brine has been diluted. These areas developed over the course of the 215-year simulation and appear to be located where the aquifer geometry and boundary conditions favor upward flow. The areas gradually expanded during the simulation as upward flow was diverted through them, further diluting the brine pool. Simulated upward flow in the vicinity of OD-1804 isolated the southern end of the brine pool, increasing the size of the mixing zone around the pool and the rate of brine dissipation (fig. 16A). Whether such processes are an accurate representation of aquifer conditions or an artifact of the model-grid resolution is unclear.

The mass of chloride in the brine pool was depleted in the 215-year simulation through both mixing and brine withdrawals. Simulated brine withdrawals accounted for about one-third of the chloride lost from the brine pool from 1820 to 1920, while the most substantial natural discharges were to Onondaga Creek and Spencepatrick Spring (fig. 17). Ninemile Creek became the largest chloride discharge area in 1945 following the application of Solvay waste, and remains so today. Chloride discharges to Onondaga Lake and the Seneca River averaged about 5 percent of the total during the 215-year period. Removal of brine through pumping substantially reduced chloride concentrations in the lower portion of the brine pool, as indicated by the simulated shrinkage of the 130 g/L isosurface between 1820 and 1920 (fig. 18). Simulated chloride concentrations at the northern end of the Onondaga Trough decreased slightly from 1920 to 2005.

Effect of Waste Application in the Ninemile Valley

Simulated chloride concentrations in the Ninemile Valley increased substantially from 1945 to 1985 following the application of Solvay wastewater in waste beds A, B, and C (fig. 19). No information is available regarding chloride concentrations prior to the period of waste application, but it is unlikely that the brine pool in the Onondaga Trough extended into this valley. The bedrock surface in Ninemile Valley is more than 45 m above the bottom of the Onondaga Trough beneath Onondaga Lake, and freshwater flowing through Ninemile Valley would have flushed any saline water in the lower aquifer and discharged it to Ninemile Creek. A geochemical reaction model prepared for saline water in well OD-1026 (located between waste beds B and C) indicates a ground-water age of less than 600 years, suggesting that the saline water has a modern origin, whereas radiocarbon ages estimated for the halite brine are generally thousands of years old.

Available records indicate that the wastewater application rate in the Ninemile Valley averaged over 10 meters per year (m/yr) from 1945 through 1985, but the percentage of the wastewater that infiltrated to ground water and the chemical composition of the wastewater are unknown. A recharge rate of 7 m/yr was initially estimated by regression for saline wastewater with a chloride concentration of 60 g/L, which is similar to that measured in waste-bed overflow (Effler, 1996). The simulated chloride concentrations associated with this combination closely matched observed concentrations, but the estimated mass applied was nearly equivalent to the total volume of chloride discharged by the Solvay plant and was, therefore, unreasonable. Most of the applied wastewater is assumed to have either evaporated or discharged to Ninemile Creek and Onondaga Lake. In calibrated model 3D-A, an arbitrary application rate of 33 cm/yr was assumed for saturated brine (170 g/L); this combination resulted in a

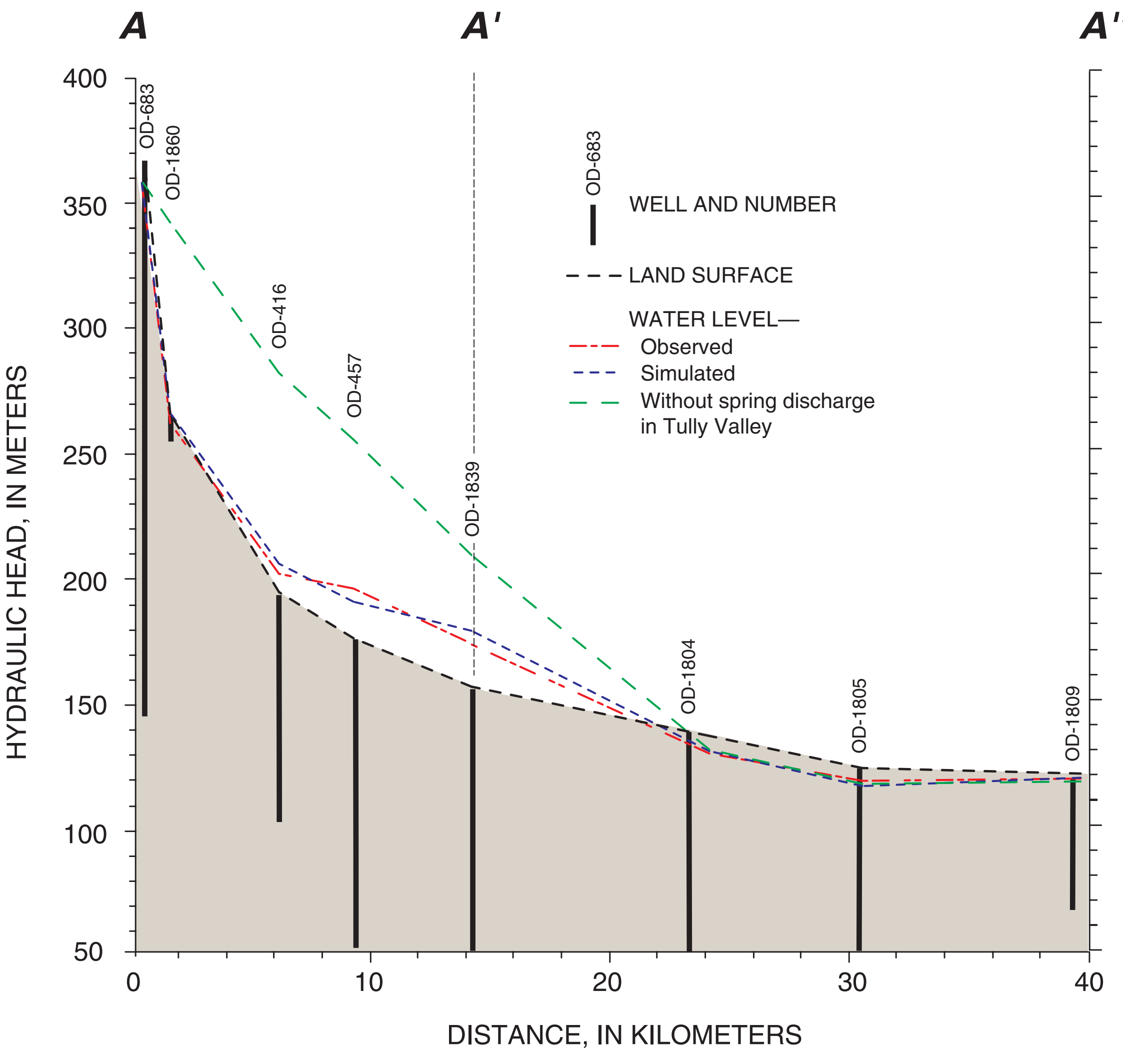

Figure 14. Generalized section A-A″ showing observed and simulated hydraulic head along the Onondaga Trough. Section location shown on figure 2.

chloride mass application equivalent to 15 percent of the total chloride produced by the plant.

The simulation indicates that under natural conditions (fig. 19A), ground water flowed eastward through the Ninemile Valley and discharged to Ninemile Creek before encountering the brine pool. After the application of saline wastewater began in 1945, freshwater was restricted to upgradient portions of the valley, and most of the ground water discharged to Ninemile Creek was saline. A clockwise circulation pattern was established in the brine pool beneath Onondaga Lake as some saline water flowed downward into the Onondaga Trough (fig. 19B); however, ground-water velocities in the brine pool remain more than an order of magnitude lower than velocities through the Ninemile Valley.

An additional series of simulations was conducted to investigate the extent of potential migration of saline water from the Solvay waste beds by varying the chloride application rate. A second solute was included in these simulations as a tracer applied in wastewater to distinguish between natural and anthropogenic sources of salinity. Chloride application rates corresponding to 15 percent, 25 percent and 100 percent of the total volume of chloride produced by the Solvay plant were considered (models 3D-A, 3D-B, and 3D-C, respectively). The results at the end of the 215-year simulation in 2005 are depicted in two pairs of figures (fig. 20). The first of each pair shows a perspective cutaway view from the southwest to illustrate the depth and extent of saline-water migration from land surface. The second figure of each pair is a plan view to illustrate the extent of migration in the lower aquifer. The simulations indicate that saline water from the Solvay waste beds moved downward and beneath Onondaga Lake, and that the size of the affected area is proportional to the assumed waste-application rate.

