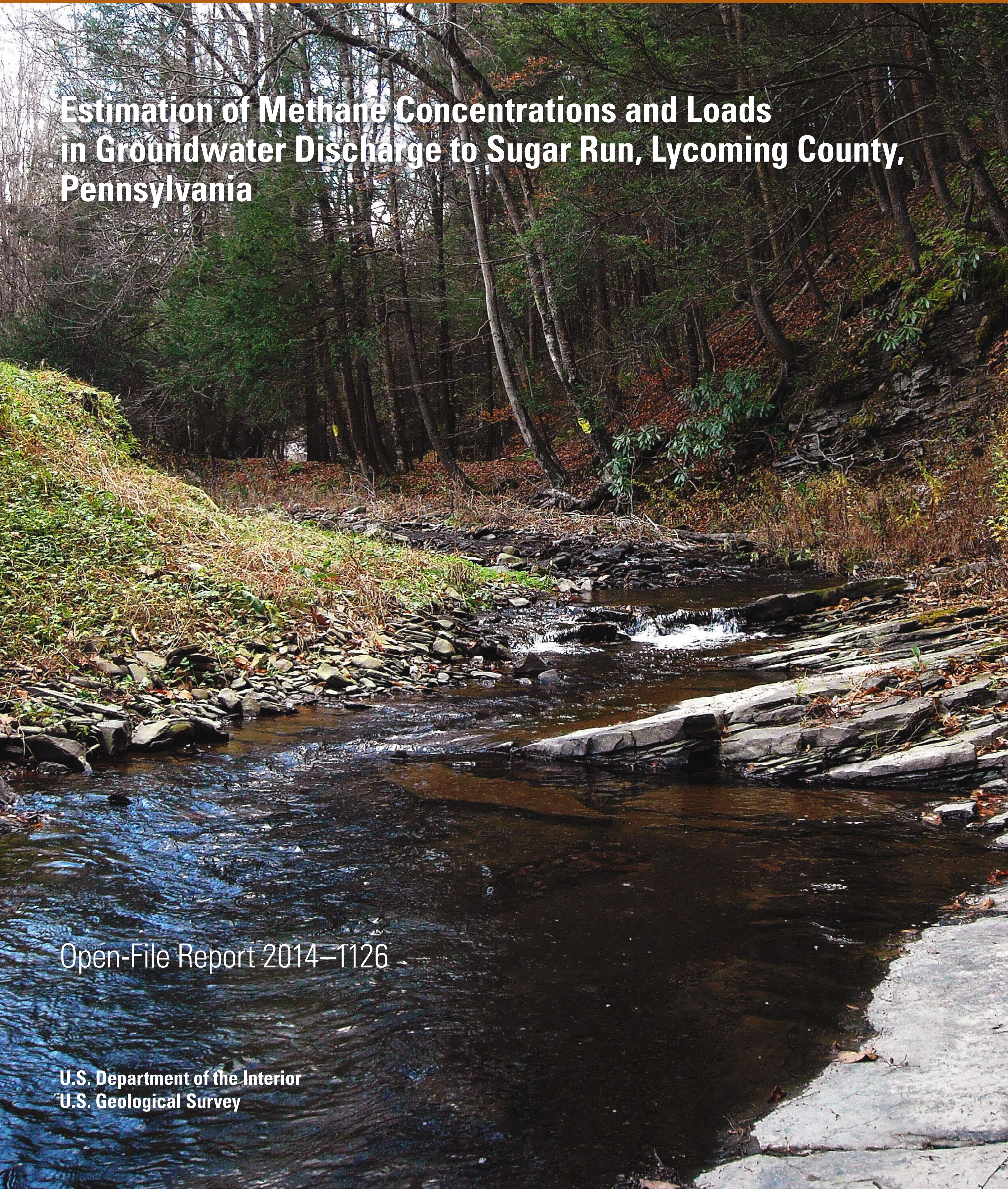
USGS
science for a changing world



Estimation of Methane Concentrations and Loads in Groundwater Discharge to Sugar Run, Lycoming County, Pennsylvania

Open-File Report 2014–1126

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

Cover. Sugar Run, Lycoming County, Pennsylvania. Photograph by Paul Grieve, Pennsylvania State University.

