

Prepared in cooperation with the New York State Department of Environmental Conservation

Dissolved Methane in New York Groundwater

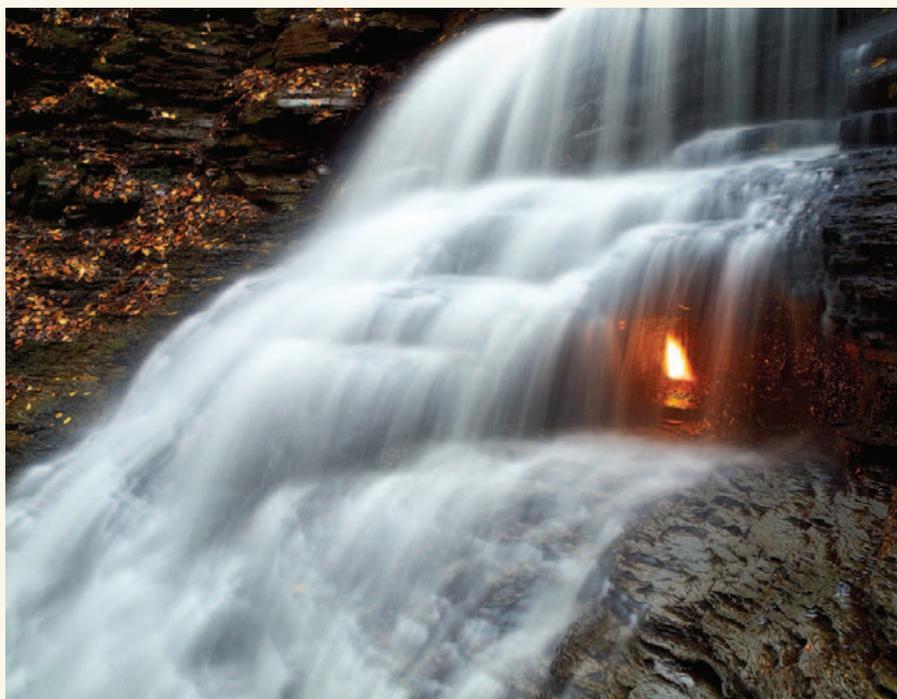
New York State is underlain by numerous bedrock formations of Cambrian to Devonian age that produce natural gas and to a lesser extent oil. The first commercial gas well in the United States was dug in the early 1820s in Fredonia, south of Buffalo, New York, and produced methane from Devonian-age black shale. Methane naturally discharges to the land surface at some locations in New York. At Chestnut Ridge County Park in Erie County, just south of Buffalo, N.Y., several surface seeps of natural gas occur from Devonian black shale, including one behind a waterfall (fig. 1). Methane occurs locally in the groundwater of New York; as a result, it may be present in drinking-water wells, in the water produced from those wells, and in the associated water-supply systems (Elt Schlager and others, 2001).

The natural gas in low-permeability bedrock formations has not been accessible by traditional extraction techniques, which have been used to tap more permeable sandstone and carbonate bedrock reservoirs. However, newly developed techniques involving horizontal drilling and high-volume hydraulic fracturing have made it possible to extract previously inaccessible natural gas from low-permeability bedrock such as the Marcellus and Utica Shales. The use of hydraulic fracturing to release natural gas from these shale formations has raised concerns with water-well owners and water-resource managers across the Marcellus and Utica Shale region (West Virginia, Pennsylvania, New York and parts of several other adjoining States). Molofsky and others (2011) documented the widespread natural occurrence of methane in drinking-water wells in Susquehanna County, Pennsylvania. In the same county, Osborn and others (2011) identified elevated methane concentrations in selected drinking-water wells in the vicinity of Marcellus gas-development activities, although pre-development samples were not available for comparison. In order to manage water resources in areas of gas-well drilling and hydraulic fracturing in New York, the natural occurrence of methane in the State's aquifers needs to be documented. This brief report presents a compilation of data on dissolved methane concentrations in the groundwater of New York available from the U.S. Geological Survey (USGS) National Water Information System (NWIS) (<http://waterdata.usgs.gov/nwis>).