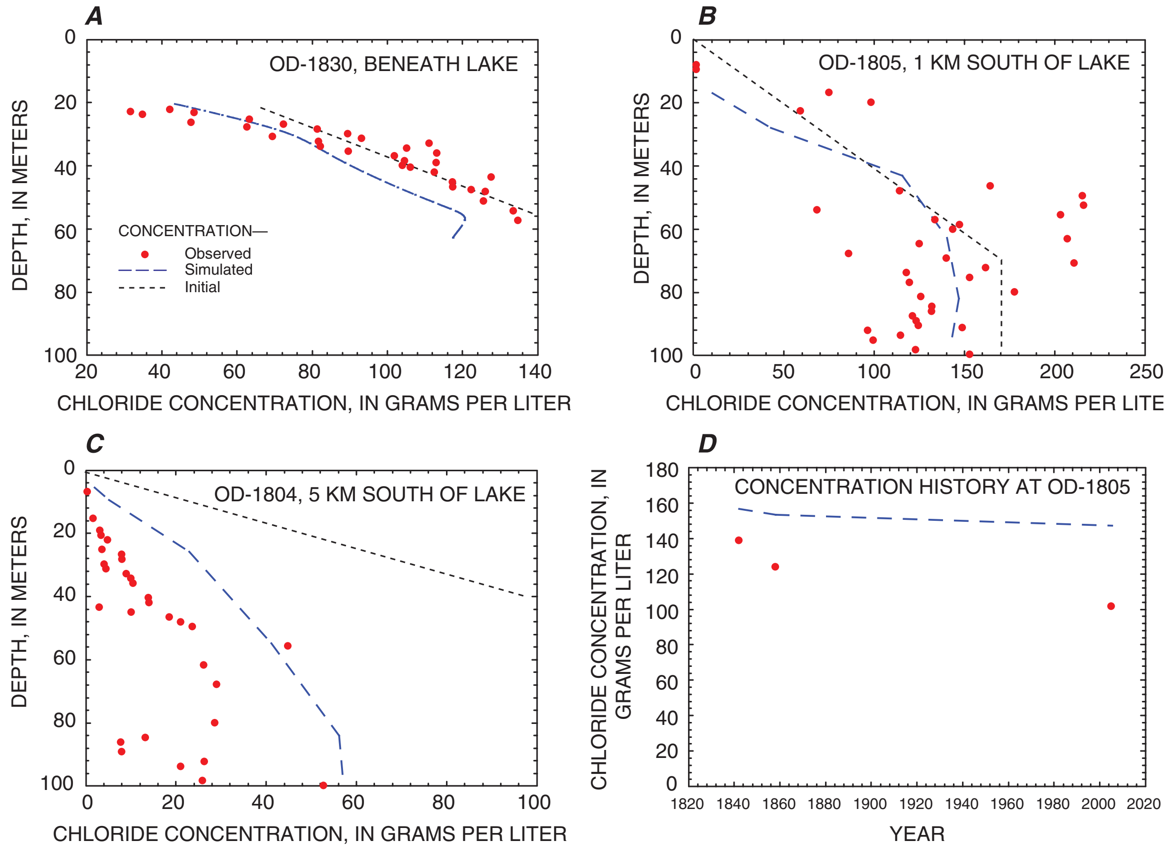

Figure 15. Depth profiles of observed and simulated chloride concentrations at: (*A*) OD-1830, beneath Onondaga Lake, (*B*) OD-1805, 1 kilometer south of lake, and (*C*) OD-1804, 5 kilometers south of lake, (*D*) chloride concentration history at OD-1805.

The predicted percentage of saline wastewater at well OD-1831 ranges from 18 percent for model 3D-A to 60 percent for model 3D-C. The results for model 3D-B (36 percent) are closest to the percentage computed for well OD-1831 (40 percent) from measured values of δD and $\delta^{18}O$, which suggests that an application rate equal to 25 percent of the total volume of chloride discharged produces a reasonable representation of the extent of migration. These results are dependent on the assumed geometry of the aquifer system. A similar distribution of wastewater migration could be obtained with a smaller waste-application rate if the thickness of the confining layer separating the waste beds from the lower aquifer were also decreased.

Model Sensitivity

Variable-density model 3D-A provides a reasonable representation of current (2005) conditions in the aquifer system within the Onondaga Trough. The model produces an acceptable match to measured water levels and chloride concentrations, and to estimates of water and chloride discharges. The model is based on a generalized conception of a complex stratigraphic setting, however, and some model parameters cannot be estimated and are uncertain. The initial chloride concentration on which the calibration is based also is uncertain because the model is calibrated to a relatively short period of the nearly 17,000-year history of the aquifer system. The two most significant parameters that cannot be estimated through model calibration are the hydraulic conductivity of the lacustrine silt and sand confining layer (K_{lac}) that overlies the basal sand and gravel, and the dispersivities of the aquifer materials.

Confining-Layer Permeability

Model sensitivity to the value of K_{lac} was investigated in a separate regression with model 3D-D, in which the value of this parameter was reduced by an order of magnitude to 0.03 m/d and the four most sensitive parameters were estimated. The resulting sum-of-squared errors (SSE) increased by about 10 percent. Most of the estimated

Table 7. Simulated water budget for aquifer system in the Onondaga Trough in model 3D-A.

[m^3/d, cubic meters per day; <, less than]

Source	Inflow volume, m^3/d	Percent	Discharge	Outflow volume, m^3/d	Percent
Recharge from precipitation	56,700	97	Streams		
Underflow			Onondaga Creek	28,600	49
Tully Valley	1,500	3	West Branch Creek	9,000	15
Ninemile Valley	300	< 1	Ninemile Creek	5,200	9
			Springs		
			Mudboils	3,100	5
			Landslides	3,800	6
			Spencepatrick	900	2
			West Branch marsh	7,900	14
			Onondaga Lake and Seneca River	100	< 1
Total	58,500	100	Total	58,500	100

parameter values were unchanged, with the exception of the hydraulic conductivity of the basal sand and gravel in the lower aquifer (K_{basal}) which increased by over 60 percent to 120 m/d (table 8). The effect of the larger value of K_{basal} was to increase the heads in the lower aquifer within the brine pool to maintain the upward discharge of saline water through the confining layer.

Dispersion

Values of longitudinal and transverse dispersivity could not be estimated in model simulations because grid resolution and the implicit FD scheme with upstream weighting introduced numerical dispersion into the solution for chloride concentrations. Model sensitivity to reducing numerical dispersion was assessed by comparing the results of model 3D-A with two additional models, 3D-E and 3D-F. In model 3D-E, numerical dispersion was reduced by dividing the grid and layer spacing by one-half, creating a grid that contained over 650,000 active cells with a maximum layer thickness of 15 m. Model 3D-F used the total-variation-diminishing (TVD) method to minimize numerical dispersion with the original model grid specified in model 3D-A; the specified dispersivity value was 1 m.

Simulations with model 3D-E (refined grid spacing) required 4 hours of computation time using a 3.2-Ghz Pentium D processor, which is about six times longer than the time required for calibrated model 3D-A. The regression conducted with model 3D-E yielded an SSE that was 10 percent less than that of model 3D-A, indicating that reducing numerical dispersion produced a better model fit (table 8). The estimated parameter values were unchanged, with the exception of K_{basal} which was increased nearly 100 percent to 140 m/d. Simulated chloride-concentration profiles at wells OD-1830 and OD-1805 were similar to those computed with model 3D-A, but simulated concentrations at OD-1804 near the south end of the brine pool were higher (fig. 21). The simulated mass of chloride in storage declined throughout the 215-year simulation in both models 3D-A and 3D-E, with the exception of the period between 1945 and 1985 when the Solvay waste application temporarily increased the chloride mass in storage (fig. 22A). Over 9 million Mg of chloride were removed from storage during the 215-year simulation with model 3D-A; a similar amount was removed with model 3D-E, which started with less chloride mass. A separate simulation run with model 3D-E using calibrated parameter values from model 3D-A produced the same decline in chloride mass, indicating that reducing the grid and layer spacing by one half had no effect on the loss of mass from the aquifer system.