Estimation of Methane Concentrations and Loads in Groundwater Discharge to Sugar Run, Lycoming County, Pennsylvania

By Victor M. Heilweil, Dennis W. Risser, Randall W. Conger, Paul L. Grieve, and Scott A. Hynek

Open-File Report 2014–1126

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit http://www.usgs.gov or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit http://www.usgs.gov/pubprod

To order this and other USGS information products, visit http://store.usgs.gov

Suggested citation:
Heilweil, V.M., Risser, D.W., Conger, R.W., Grieve, P.L., and Hyneck, S.A., 2014, Estimation of methane concentrations and loads in groundwater discharge to Sugar Run, Lycoming County, Pennsylvania: U.S. Geological Survey Open-File Report 2014–1126., 31 p., *http://dx.doi.org/10.3133/ofr20141126*.

ISSN 2331-1258 (online)

Acknowledgments

The authors would like to thank D. Kip Solomon (University of Utah) for providing valuable insight into applying stream-reach mass-balance methods for quantifying methane loads in groundwater, and Susan Brantley and Todd Sowers (Pennsylvania State University) for analytical support of the November 2013 Sugar Run synoptic study. Thanks also go to Olivia Miller (University of Utah) for assistance in developing the conceptual model diagram, Peter Cook (Commonwealth Scientific and Industrial Research Organization) for the one-dimensional stream transport code for simulating groundwater inflow and gas transfer, and Lisa Senior and John Solder (U.S. Geological Survey) for their helpful peer review comments and suggestions.

Contents

Figures

Tables

Conversion Factors

SI to Inch/Pound

Multiply	By	To obtain
	Length	
centimeter (cm)	0.3937	inch (in.)
millimeter (mm)	0.03937	inch (in.)
meter (m)	3.281	foot (ft)
kilometer (km)	0.6214	mile (mi)
	Area	
square kilometer (km^2)	0.3861	square mile (mi^2)
	Flow rate	
meter per day (m/d)	3.281	foot per day (ft/d)
cubic meter per second (m^3/s)	35.31	cubic foot per second (ft^3/s)
	Mass	
kilogram (kg)	2.205	pound, avoirdupois (lb)

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

°F=(1.8×°C)+32

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

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

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

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

Estimation of Methane Concentrations and Loads in Groundwater Discharge to Sugar Run, Lycoming County, Pennsylvania

By Victor M. Heilweil, Dennis W. Risser, Randall W. Conger, Paul L. Grieve[1], and Scott A. Hynek[1]

Abstract

A stream-sampling study was conducted to estimate methane concentrations and loads in groundwater discharge to a small stream in an active shale-gas development area of northeastern Pennsylvania. Grab samples collected from 15 streams in Bradford, Lycoming, Susquehanna, and Tioga Counties, Pa., during a reconnaissance survey in May and June 2013 contained dissolved methane concentrations ranging from less than the minimum reporting limit (1.0) to 68.5 micrograms per liter (µg/L). The stream-reach mass-balance method of estimating concentrations and loads of methane in groundwater discharge was applied to a 4-kilometer (km) reach of Sugar Run in Lycoming County, one of the four streams with methane concentrations greater than or equal to 5 µg/L. Three synoptic surveys of stream discharge and methane concentrations were conducted during base-flow periods in May, June, and November 2013. Stream discharge at the lower end of the reach was about 0.10, 0.04, and 0.02 cubic meters per second, respectively, and peak stream methane concentrations were about 20, 67, and 29 µg/L. In order to refine estimated amounts of groundwater discharge and locations where groundwater with methane discharges to the stream, the lower part of the study reach was targeted more precisely during the successive studies, with approximate spacing between stream sampling sites of 800 meters (m), 400 m, and 200 m, in May, June, and November, respectively. Samples collected from shallow piezometers and a seep near the location of the peak methane concentration measured in streamwater had groundwater methane concentrations of 2,300 to 4,600 µg/L. These field data, combined with one-dimensional stream-methane transport modeling, indicate groundwater methane loads of 1.8 ±0.8, 0.7 ±0.3, and 0.7 ±0.2 kilograms per day, respectively, discharging to Sugar Run. Estimated groundwater methane concentrations, based on the transport modeling, ranged from 100 to 3,200 µg/L. Although total methane load and the uncertainty in calculated loads both decreased with lower streamflow conditions and finer-resolution sampling in June and November, the higher loads during May could indicate seasonal variability in base flow. This is consistent with flowmeter measurements indicating that there was less inflow occurring at lower streamflow conditions during June and November.