Methane

Methane originates from several different sources. Biogenic methane is produced through biologic decomposition of organic matter at shallow depths and low temperatures in places such as swamps or landfills, or within glacial deposits that have decomposing organic matter—often termed "drift gas." Thermogenic methane is produced from organic matter buried millions of years ago, which has undergone physical and chemical changes at great temperature and pressure; other hydrocarbons such as ethane, propane, and butane, or oil also can be produced thermogenically.

Methane is a colorless, odorless, tasteless gas that can be flammable or explosive. It can trigger an explosion in enclosed/confined spaces containing oxygen, coupled with an ignition source (an open flame or an electrical spark). Methane can act as an asphyxiate by displacing air in structures and replacing oxygen in animal circulatory systems; burning methane also can produce other toxic gases such as carbon monoxide (Elt Schlager and others, 2001).



Photograph by Matthew Conheady (www.nyfalls.com)

Figure 1. Gas flame from natural gas seep at Chestnut Ridge County Park, Eternal Flame Falls, Erie County, New York.

Historic Accounts of Natural Gas Springs in New York

Otisco Lake—Easternmost Finger Lake, Onondaga County, N.Y.

From the Skaneateles Historical Society's Girl Scout Scrapbook, Skaneateles, N.Y., December, 1942.

"Troop 57 Does Out-Door Cooking in a New Way"

"We've heard of a lot of ways to do outdoor cooking but Troop 57 of Skaneateles certainly pulled a new one out of the bag recently. The girls hiked along Otisco Lake through Puddin' Mill Gorge where they cooked their lunch with natural gas which came up through the creek bed."

Oak Orchard Acid Springs—Northern Genesee County, N.Y.

From S.E. North, 1899, "History of Alabama, New York—from our county and its people a descriptive and biographical record of Genesee County New York" accessed August 2009 at: <http://history.raysplace.com/ny/alabama-ny.htm>.

"Alabama Sour Springs" also called "Oak Orchard Acid Springs," celebrated for their medicinal purposes, are located on road 7, in the southern part of the town, in the "swamp" on a little elevation two and a half to four feet above the surrounding surface, within a circle of 50 rods, and no two alike: eight in all have been discovered and analyzed, three of which are of an acid nature, one sulphur, one magnesia, one iron and one of a gaseous nature, affording gas enough to light 50 ordinary gas burners."

In groundwater, methane can be dissolved or in a gaseous state. When methane is dissolved, it acts like the carbon dioxide gas used in carbonated beverages, where the gas is held within the fluid under the confining pressure of the sealed container. When the container is opened, pressure is reduced and some of the gas comes out of solution, which causes bubbling and fizzing in the beverage. In aquifers, methane may be confined by overlying fine-grained deposits or unfractured bedrock. Dissolved methane concentrations in confined aquifers can be much greater than the saturation concentration at atmospheric pressure. As groundwater enters a well at atmospheric pressure, the natural gas can be released from the water, which can cause a column of gas to form above the water surface in the well or be released within a pressure tank, at faucets inside a home, or in structures enclosing the well, where it can become flammable or explosive as a result (Eltschlager and others, 2001).

Methane reaches saturation in water at 28 milligrams per liter (mg/L) at atmospheric pressure and becomes flammable in air at about 5 percent by volume (Eltschlager and others, 2001). The Office of Surface Mining recommends that methane concentrations greater than 28 mg/L in well water

should be addressed immediately by removing any potential ignition source and venting the gas away from confined spaces (Eltschlager and others, 2001). The Office of Surface Mining also recommends that methane concentrations ranging from 10 to 28 mg/L in water (or 3 to 5 percent by volume in air) signify an action level where the situation should be closely monitored, and if the concentration increases, the area should be vented to prevent methane gas buildup. Concentrations of methane less than 10 mg/L in water (or 1 to 3 percent by volume in air) are not as great a concern, but the gas should be monitored to observe if the concentrations increase over time (Eltschlager and others, 2001). Homeowners should contact their local or New York State Health Department for further information about measuring and mitigating "action level" methane concentrations (as previously defined) in their water wells or in their homes.