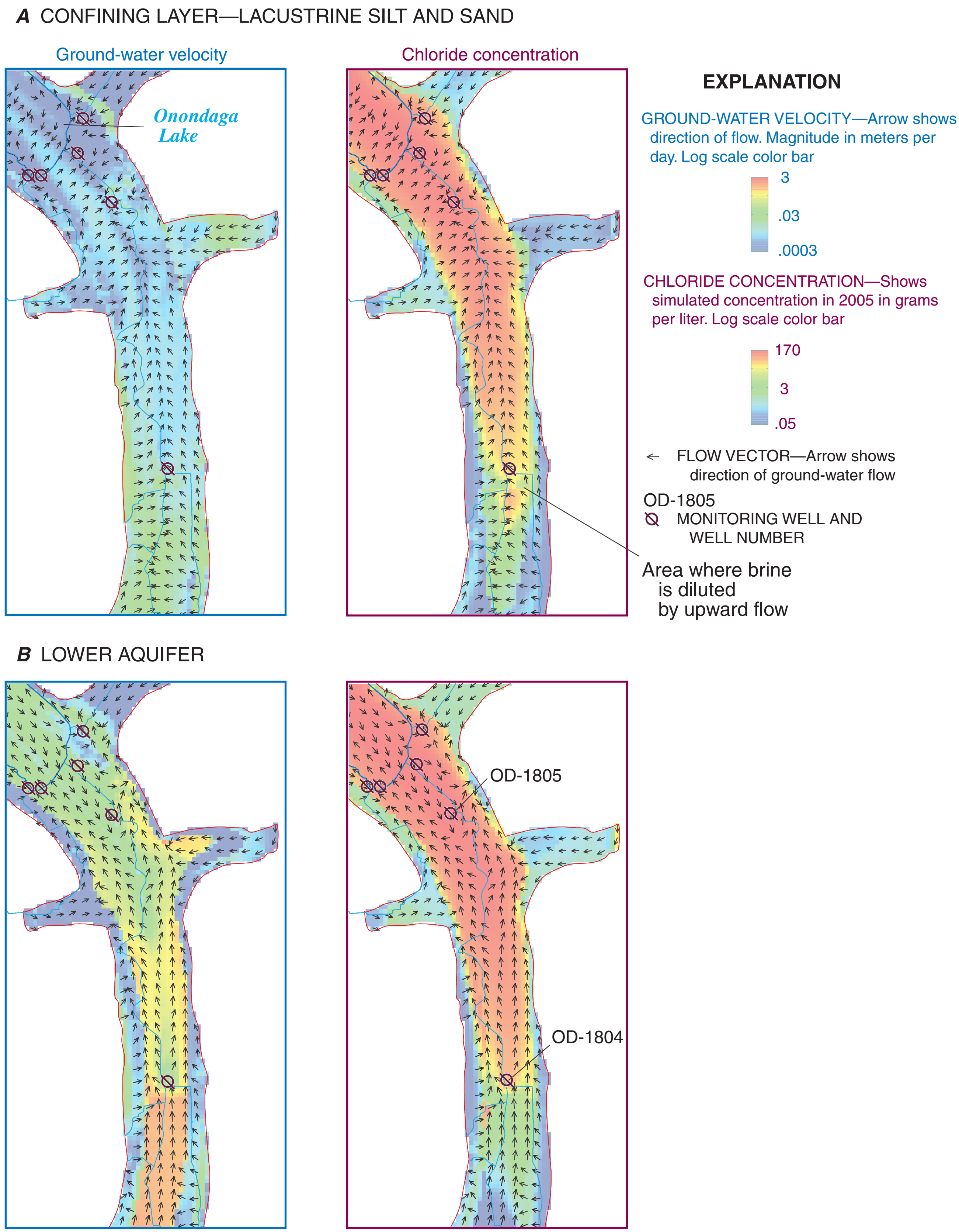

Figure 16. Simulated chloride concentration and ground-water velocity near the southern end of the brine pool under current conditions (2005) in: (*A*) confining layer and (*B*) lower aquifer.

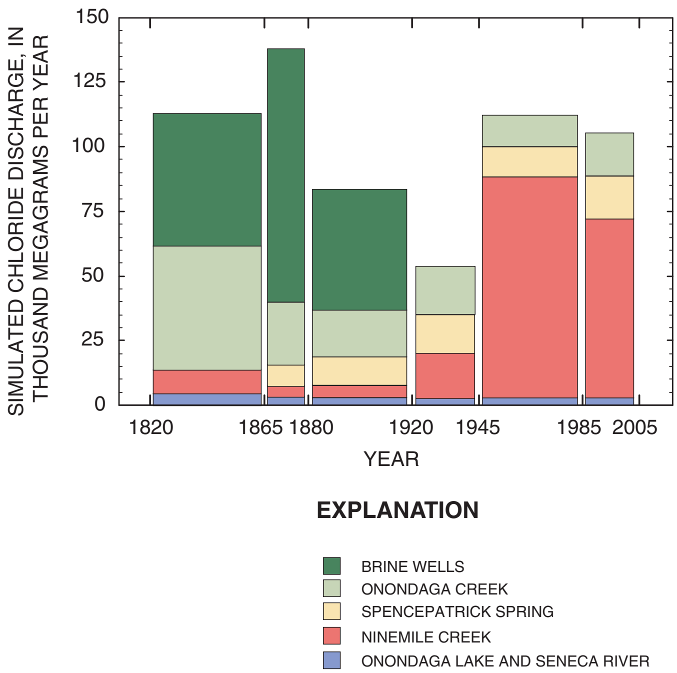

Figure 17. Mass flows of chloride discharged from aquifer system during 215-year simulation.

The simulation with model 3D-F using the TVD method required time steps of less than one day to solve the transport equations, resulting in a computation time of over 110 hours. It was, therefore, impractical to calibrate this model through regression or to conduct a sensitivity analysis. As expected, the application of the TVD method reduced numerical dispersion, producing concentration profiles that varied abruptly rather than smoothly with depth (fig. 21). The SSE of model 3D-F increased over 60 percent to 2,220 m, indicating a poor model fit; adjustments to the parameter values could have reduced model error if calibration had been possible. The rate of chloride mass loss during the 215-year simulation was about 20 percent less than in model 3D-A (fig. 22A), suggesting that numerical dispersion plays a significant role in controlling the mass lost from the system.

Grid Resolution and Numerical Dispersion

Simulation studies of the salt-pool experiment discussed previously suggest that a high degree of spatial resolution is required to limit numerical dispersion and accurately represent the sharp interface that arises between waters with a large density contrast. Langevin and Guo (2006) found that 700,000 cells were not sufficient to attain grid convergence in simulations of the salt-pool experiment when using the implicit FD method with central-in-space weighting, which offers less numerical dispersion than upstream weighting used in this study. Johannsen and others (2002) concluded that over 17 million nodes were required to accurately simulate the same problem. The 3D models of the Onondaga Trough described herein do not contain the degree of spatial resolution recommended by these studies, although the grid spacing in model 3D-E (50 m) does approach the level suggested by Johannsen and others (2002) for field studies (30 m). It is not clear, however, that a sharp interface exists at the edges of the brine pool in the Onondaga Trough. Concentration profiles constructed from data collected at a spacing of less than 2 m do not depict an abrupt transition from saturated brine to saline water, and scatter in the data likely results from heterogeneity in material properties. The numerical dispersion associated with the application of the implicit FD method can be interpreted as mimicking the actual dispersive properties of the aquifer material. The simulated chloride-concentration distribution and, therefore, density distribution within the brine pool are reasonably accurate depictions of actual conditions. The width of the mixing zone bordering the periphery of the pool is probably overestimated, however, especially in the vertical direction as a result of the maximum 30-m layer spacing.

One significant consequence of numerical dispersion owing to the grid spacing used in model 3D-A is that the rate of chloride-mass loss from the aquifer system is overestimated. As mentioned previously, mass is lost from the brine pool through spreading into the mixing zone, resulting in dissipation of the pool. This mass is then discharged to model boundaries by upward-flowing ground water and lost to the aquifer system. Over 25 percent of the chloride mass was lost over the course of the 215-year simulation with model 3D-A. In the simulation with model 3D-F (TVD method), the reduced numerical dispersion decreased the rate of mass loss from the system (18 percent), but mass loss was still substantial. Although measured chloride concentrations have declined from 1842 to 2005 (fig. 15D), most of the decline probably resulted from pumping between 1797 and 1926, and not from natural discharges.