Introduction

Natural-gas production from shale-gas formations has increased rapidly in the United States because of technological advances allowing extraction from unconventional resources due to the widespread use of horizontal drilling and hydraulic fracturing (Dammel and others, 2011; Nicot and Scanlon, 2012; Schnoor, 2012). As a consequence of these developments, previously unexploited regions of the country are experiencing intensive development of natural gas resources (Kappel and others, 2013). There is widespread public concern about the environmental effects of unconventional gas development on surface-water and groundwater resources (Pelly, 2003; Kargbo and others, 2010). Some studies have indicated increased methane concentrations in overlying aquifers associated with shale-gas development (Osborn and others, 2011; Jackson and others, 2013). Such interpretations remain controversial, partly because of the lack of publically available pre-development groundwater quality data. The effects of stray gas on groundwater quality are also difficult to assess in active development areas because of the uncertainty as to whether existing monitoring wells are located along the same groundwater flowpaths affected by development (Vidic and others, 2013; Brantley and others, 2014).

[1]Pennsylvania State University.

The Marcellus Formation shale-gas play in northeastern Pennsylvania is one such area of drilling for unconventional natural gas (fig. 1). Depths to the base of the Marcellus Formation in Susquehanna, Bradford, Tioga, Lycoming, and Sullivan Counties range from 0 to about 9,000 feet (MCOR, 2014). The presence of methane has been documented in water wells overlying the Marcellus in northeastern Pennsylvania (Boyer and others, 2011; Osborn and others, 2011; Molofsky and others, 2013; Sloto, 2013), but publicly available data are sparse. Methane occurrence in groundwater in Tioga County has been documented before the onset of the Marcellus play in northern Pennsylvania (Breen and others, 2007). The history of natural-gas production in Tioga County spans much of the 20th century, and gas-storage fields (Lytle, 1963) are developed in the sandstone reservoirs that overlie the Marcellus Formation and are active as storage reservoirs for natural gas transported via pipeline through northern Pennsylvania. Additional information is needed to better understand the occurrence and distribution of groundwater methane in order to assess potential effects from gas development.

A method using stream-based methane sampling was recently developed to estimate methane loads in groundwater and potential groundwater contamination at the watershed scale (Heilweil and others, 2013), based on the conceptual model of thermogenic methane transport from a hydraulically fractured natural gas reservoir into an overlying aquifer/stream system (fig. 2). Methane in groundwater discharging to the stream, however, may also include biogenic methane. Potential biogenic sources include anaerobic decay of organic matter from agricultural sources, waste disposal, riparian zones, swamps, and shallow groundwater. In order to differentiate between biogenic and thermogenic methane sources, however, other geochemical tracers in streamwater (such as hydrocarbon ratios and the stable carbon and hydrogen isotopes of methane and ethane) are also needed. Potential migration pathways for thermogenic methane to move from deep shale reservoirs into overlying aquifers include dissolved gas in upwardly migrating fluids or stray gas moving through fractures, faults, and improperly completed well bores. Groundwater from these aquifers can discharge to wells, springs, or gaining stream reaches. The converging of groundwater flow paths at points of discharge (springs, gaining streams) can provide a flow-weighted and integrated sample, indicative of watershed-scale groundwater quality, including dissolved thermogenic methane and other potential contaminants from natural gas development activities. This streamwater-sampling-based methane monitoring approach, if successful, may provide a much broader evaluation than reported studies that are based on the sampling of water wells (Breen and others, 2007; DiGuilio and others, 2011; Osborn and others, 2011). Importantly, the information gained from the study of gaining stream reaches can integrate information about groundwater over km-scale distances that are more representative of regional aquifer conditions than point samples from monitoring wells.