New York Bedrock and Natural Gas and Oil Stratigraphy

The stratigraphic column from Hill and others (2003) (fig. 2) shows that at least some natural gas has been developed from almost all the bedrock formations in New York State, indicating that bedrock units yielding some volume of methane are widespread. Therefore, any open borehole such as a water well, potentially could contain methane gas. Even though there are many gas-producing formations, relatively little data exist citing the occurrence, distribution, and concentration of methane in groundwater.

Dissolved Methane Concentration Data in New York

The collection of dissolved methane concentrations in groundwater by the USGS in New York coincided with groundwater age-dating applications for aquifer studies in the late 1990s. Various tracers can be used to date groundwater including tritium (Solomon and others, 1993), chlorofluorocarbons (CFC) (Plummer and others, 2006), and sulfur hexafluoride (SF₆) (Busenberg and Plummer, 2000). As part of the age-dating method, dissolved gas samples (nitrogen, argon, carbon dioxide, oxygen, and methane) are collected and analyzed to help determine the time when groundwater recharge occurred. When the age-dating results are reported, the supporting dissolved gas data (including methane) are sometimes included. Methane data from such previous age-dating studies (Komor, 2002; Yager and others, 2007) have been compiled for this report.

Since 2002, the USGS, in cooperation with New York State Department of Environmental Conservation (NYSDEC), has conducted groundwater-quality monitoring assessments in major river basins in New York (<http://ny.water.usgs.gov/projects/305b/>). Since 2009, these assessments have included sampling for dissolved gases, including methane (Nystrom, 2011, 2012, and Reddy and Risen, 2011). By 2011, methane had been sampled in 8 of the 14 major river basins in the State. These data, combined with those from groundwater age-dating analyses, yielded dissolved methane concentrations from water wells at 239 locations in New York from 1999 to 2011 (fig. 3).