The simulated rate of mass loss is not sustainable over long periods of time. In a separate simulation with model 3D-A that neglected the effects of pumping and waste application, the mass of chloride in the brine pool declined 50 percent in 1,000 years (fig. 22B). This result is inconsistent with a hypothesis based on geochemical modeling that suggests that the halite brine was formed from dissolution by glacial melt water and has persisted in the aquifer system for as much as 16,500 years. This discrepancy suggests that either (1) the rate of mass loss estimated by model 3D-A is too large, or (2) that the hypothesis that the brine pool was derived from a relict source of salt is incorrect. In either case, model 3D-A (with a maximum layer spacing of 30 m) is not suitable for simulating the long-term behavior of this aquifer system.

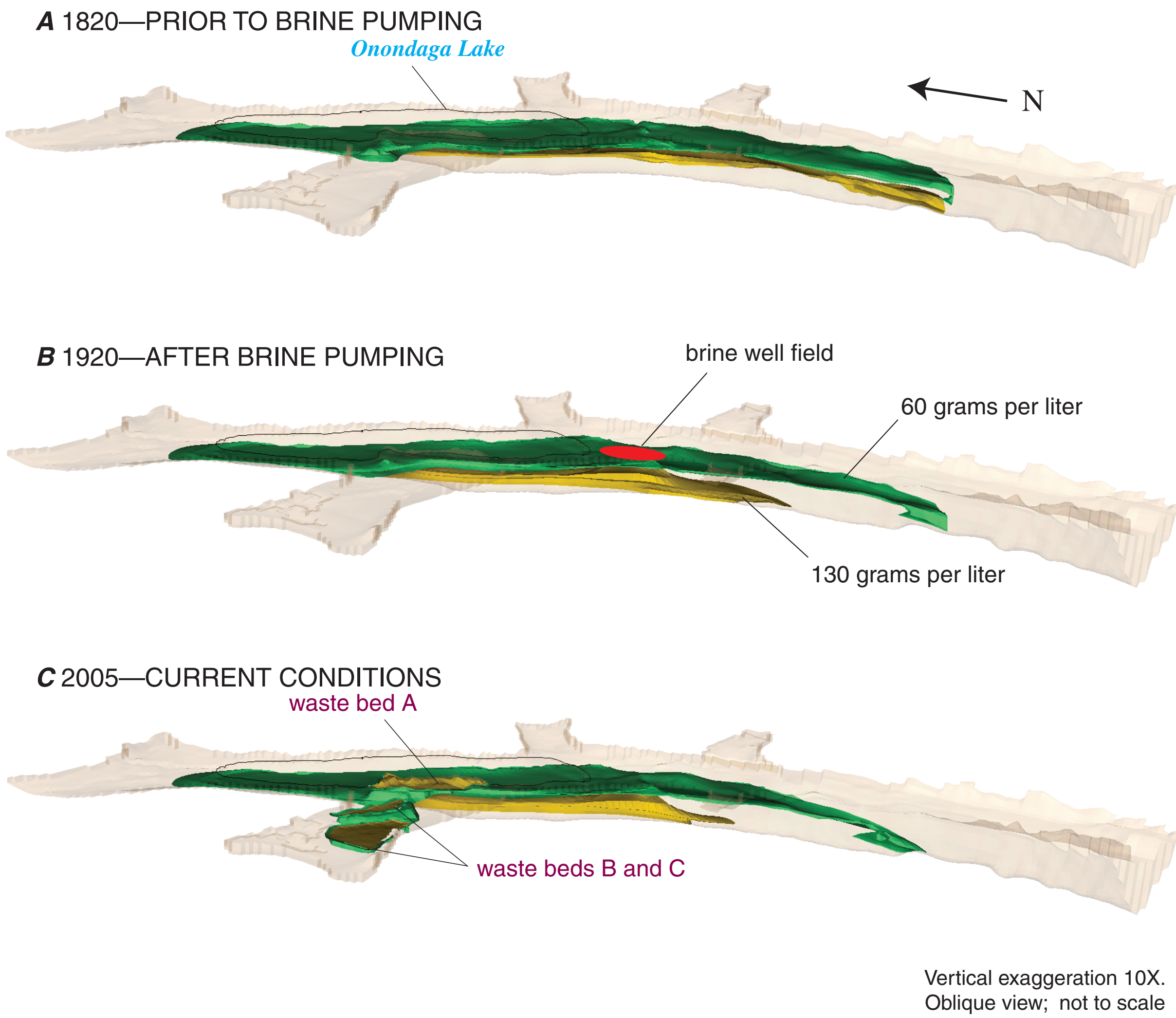

Figure 18. Isosurfaces of equal chloride concentration during 215-year simulation in (*A*) 1820, prior to brine pumping, (*B*) 1920, after brine pumping; and (*C*) 2005, current conditions.

Two-Dimensional Variable-Density Cross-Sectional Flow Model

A two-dimensional (2D) variable-density, transient ground-water-flow model of the glacial-drift aquifer system in the Onondaga Trough was constructed by using SEAWAT to assess the hypothesis that the brine pool could have persisted in the aquifer system for 16,500 years. The 2D model afforded a higher degree of resolution than the 3D model, while still permitting simulation of a long time period within an acceptable computation time. The model simulated flow in the vertical section A-A” (fig. 3) along the longitudinal axis of the Onondaga Trough from the Valley Heads Moraine through Onondaga Lake. Four finite-difference grids with different column and layer spacing were used to assess the effect of numerical dispersion on model results (table 9). The 2D cross-sectional model cannot represent converging ground-water flow where the two tributary valleys (West Branch Valley and Ninemile Valley) intersect the Onondaga Trough. Ground-water flow in the Onondaga Trough is mainly parallel to the line of section north of the West Branch Valley, however, so the model provides a reasonable simulation of flow conditions in the vicinity of the brine pool.

Model Design

The transient simulation was divided into two periods: (1) a 2,000-year period that represented dissolution of halite and accumulation of brine in the glacial sediments, and (2) a 15,000-year period following cessation of dissolution that represented flushing and dilution of the brine by fresh ground water. Flow and transport equations were explicitly coupled using a one timestep lag, and the implicit FD method with