Approach

The objective of this study was to demonstrate the use of measurements of dissolved methane concentrations in a stream (hereafter “stream methane”) for estimating dissolved methane concentrations in groundwater inflow to the stream (hereafter “groundwater methane”) and methane loads of groundwater discharge to streams. The approach began with reconnaissance-level sampling of a selected group of streams located in areas of ongoing shale-gas development in the Marcellus Formation shale-gas play of northeastern Pennsylvania to identify the range of stream methane in the area. Streams in Bradford, Lycoming, Susquehanna, and Tioga Counties were selected that were easy to access for sampling and were representative of the differing physiography, land cover, and underlying geology of the area. Some stream sampling sites were located near areas where groundwater with methane concentrations elevated above background levels had been reported. One site in Tioga County is in an area of underground storage fields for natural gas (Lytle, 1963). Samples for methane analysis were collected from 15 streams, and stream characteristics were measured during base-flow conditions during May and June 2013.

Sugar Run in Lycoming County was selected for more detailed investigation. Three synoptic studies (May 21, June 27, and November 12, 2013) of stream and shallow groundwater methane in and adjacent to Sugar Run were conducted during base-flow conditions. The synoptic studies consisted of stream-methane sampling and stream-discharge measurements at the sub-kilometer (km) scale. The sampling resolution was increased with each successive sampling synoptic study in order to pinpoint areas with methane-laden groundwater discharge to the stream. Thus, the sample spacing decreased from about 800 meters (m) to 400 m to 200 m during the three successive synoptic studies. Near-stream groundwater samples were collected (from temporary piezometers installed in the streambed and a groundwater seep) for methane analysis in order to determine groundwater methane concentrations prior to mixing and dilution with streamwater. These stream and groundwater data were compiled into a series of preliminary stream-methane transport numerical models for estimating methane concentrations and loads in groundwater discharge to Sugar Run.

Purpose and Scope

This report presents the results of reconnaissance sampling of methane in 15 streams in northeastern Pennsylvania and three synoptic studies of stream discharge, stream methane, and groundwater methane conducted during May, June, and November 2013 along a gaining reach of Sugar Run, Lycoming County, Pennsylvania. The stream-reach mass-balance method was used to estimate methane concentrations and loads in groundwater discharge to Sugar Run.