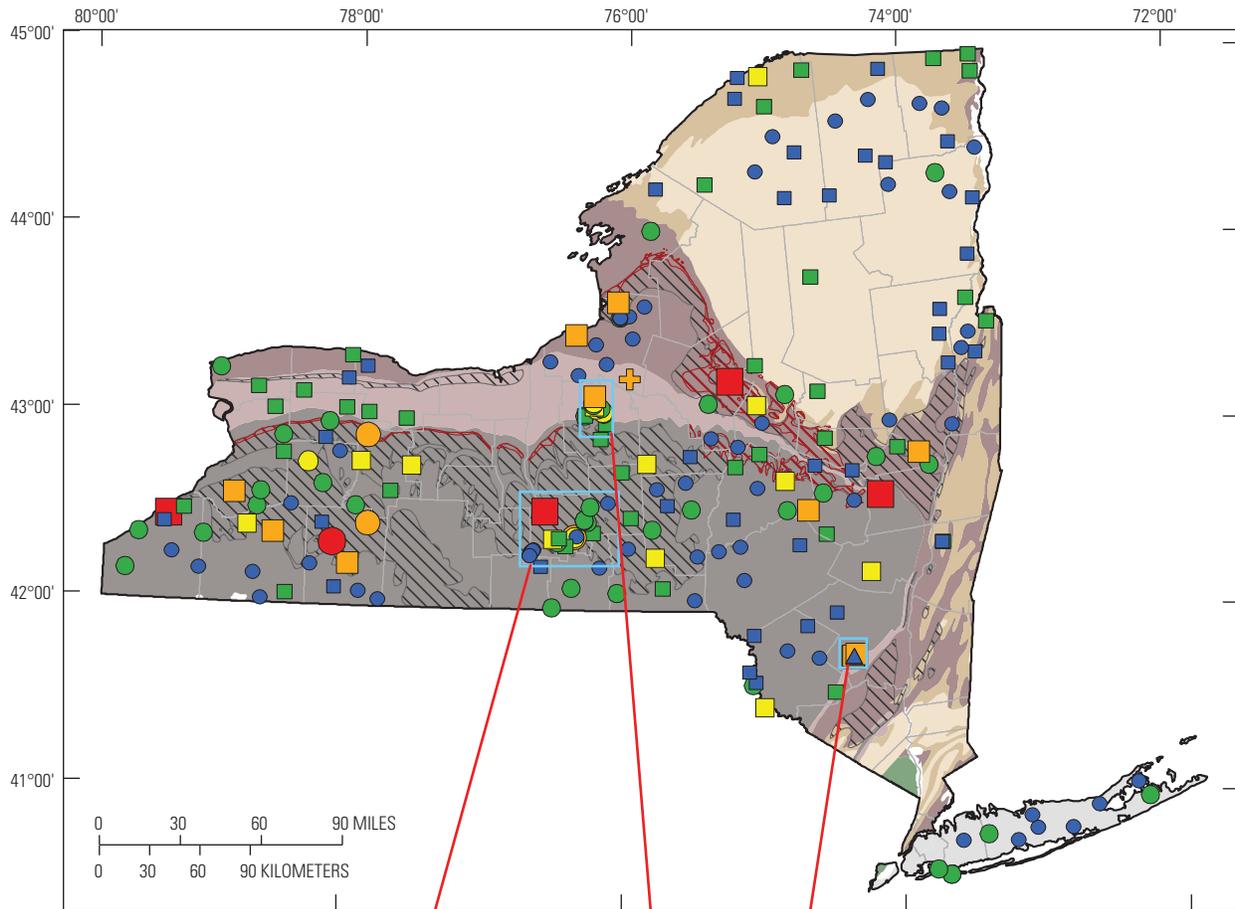
Stratigraphic Column of New York; Oil and Gas Producing Horizons
(From Hill and others, 2003)

PERIOD	GROUP	UNIT	LITHOLOGY	THICKNESS (feet)	PRODUCTION	
PENNSYLVANIAN	Pottsville	Olean	Ss, cgl	75 - 100		
	MISSISSIPPIAN	Pocono	Knapp	Ss, cgl	5 - 100	
DEVONIAN		UPPER	Conewango	Riceville	Sh, ss, cgl	70
	Conneaut		Chadakooin	Sh, ss	700	
			Canadaway	Undiff	Sh, Ss	1,100 - 1,400
	Perrysburg-Dunkirk			Sh, ss	Oil, Gas	
				Sh, ss		
	West Falls		Java	Sh, ss	365 - 125	
			Nunda	Sh, ss		Oil, Gas
		Rhinestreet	Sh			
	Sonyea	Middlesex	Sh	0 - 400	Gas	
	Genesee	Genesee	Sh	0 - 450	Gas	
	MIDDLE	Hamilton	Tully	Ls	0 - 50	Gas
			Moscow	Sh	200 - 600	
			Ludlowville	Sh		
Skaneateles			Sh			
Marcellus			Sh	Gas		
Onondaga		Ls	30 - 235	Gas, Oil		
LOWER		Tristates	Oriskany	Ss	0 - 40	Gas
		Helderberg	Manlius	Ls	0 - 10	
			Rondout	Dol		
SILURIAN		UPPER	Salina	Akron	Dol	0 - 15
	Camillus			Sh, gyp	450 - 1,850	
	Syracuse			Dol, sh, slt		
	Vernon			Sh		Gas
	Lockport		Lockport	Dol		150 - 250
	LOWER	Clinton	Rochester	Sh	125	Gas
			Irondequoit	Ls		
			Sodus/Oneida	Sh/cgl	75	Gas
			Reynales	Ls		
		Medina	Thorold	Ss		
			Grimsby	Sh, ss	75 - 150	Gas
ORDOVICIAN	UPPER		Whirlpool	Ss	0 - 25	Gas
			Queenston	Sh	1,100 - 1,500	Gas
			Oswego	Ss		Gas
			Lorraine	Sh		
	MIDDLE	Trenton-Black River	Utica	Sh	900 - 1000	Gas
			Trenton	Ls	425 - 625	Gas
	LOWER	Beekmantown	Black River	Ls	225 - 550	Gas
			Tribes Hill-Chuctanunda	Ls	0 - 550	
CAMB.	UPPER		Little Falls	Dol	0 - 350	
			Galway	Dol, ss	575 - 1,350	Gas
			Potsdam	Ss, dol	75 - 500	Gas
PRECAMBRIAN			Gneiss, marble, quartzite			