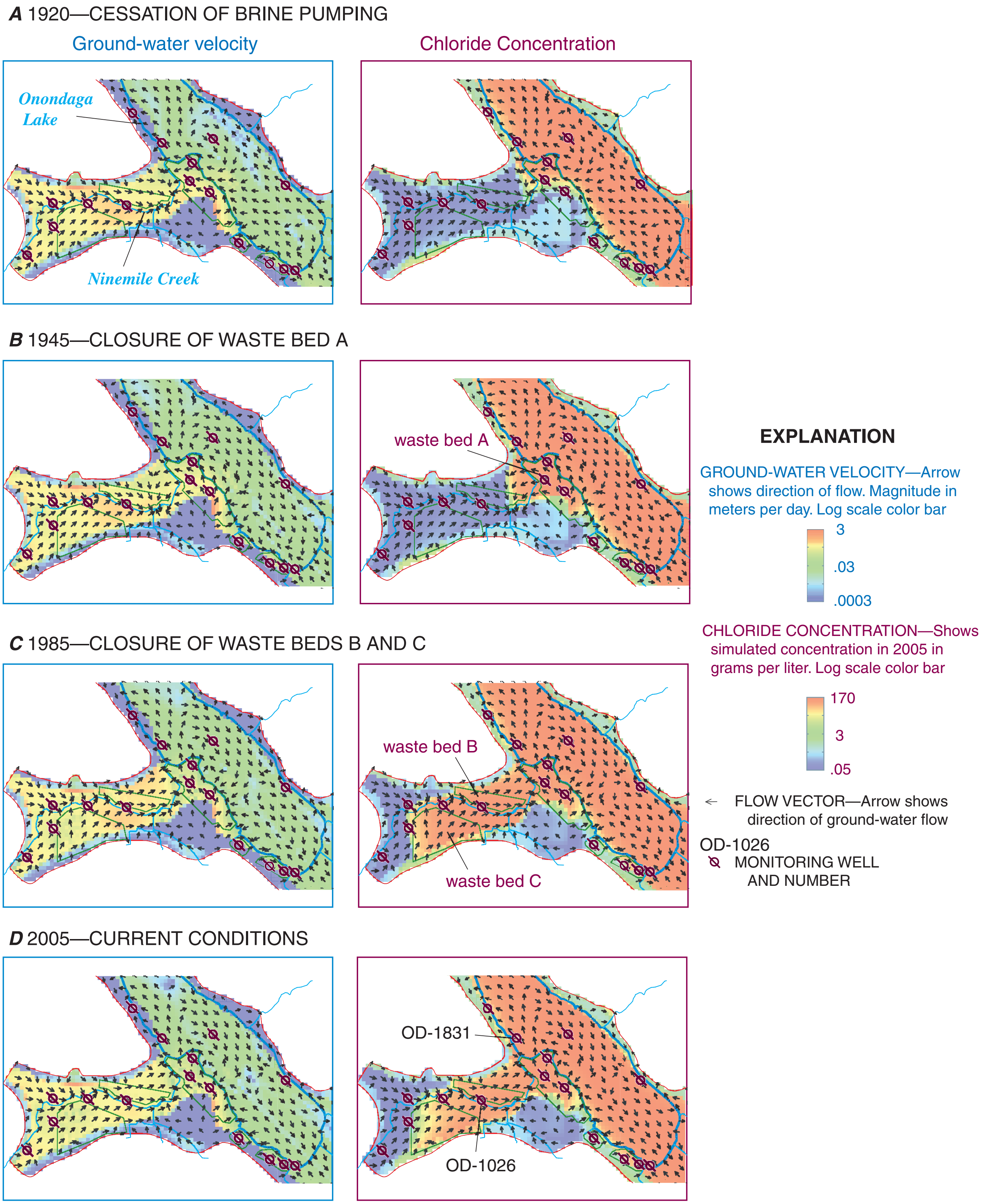

Figure 19. Simulated chloride concentration and ground-water velocity in the Ninemile Valley in (*A*) 1920, cessation of brine pumping, (*B*) 1946, closure of waste bed A, (*C*) 1985, closure of waste beds B and C, and (*D*) 2005, current conditions.

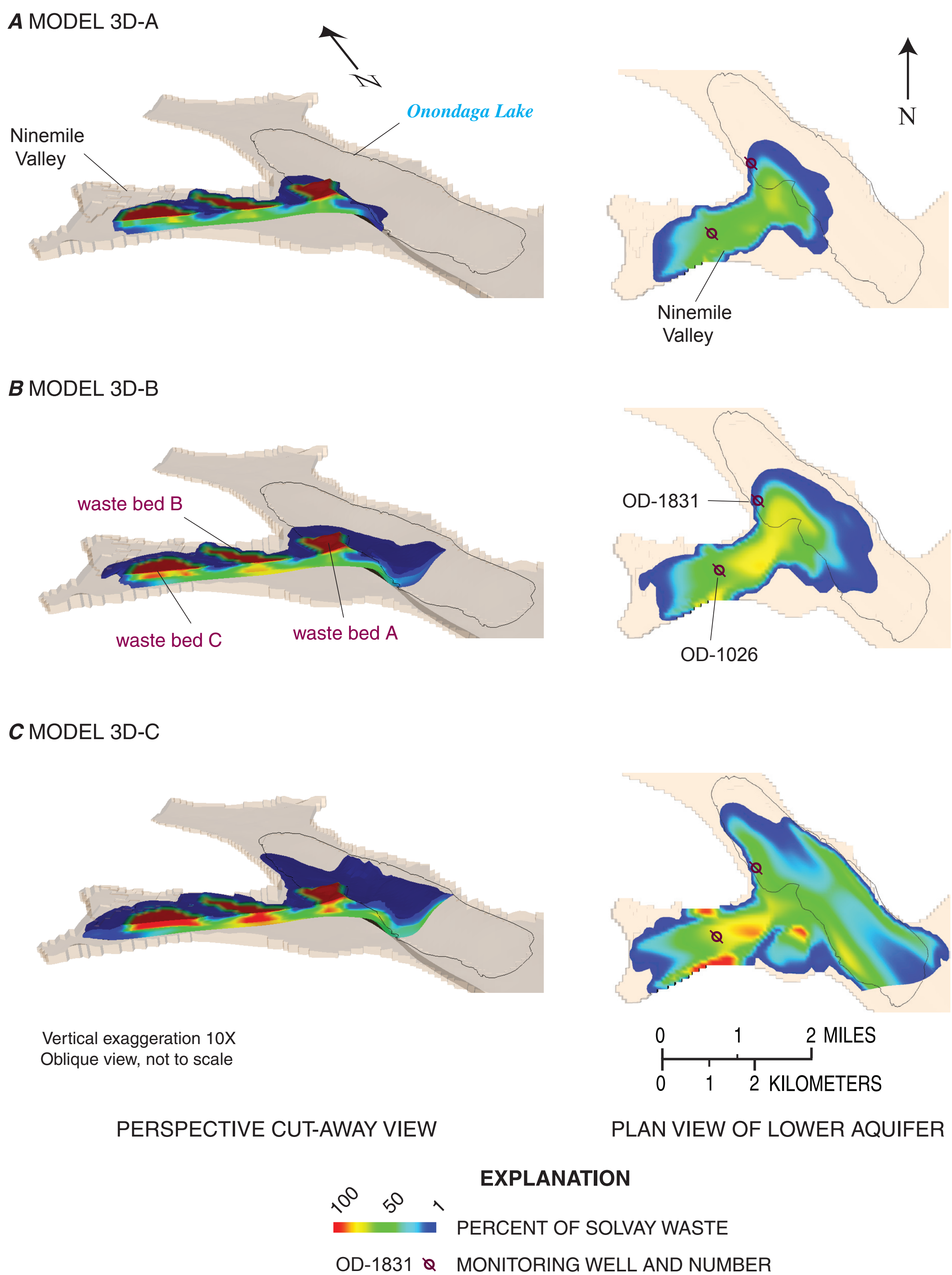

Figure 20. Simulated extent of saline water migration from Solvay waste beds in 2005 under three conditions based on percent of waste chloride application (*A*) model 3D-A, 15 percent, (*B*) model 3D-B, 25 percent, and (*C*) model 3D-C, 100 percent.

Table 8. Sensitivity of estimated model parameters to optimized alternative three-dimensional models.

[m/d, meters per day; m², meters squared]

Parameter	Model 3D-A[a]	Model 3D-D[b]	Model 3D-E[c]
Hydraulic conductivity, m/d			
Alluvial sand and gravel	2.1	2.1	1.1
Basal sand and gravel	72	120	140
Rural recharge, cm/yr	42	40	38
Threshold for saturated Cl, m	70	80	73
Model error			
Sum of squared errors, m²	1,348	1,485	1,204

[a]Calibrated model.

[b]Hydraulic conductivity of lacustrine silt and sand = 0.03 m/d.

[c]Model grid reduced by one-half.