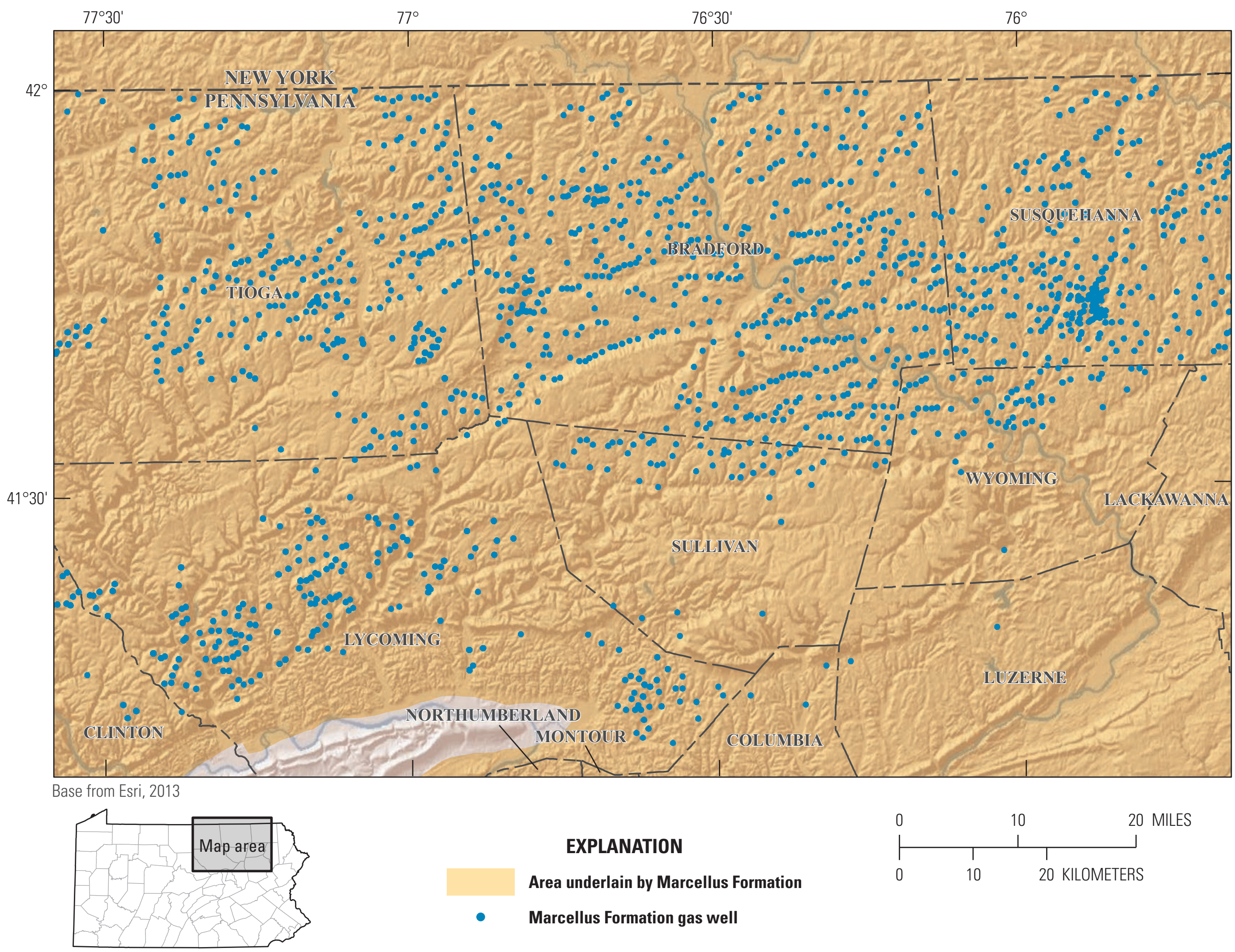


Figure 1. Marcellus Shale gas wells drilled in northeastern Pennsylvania as of July 20, 2013 (well locations from FracTracker, 2013).