EXPLANATION

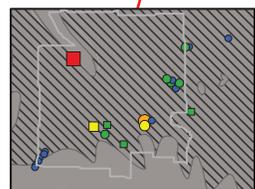
Lithology			
Primary bedrock		Secondary bedrock	
Sh	Shale	cgl	Conglomerate
Ss	Sandstone	gyp	Gypsum
Ls	Limestone	slt	Siltstone
Dol	Dolostone		

Figure 2. Bedrock stratigraphic column for New York State, indicating time period, bedrock groups, unit names, lithology, average thickness, and if the unit could produce natural gas or oil.

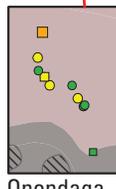


Base from U.S. Geological Survey digital data

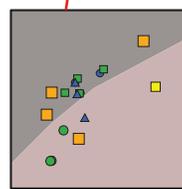
Geologic ages modified from Schruben and others, 1994: 1:2,500,000
 Shale rock outcrops modified from Fisher and others, 1970: 1:250,000



Tompkins County area



Onondaga County area



Ulster County area

EXPLANATION

Dissolved methane concentrations, in milligrams per liter

- ▲ Non-detect (<0.001), Spring
- Non-detect (<0.001), Bedrock
- Non-detect (<0.001), Unconsolidated
- 0.001 to 1, Bedrock
- 0.001 to 1, Unconsolidated
- 1.01 to 10, Bedrock
- 1.01 to 10, Unconsolidated
- ⊕ 10.1 to 28, Unknown
- 10.1 to 28, Bedrock
- 10.1 to 28, Unconsolidated
- >28, Bedrock
- >28, Unconsolidated

Bedrock geology

- ▨ Marcellus and Utica shale outcrops
- ▨ Other black and gray shale outcrops

Geologic age

- Cretaceous and Cenozoic unconsolidated
- Triassic
- Devonian
- Silurian
- Upper and Middle Ordovician
- Lower Ordovician and Upper Cambrian
- Precambrian

Figure 3. Location of wells and dissolved methane concentrations in New York groundwater, 1999–2011.