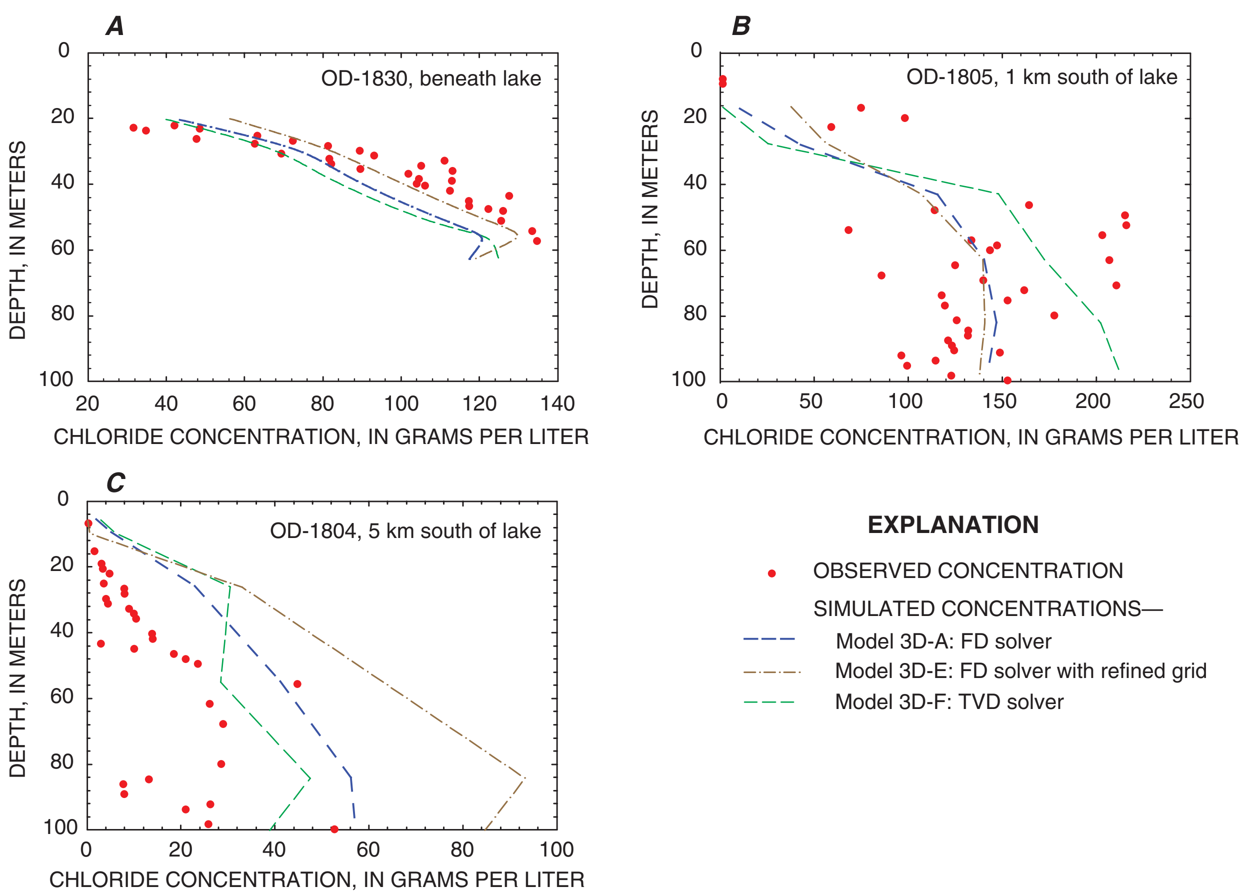

Figure 21. Depth profiles showing sensitivity of simulated chloride concentrations to model grid spacing (model E) and TVD method (model F): (*A*) well OD-1830, beneath Onondaga Lake, (*B*) well OD-1805, 1 kilometer south of lake, and (*C*) well OD-1804, 5 kilometers south of lake.

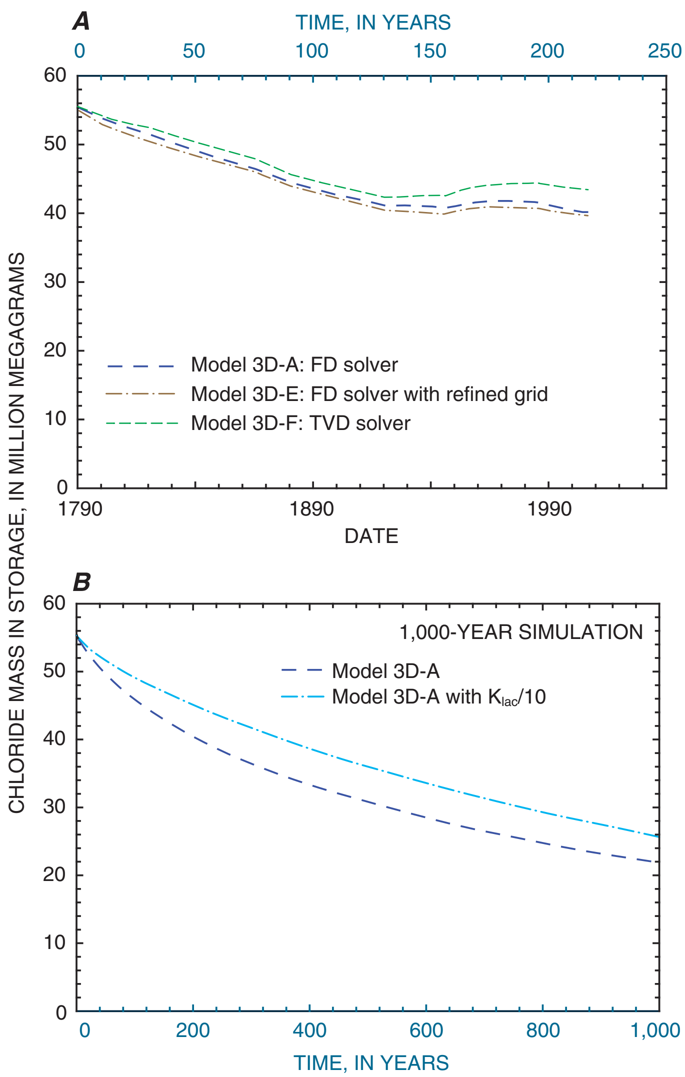

Figure 22. Simulated chloride mass in storage: (*A*) during 215-year simulation, and (*B*) during 1000-year simulation.

upsteam weighting was used to solve the advection equation. Model-layer spacing ranged from 15 m in models 2D-A and 2D-B to 1.5 m in model 2D-D.

Constant head and drain boundaries were specified: (1) at land surface to represent recharge on the moraine and discharge to Onondaga Lake and its inlet, Onondaga Creek; and (2) in the Tully Valley to represent underflow through the moraine and discharge from confined aquifers through springs in the area of mudboil activity (fig. 23A). A constant concentration boundary was specified in the initial time period to represent a salt source where halite beds subcrop on the bedrock valley floor and establish the brine pool. During the second time period, this boundary condition was removed and the brine pool was diluted by the continuing flow of freshwater from the south. Chloride was selected as the migrating solute in the transport simulation because the relation between chloride and density in brine samples is relatively linear (fig. 11). Specified hydraulic and transport properties were based on estimated values for model 3D-A presented earlier (table 5).

Simulation of Brine Origin

Simulation results indicate that the brine pool has had sufficient time to migrate from the halite subcrop area to the northern end of the Onondaga Trough. The simulated mass of chloride in the aquifer system in all of the models approaches a maximum after 2,000 years when sediments downgradient of the halite subcrop become nearly saturated (fig. 24A). Simulated chloride concentrations then decline rapidly following the cessation of halite dissolution, but reach a nearly constant mass after about 7,000 years that is depleted very slowly. Models with the less refined grids and more numerical dispersion (models 2D-A and 2D-B) predicted 23 percent less mass remaining in the aquifer system after 15,000 years than the more refined grid in model 2D-C. The increased accuracy required an increase in computation time from 0.5 and 0.6 hours with models 2D-A and 2D-B, respectively, to 5.8 hours with model 2D-C using a 2-Ghz Pentium D processor. Using the more accurate TVD numerical method instead of the FD method in model 2D-B also reduced numerical dispersion—this simulation produced 30 percent and 10 percent more mass than using the FD method with either model 2D-A or 2D-B, respectively, but the computation time increased to 140 hours. The most refined grid (model 2D-D) produced a chloride mass nearly equal to that of model 2D-B using TVD, however, and required a computation time of only 20 hours.

Chloride concentrations simulated by using the refined grid with a layer spacing of 3 m (model 2D-C) are in good agreement with measured concentrations in pore-water samples extracted from sediment cores in three boreholes (fig. 24B-D). Model 2D-C appears to best represent the actual rate of spreading in the brine pool because measured concentrations are matched closely at well OD-1804, located near the south end of the pool. At this location, brine is dissipated by mixing with fresher water. The other models produce simulated concentrations that are too low at this location and thus either overestimate or underestimate the rate of spreading. Flow patterns within the simulated section were depicted using the results of model 2D-C and MODPATH (Pollock, 1994) to compute flow paths from a set of starting points spaced throughout the brine pool. The flow paths were then generalized to illustrate flow directions within the section (fig. 23B). Simulation results indicate that the velocity field is relatively stable over a 20,000-year period.