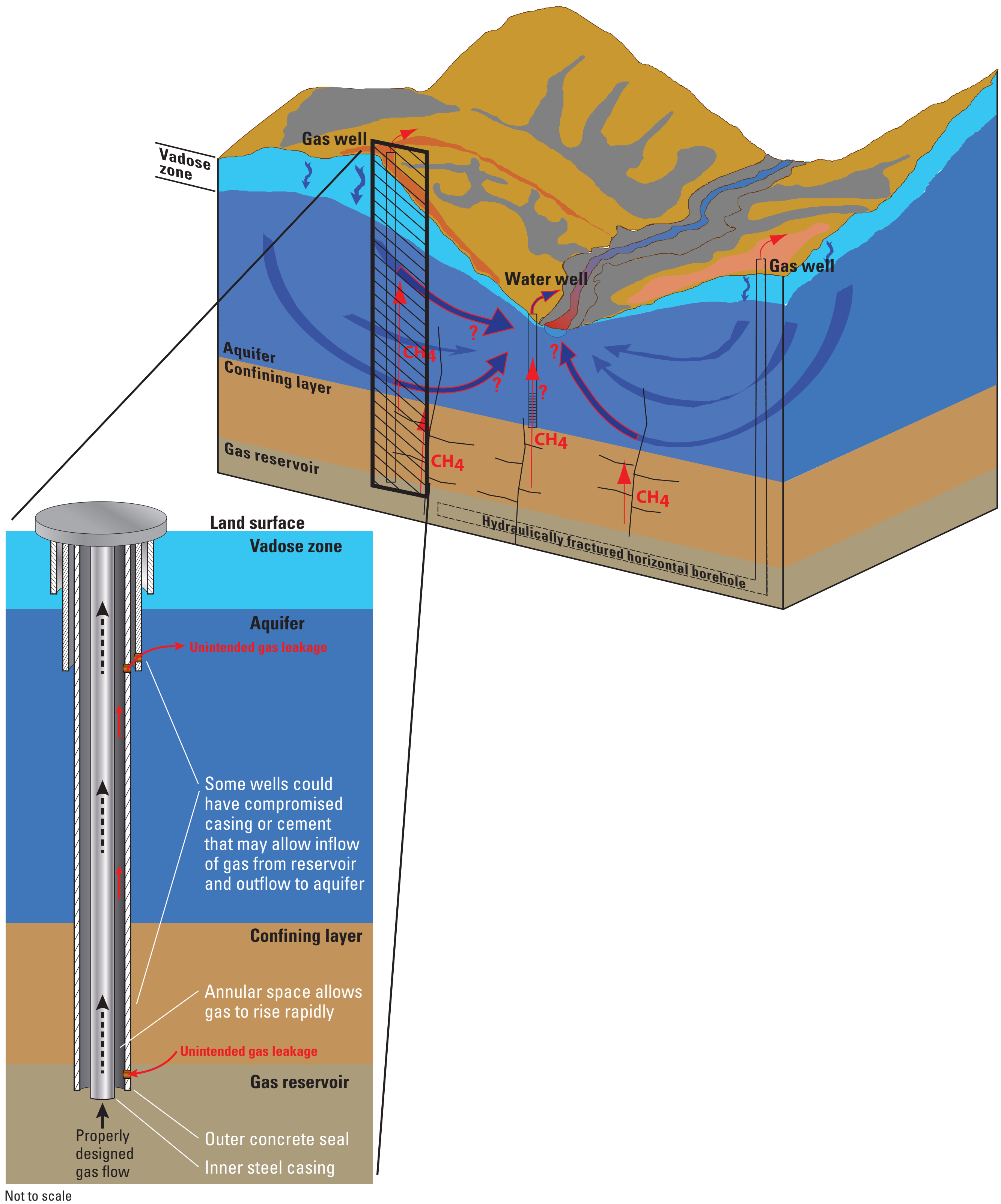


Figure 2. Conceptual diagram of methane transport from a hydraulically fractured gas reservoir to an overlying aquifer/stream system. The relatively small vertical extent of the confining layer is a simplification; in many areas of natural gas development, the aquifer and gas reservoir may be vertically separated by many thousands of meters (modified from Heilweil and others, 2013; CH_4, methane).

Methods

Sampling Procedures

Measurement of stream discharge and other stream characteristics, along with the collection of stream samples for methane analysis, were completed on the same day for each of the three synoptic studies. Discharge was measured using a SonTek/YSI FlowTracker acoustic Doppler current profiler. The synoptic studies were conducted during days when the streams were at base flow. The empirical equation $N = (A \times 0.3861)^{0.2}$ was used to estimate the approximate number of days (N) after a storm until base-flow conditions were reached, where A is the basin area in square kilometers (Linsley and others, 1975, p. 230). From the equation, base-flow conditions for the 16.7-square-kilometer (km^2) Sugar Run watershed likely would be reached about 1.5 days after a storm peak. For the May, June, and November synoptic studies, samples were collected 10, 13, and 5 days after storm peaks, respectively. The flow was steady, and the water was clear during all three sampling events, indicating that water was contributed predominantly by groundwater discharge. Although there is not a streamgage on Sugar Run to verify base-flow conditions during the 3 days when the synoptic studies were conducted, the flow at the nearby streamgage on Muncy Creek near Sonestown (station 01552500) was predominantly base flow. This was determined by hydrograph separation using the U.S. Geological Survey's HYSEP (Hydrograph Separation) local minimum method of Pettyjohn and Henning (1979) as implemented by Sloto and Crouse (1996). The flow in Muncy Creek near Sonestown, which drains a 62-km^2 watershed, was entirely base flow on May 21 and June 27. On November 12, about 82 percent of the streamflow in Muncy Creek near Sonestown was characterized as base flow, but because the watershed upstream from that stream gage is four times larger than the Sugar Run watershed, base-flow conditions were probably established more rapidly in Sugar Run. Stream discharge at the lower end of the study reach in Sugar Run was about 0.10, 0.04, and 0.02 cubic meters per second (m^3/s), respectively, during the three synoptic studies. High flows that occur on average once in 2 years were estimated to reach 9.65 m^3/s by using the Roland and Stuckey (2008) StreamStats regression program.