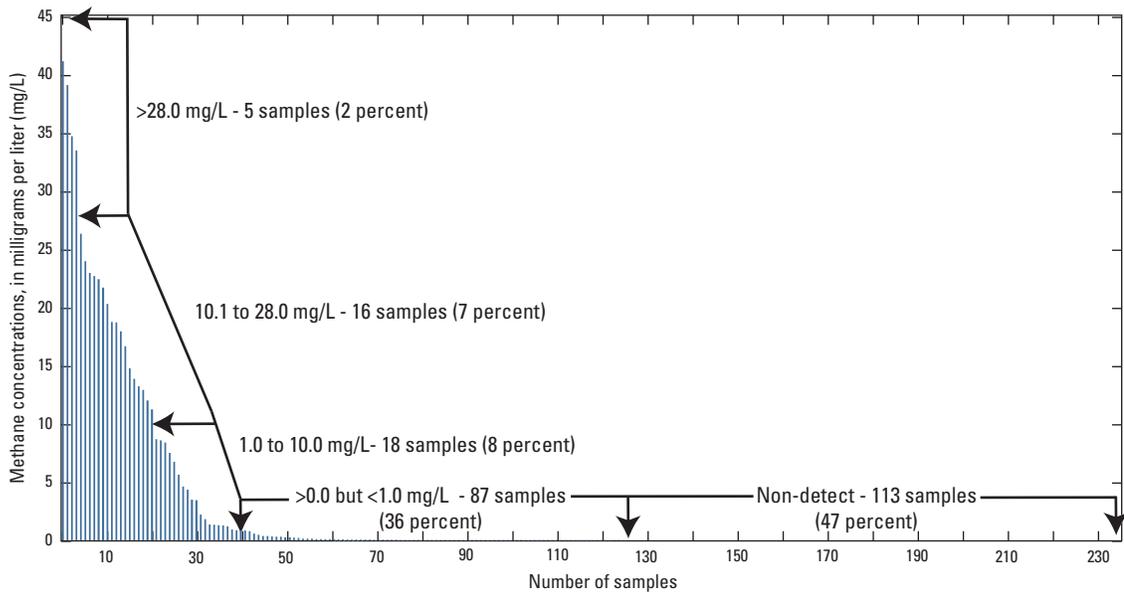


Figure 4. Histogram showing methane concentration by concentration range in groundwater in New York, 1999–2011.

Results

Samples collected through 2011 indicate that concentrations of methane in groundwater from most wells measured (91 percent of the wells) were at or below the Office of Surface Mining action level of 10 mg/L (Eltschlager and others, 2001), and a large number of wells (47 percent) had no detectable methane (fig. 4 and table 1). However, methane concentrations from several wells exceeded 10 mg/L (9 percent); in five cases, the measured concentrations were greater than 28 mg/L (2 percent).

Methane was detected in both unconsolidated and bedrock aquifers across New York (table 1 and fig. 4). In unconsolidated aquifers, 93 percent of the wells had non-detect to low-level methane concentrations (methane concentrations <1 mg/L), and less than 1 percent of the wells (one well) was greater than the saturation value of 28 mg/L. The greater methane concentrations are most likely associated with confined glacial aquifers over black shale bedrock. In bedrock formation aquifers, 73 percent of the methane concentrations were less than 1 mg/L, while nearly 4 percent had concentrations

greater than 28 mg/L across the State. Three of the four highest methane values in bedrock wells were associated with Devonian-aged black shale bedrock; in total, many of the greater methane concentrations were most likely associated with wells drilled into these shales (fig. 3).

The 1999–2011 analysis of dissolved methane in groundwater in New York is meant to document the natural occurrence of methane in the States aquifers. The data describing the occurrence of methane come from a limited dataset collected for general groundwater quality under the 305B program or were associated with the age-dating of groundwater. While many of the greater concentrations of dissolved methane appear to be associated with wells drilled in black shale bedrock or in unconsolidated deposits overlying black shale bedrock, the limited set of existing data does not allow a more concise analysis at this time. This study does indicate the need for continued collection of methane data and analysis for individual and public water-supply wells to document methane concentrations for water wells in New York State.

Table 1. Distribution of dissolved methane concentrations by geologic age.

[<, less than; >, greater than]

Geologic age of water-bearing formation	Number of wells by methane concentration (in milligrams per liter)					Number of wells	Percent of wells
	Non-detect	< 1.0	1.0–10.0	10.1–28.0	> 28.0		
Pleistocene & Upper Cretaceous (glacial) deposits	75	45	5	3	1	129	54
Devonian	14	19	10	7	3	53	22
Silurian	2	8	1	2	0	13	5
Upper and Middle Ordovician	3	5	1	3	1	13	5
Lower Ordovician & Upper Cambrian	7	6	1	0	0	14	6
Precambrian	9	4	0	0	0	13	5
Unknown & other (springs)	3	0	0	1	0	4	2
Number of wells and springs	113	87	18	16	5	239	
Percent of wells and springs	47	36	8	7	2		100