Fresh ground water from upgradient areas south of the brine pool flows upward and over the southern end of the pool, creating a mixing zone where brine is continually removed from the pool. Flow through the freshwater portion of the section exits the aquifer system within 8,000 years. Flow is much slower within the brine pool, with the exception of a

Table 9. Spatial discretization and computation times associated with two-dimensional model simulations.

[m, meters; hr, hours]

	Model			
	2D-A	2D-B	2D-C	2D-D
Grid spacing, m				
Column	152	76	76	76
Layer	15	15	3	1.5
Active cells	2,695	5,390	23,030	45,080
Computation time, hr	0.5	0.6	5.8	20

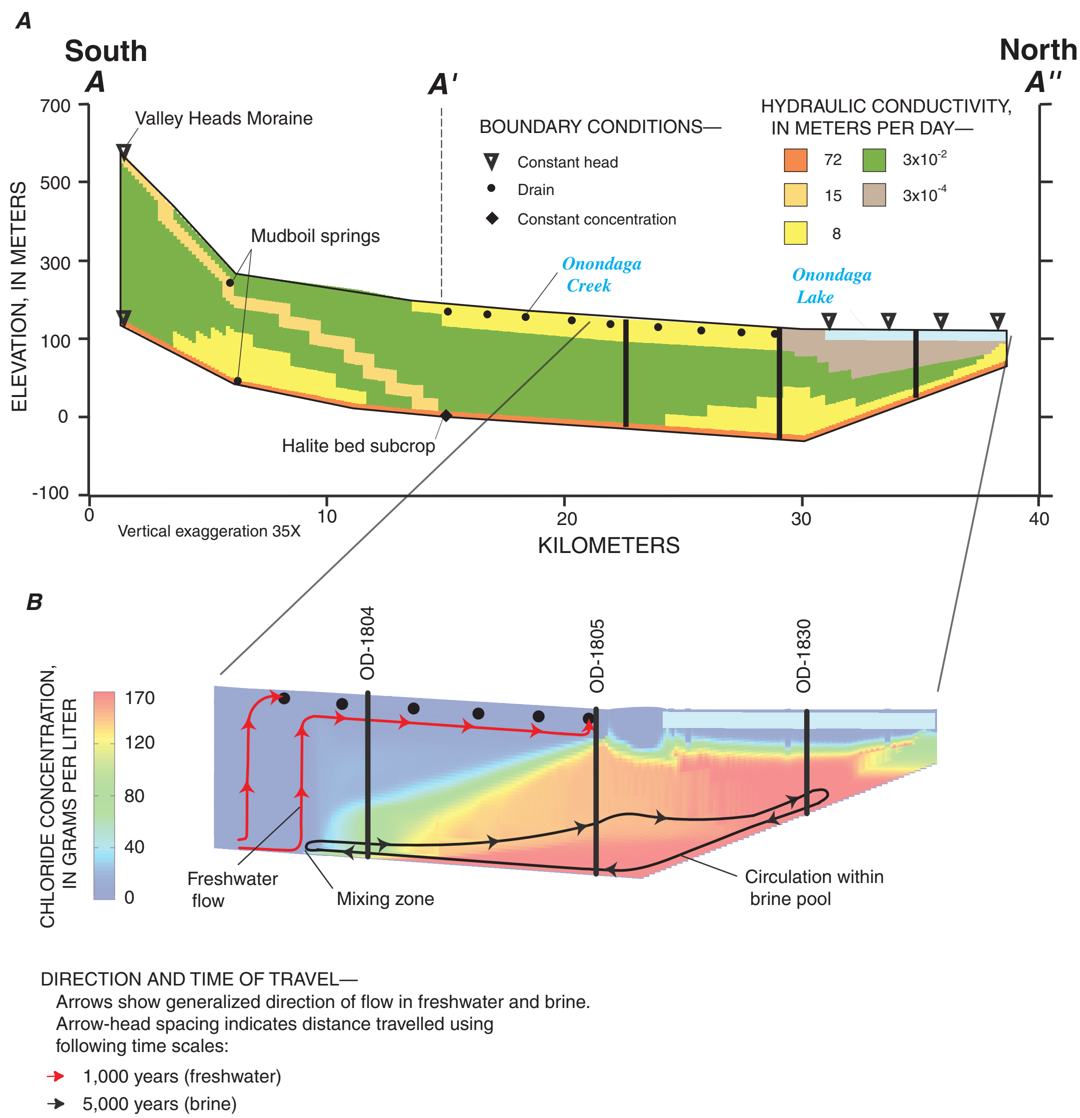

Figure 23. (*A*) Design of two-dimensional variable-density flow model, and (*B*) chloride concentrations at the end of 17,000-year simulation with model 2D-C.

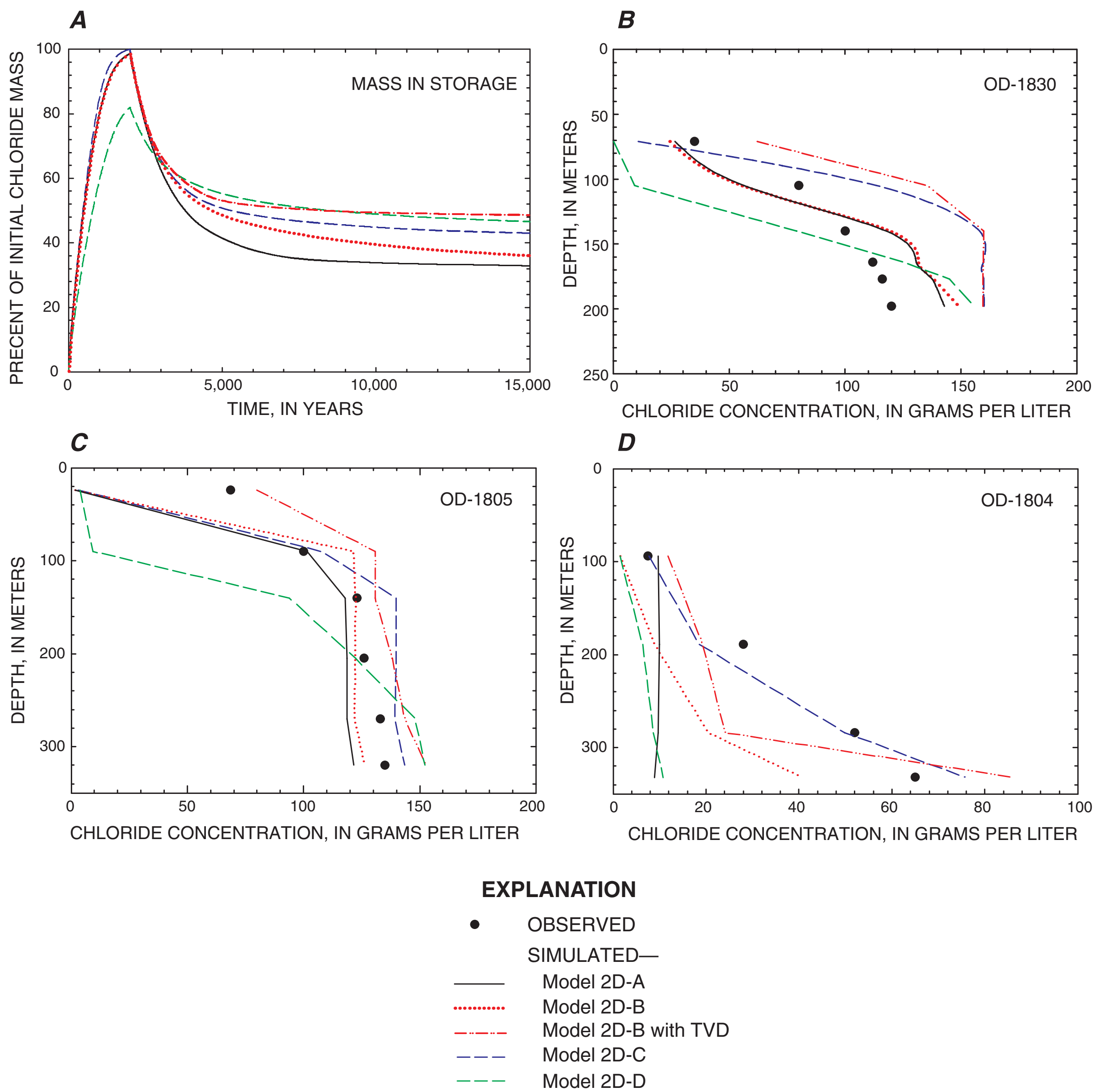

Figure 24. Chloride mass and concentration profiles simulated with 2D models: (*A*) percent of initial mass remaining in aquifer system; (*B*) well OD-1830, beneath Onondaga Lake; (*C*) well OD-1805, 1 kilometer south of lake; and (*D*) well OD-1804, 5 kilometers south of lake.

clockwise circulation current that traverses the base of the pool in about 10,000 years. This flow delivers saturated brine to the mixing zone at the south end of the pool and is similar to the pattern of flow observed in coastal areas where freshwater overlies a salt-water wedge. Brine also is dissipated through dispersion along the interface between fresh and saline water, and eventually discharges to Onondaga Creek where it is lost from the aquifer system. Flow beneath Onondaga Lake is virtually stagnant and little movement was indicated over a 20,000-year period.