To determine net gains to the stream caused by groundwater inflows and outflows along a study reach, the upstream flowmeter discharge measurements were subtracted from downstream discharge measurements (while accounting for any tributary surface-water inflow). Positive values indicate groundwater discharge to the stream, whereas negative values indicate stream loss to the groundwater system.

Field parameters were measured near the bottom of the stream and in the main flow channel at each stream site using a multi-parameter probe that included temperature, specific conductance, pH, and dissolved oxygen. Samples for methane concentration were collected at the same stream locations and water depths as the field-parameter measurements. Samples analyzed by the U.S. Geological Survey (USGS) Chlorofluorocarbon Laboratory (*http://water.usgs.gov/lab/*) were collected in 250-milliliter (mL) glass bottles; samples analyzed by Pennsylvania State University were collected in 1,000-mL polycarbonate bottles. While submerged in the stream, the bottles were first purged (3 bottle volumes) with streamwater using a small battery-operated submersible pump (Whale pump) that pushed water from the stream into the bottle to minimize the possibility of gas exsolution. For the 250-mL glass bottles, a bactericide (potassium hydroxide) was then added to each full sample bottle, and the bottle was again submerged in the stream and sealed with a rubber stopper. The stopper was pierced by a syringe, allowing displaced water to escape while the stopper was being inserted into the bottle neck. Removal of the syringe below the water surface and continuous submersion of the bottle during the entire sampling procedure ensured that there was no head space in the completed sample. The 1,000-mL polycarbonate bottles had a time-release bactericide capsule attached to the inside of the bottle cap. Methane concentrations in samples from the May and June synoptic studies along Sugar Run were measured in replicate by the USGS using a Hewlett Packard model 5890 gas chromatograph with a Flame Ionization Detector with a minimum reporting limit of 1.0 micrograms per liter (µg/L) and precision of ±0.5 µg/L. In this report, concentrations in samples that had USGS replicate laboratory results less than the 1.0 µg/L minimum reporting limit are defined as "estimated" values. In addition, replicate samples for eight stream sites were collected on May 22, 2013, and were analyzed by Isotech, Inc., using gas chromatography with a reported precision of ±5 percent (table 1, at end of report). Methane concentrations for the November synoptic study along Sugar Run were measured by Pennsylvania State University using a Hewlett Packard model 5830 gas chromatograph and Flame Ionization Detector with a minimum reporting limit of 0.1 µg/L and precision of less than or equal to (≤) 2 percent.

Drive-point piezometers were temporarily installed in the streambed of Sugar Run at two of the stream sampling sites on June 27, 2013, and one site on November 12, 2013. The ¾-inch-diameter piezometers were driven with a slide hammer to depths of 1 to 3 feet below the streambed. Penetration was difficult because of the cobble-lined streambed and shallow bedrock. Vinyl tubing was inserted into the piezometer, and water was purged with a peristaltic pump at a low pumping rate to minimize the possibility of pulling in streamwater and (or) degassing. After the discharge was free of sediment, a water sample was collected by inserting the discharge tube into the bottom of the bottle. When full, the bottle was submerged in the stream while water was continuously being pumped, allowing water in the bottle to continuously overflow until about three sample volumes had flushed through. The same preservative and capping procedures as described above were used.

Modeling

Stream-discharge measurements and stream methane were used in a stream reach mass-balance model to evaluate methane concentrations and loads coming into Sugar Run from groundwater inflow. Assuming that microbial consumption or production of methane is minimal, the mass balance used for this modeling (based on Heilweil and others, 2013) is

$$Q\,\partial C/\partial x = I(C_{gw} - C) - \lambda_{CH4} DwC\,, \qquad (1)$$

where

- Q is stream discharge, in cubic meters per day (m^3/d);
- I is groundwater inflow per unit stream length, in square meters per day (m^2/d);
- C is stream methane, in µg/L;
- C_{gw} is groundwater methane, in µg/L;
- λ_{CH4} is gas transfer coefficient of methane exsolution from the stream to the atmosphere, in 1 per day (1/d);
- D is stream depth, in meters (m);
- w is stream width, in m; and
- x is the downstream distance coordinate, in m.