References

- Busenberg, E., and Plummer, L.N., 2000, Dating young ground water with sulfur hexafluoride—Natural and anthropogenic sources of sulfur hexafluoride: *Water Resources Research*, v. 36, p. 3011–3030.
- Eltschlager, K.K., Hawkins, J.W., Ehler, W.C., and Baldassare, Fred, 2001, Technical measures for the investigation and mitigation of fugitive methane hazards in areas of coal mining: U.S. Department of the Interior, Office of Surface Mining Reclamation and Enforcement, 125 p., at <http://www.techtransfer.osmre.gov/NTTMainSite/Library/hbmanual/methane/methane.pdf>.
- Fisher, D.W., Isachsen, Y.W., and Rickard, L.V., 1970, Geologic map of New York State: Albany, N.Y., New York State Museum Map and Chart Series no. 15, scale 1:250,000.
- Hill, D.G., Lombardi, T.E., and Martin, J.P., 2003, Fractured shale gas potential in New York, accessed December 2011, at http://www.pe.tamu.edu/wattenbarger/public_html/Selected_papers/--Shale%20Gas/fractured%20shale%20gas%20potential%20in%20new%20york.pdf.
- Komor, S.C., 2002, Groundwater age dating in community wells in Oswego County, New York: U.S. Geological Survey Open-File Report 01–032, 16 p., at <http://ny.water.usgs.gov/pubs/of/of01232/>.
- Molofsky, L., Connor, J., Wylie, A., and Wagner, T., 2011, Methane in Pennsylvania water wells unrelated to Marcellus shale fracturing: *Oil and Gas Journal*, v. 109, no. 49, 12 p. at <http://www.ogj.com/1/vol-109/issue-49/exploration-development/methane-in-pennsylvania-water-full.html>.
- Nystrom, E.A., 2011, Groundwater quality in the Lake Champlain Basin, New York, 2009: U.S. Geological Survey Open-File Report 2011–1180, 42 p., at <http://pubs.usgs.gov/of/2011/1180/>.
- Nystrom, E.A., 2012, Groundwater quality in the Delaware and St. Lawrence River Basins, New York, 2010: U.S. Geological Survey Open-File Report 2011–1320, 58 p., at <http://pubs.usgs.gov/of/2011/1320/>.
- Osborn, S.G., Avner, Vengosh, Warner, N.R., and Jackson, R.B., 2011, Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing: *Proceedings of the National Academy of Sciences*, 5 p., at www.pnas.org/cgi/doi/10.1073/pnas.1100682108.
- Plummer, L.N., Busenberg, E., and Böhlke, J.K., among authors of the International Atomic Energy Agency (IAEA), 2006, Use of chlorofluorocarbons in hydrology—A guidebook, STI/PUB/1238, 277 p., 111 figs.
- Reddy, J.E., and Risen, A.J., 2012, Groundwater quality in the Upper Susquehanna River Basin, New York, 2009: U.S. Geological Survey Open-File Report 2012–1045, 29 p., at <http://pubs.usgs.gov/of/2012/1045/>.
- Schruben, P.G., Arndt, R.E., Bawiec, W.J., King, P.B., and Beikman, H.M., 1994, Geology of the conterminous United States at 1:2,500,000 scale—A digital representation of the 1974 P.B. King and H.M. Beikman Map: U.S. Geological Survey Digital Data Series DDS–11.
- Solomon, D.K., Schiff, S.L., Poreda, R.J., and Clarke, W.B., 1993, A validation of the 3H/3He method for determining groundwater recharge: *Water Resources Research*, v. 29, no. 9, p. 2951–2962.
- Yager, R.M., Kappel, W.M., and Plummer, L.N., 2007, Halite brine in the Onondaga trough near Syracuse, New York—Characterization and simulation of variable-density flow: U.S. Geological Survey Scientific Investigations Report 2007–5058, 40 p., at <http://pubs.usgs.gov/sir/2007/5058>.



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