Conclusions

A halite brine pool (saturation ranging from 45 to 80 percent) lies within glacial-drift deposits that fill the Onondaga Trough, a 40-km long bedrock valley deepened by Pleistocene ice near Syracuse, N.Y. Halite brine that discharged from springs and was pumped from wells around the southern end of Onondaga Lake became the most important source of salt in the United States in the first part of the 19th century. The halite brine was later utilized in the production of soda ash at a chemical plant on the west shore of the lake from 1888 to 1986. Runoff of saline water from waste beds filled by saline slurry discharged by the plant caused hypersaline conditions in Onondaga Lake by the middle of the 20th century, resulting in chemical stratification of lake water and failure of spring turnover. The regional, three-dimensional ground-water-flow model developed in this study provides a qualitative and quantitative description of how ground water flows through the aquifer system in the Onondaga Trough, and simulates changes that have occurred in the aquifer system as a result of anthropogenic development. The simulated distributions of hydraulic head and ground-water density provide a basis for further studies aimed at designing remedial efforts to cleanup Onondaga Lake.

The position of the brine pool at the northern end of the Onondaga Trough, 15 km north of the halite beds in the Silurian Syracuse Formation that are the assumed salt source, can be explained by two hypotheses. Under the first hypothesis, the brine pool was derived from a relict source of salt that was dissolved by glacial melt water and then migrated through glacial sediments to its current position, where it is slowly being depleted. Under the second hypothesis, the brine pool is sustained indefinitely by a continuing salt source in the bedrock through upward flow that discharges into the glacial sediments beneath Onondaga Lake. The geochemical and isotopic compositions of the brine support the first hypothesis. The brine differs markedly from that of saline bedrock waters obtained from wells adjacent to the trough in that: (1) the chloride to bromide ratio of brine samples is much larger, (2) the stable isotope values of hydrogen and oxygen (δD and $\delta^{18}O$) are more enriched, and (3) boron isotope values ($\delta^{11}B$) are lower than those of the saline bedrock waters. Geochemical modeling with NETPATH indicates that the brine could have formed from a mixture of freshwater and saline bedrock water that reacted with halite, gypsum and cation exchange of calcium for sodium. The estimated radiocarbon age of this mixture (16,700 years) is consistent with the timing of deglaciation in the Onondaga Trough and suggests that the freshwater was derived from glacial melt water.

A three-dimensional (3D) variable-density model of the aquifer system within the Onondaga Trough based on the first hypothesis was calibrated to measured water levels and estimates of water and chloride discharges. The initial chloride distribution in the brine pool in 1790 was computed as a linear function of increasing concentration with depth, but limited by a maximum concentration of 170 g/L. The 3D model provided a reasonable representation of concentration and density distributions within glacial sediments over a 215-year period from 1790 to 2005. Model results indicate that freshwater flows northward through the trough from the Tully and West Branch Valleys, but is diverted upward and around the southern end of the brine pool. Simulated concentration and velocity distributions indicate that brine is slowly depleted through a mixing zone formed by the upward flow of freshwater, and that the mass of brine entrained in the upward flow is eventually lost to the aquifer system where it discharges to Onondaga Creek. Model simulations also indicate that saline water from waste-disposal beds associated with the former chemical plant could have migrated downward and spread laterally beneath Onondaga Lake.

One important limitation of the 3D model is that the computed rate of mass depletion from the brine pool is too large to support the brine pool over its assumed residence time of 16,500 years. Additional model simulations indicated that decreasing the grid spacing and using a more accurate numerical method would decrease numerical dispersion and, thereby, reduce the computed mass-depletion rate. Construction and calibration of a 3D model capable of accurately simulating movement of brine in the Onondaga Trough over a 16,500-year period would require a processor 100 times faster than those available today, however, or an improved implementation of a mathematical algorithm to solve the advection-dispersion equation.

Variable-density flow simulations with a two-dimensional (2D) cross-sectional model were conducted for a 17,000-year period to assess the hypothesis that the brine pool could have persisted in the aquifer system since deglaciation of the Onondaga Trough. The 2D model afforded a higher degree of resolution than the 3D model, while still permitting simulation of a long time period within an acceptable computation time. Model results support the hypothesis that the halite brine is derived from dissolution of halite by glacial melt water. The 2D simulations indicate that the brine could have migrated more than 15 kilometers from the halite subcrop area to the northern end of the trough and remained in the glacial sediments for 16,500 years, as suggested by radiocarbon dating.

Model results do not rule out the second hypothesis that the brine pool is sustained through a continuing salt source within the bedrock beneath the Onondaga Trough. This possibility could be investigated by drilling a deep test hole to bedrock in the center of the trough south of the brine pool to obtain samples of bedrock water. The geochemistry of these samples could then be analyzed to determine whether the halite brine may be derived from the bedrock water. Alternatively, the level of brine saturation in the pool could be monitored for a sufficiently long period of time, possibly 100 years, to establish whether the mass of brine is slowly depleted over time or could be sustained indefinitely.

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Appendix 1. Dissolved-gas compositions of waters in the Onondaga Trough.

[Values in milligrams per liter; CH_4, methane; CO_2, carbon dioxide; N_2, nitrogen; O_2, oxygen; Ar, argon]

Station ID	Local identifier	Well Name	Date	Time	CH_4	CO_2	N_2	O_2	Ar
430243076180401	OD-1825	Camillus - deep	12/16/2004	1030	0.068	12.06	22.70	0.04	0.734
430243076180402	OD-1833	Camillus - bedrock	11/16/2004	1530	0.158	0.0	25.29	0.06	0.734
430439076143701	OD-1026	Waste bed 5L-deep	6/29/2004	1100	1.591	9.9	12.95	0.81	0.428
430402076103201	OD-1788	Carousel HA-9 - deep	9/10/2004	1100	5.043	3.58	11.4	0.05	0.495
430004076085401	OD-1804	Meachem Park - deep	9/10/2004	1500	0.135	11.54	18.63	0.43	0.663
430326076095602	OD-1805	Spencer Street - deep	6/29/2004	900	0.276	8.92	6.09	0.13	0.324
430326076095601	OD-1806	Spencer Street - shallow	11/16/2004	1100	0.183	11.34	22.33	0.08	0.710
430701076143802	OD-1809	Onondaga Lake outlet - deep	9/10/2004	1230	1.393	1.67	9.65	0.59	0.333
430332076094901	OD-1819	Spencepatrick Spring	9/10/2004	1000	0.106	14.74	10.49	0.62	0.446
430810076141002	OD-1827	Seneca River east - bedrock	11/16/2004	1430	29.291	21.27	4.45	0.0	0.169
430458076110601	OD-1829	Parkway - deep	6/14/2004	1200	0.027	0.8	7.1	1.55	0.475
430535076135401	OD-1831	West trail - deep	6/14/2004	1100	0.518	18.22	9.06	0.47	0.321
430535076135402	OD-1836	West trail - bedrock	11/16/2004	1300	1.589	13.07	26.97	0.49	0.643
425505076110401	OD-1839	West Branch - deep	8/31/2004	1230	0.025	7.83	23.73	0.3	0.777
430601076143101	OD-1848	Midway - shallow	12/16/2004	1130	0.013	0.0	25.82	0.07	0.779

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