Multiplying λ_{CH4} by D yields the gas transfer velocity of methane (K_{CH4}, in m/d). This equation illustrates that the downstream gradient in stream methane concentration ($\partial C/\partial x$) can be determined by (1) stream discharge, Q, (2) the rate of groundwater inflow to the stream, I, (3) the methane concentration of this groundwater inflow, C_{gw}, (4) the methane concentration in the stream, C, (5) the gas transfer velocity, K_{CH4}, and (6) the stream cross-sectional area (Dw). Conversely, by measuring the downstream rate of change in methane concentration, the groundwater methane load discharging to the stream can be evaluated (where methane load is the product of groundwater inflow rate and groundwater methane concentration).

For evaluating the stream-methane mass balance, a one-dimensional (1-D) stream transport model with gas exchange (Cook and others, 2003, 2006) was used to estimate groundwater methane load. On the basis of equation 1, the model includes initial streamflow at the upper end of the study reach, stream characteristics (groundwater inflow, width, depth, methane concentration) as a function of downstream distance, and gas transfer velocity. For the preliminary modeling presented in this report, the gas transfer velocity is assumed to be constant for the study reach. Because wind, water temperature, stream depth, and turbulence can all affect the gas transfer velocity, a range of values was tested to evaluate the sensitivity of results to this model parameter. The methane concentration of groundwater inflow for each gaining section was adjusted during calibration to measured stream methane. For these numerical simulations, stream gain (groundwater inflow) and stream loss (to groundwater) were specified, based on the stream discharge measurements. These gains and losses are defined in the numerical model as inflow or outflow in cubic meters per day per unit stream length, so the amount of gain or loss for each section of the reach was divided by the length of that section.

Stream Methane, Stream Discharge, and Groundwater Methane

Stream-Methane Reconnaissance

Methane samples were initially collected at nine stream sites during May 21–22, 2013; an additional six sites were sampled on June 26, 2013. The 15 sites are located in Bradford, Lycoming, Susquehanna, and Tioga Counties (fig. 3). Dissolved methane concentrations ranged from below the minimum reporting limit of 1.0 µg/L for seven streams to 68.5 µg/L in Meshoppen Creek (table 1). Four streams had methane concentrations greater than or equal to 5 µg/L (Sugar Run, Little Muncy Creek, Parks Creek, and Meshoppen Creek).

The physical characteristics and human activities within the watershed are likely to affect the occurrence and distribution of methane in streams. Some of these factors, including the density of Marcellus gas-well pads as of July 2013, are listed in table 1. The characteristics are not independent (for example, geology affects land cover), and consequently the individual effect of each characteristic is not obvious. In addition, other factors relating to gas transport and transfer may differ among streams, but some general observations can be made about measured stream methane. Streams with the highest median concentration of methane of 1.5 µg/L are in watersheds where the Lock Haven and Trimmers Rock formations, as mapped by Berg and others (1980), directly underlie more than 50 percent of the area (fig. 4). Stream samples had a lower median methane concentration of 0.71 µg/L (but the largest range of below the 1.0-µg/L minimum reporting limit to 68.5 µg/L) in watersheds where the Catskill Formation directly underlies more than 50 percent of the area. Samples with the lowest methane concentrations (not shown in figure 4) were from two stream sites in watersheds where neither the Catskill and Trimmers Rock or Lock Haven Formations underlie more than 50 percent of the area.

The concentration of methane in the 15 reconnaissance stream samples may suggest some relation to the percentage of forested lands in the watershed (fig. 5). Percentage of forested land in each basin was determined from the land use and land cover dataset of Price and others (2006) in StreamStats. Samples collected from streams in the six watersheds with greater than 70 percent forested land had methane concentrations below the minimum reporting limit of 1.0 µg/L. The possible

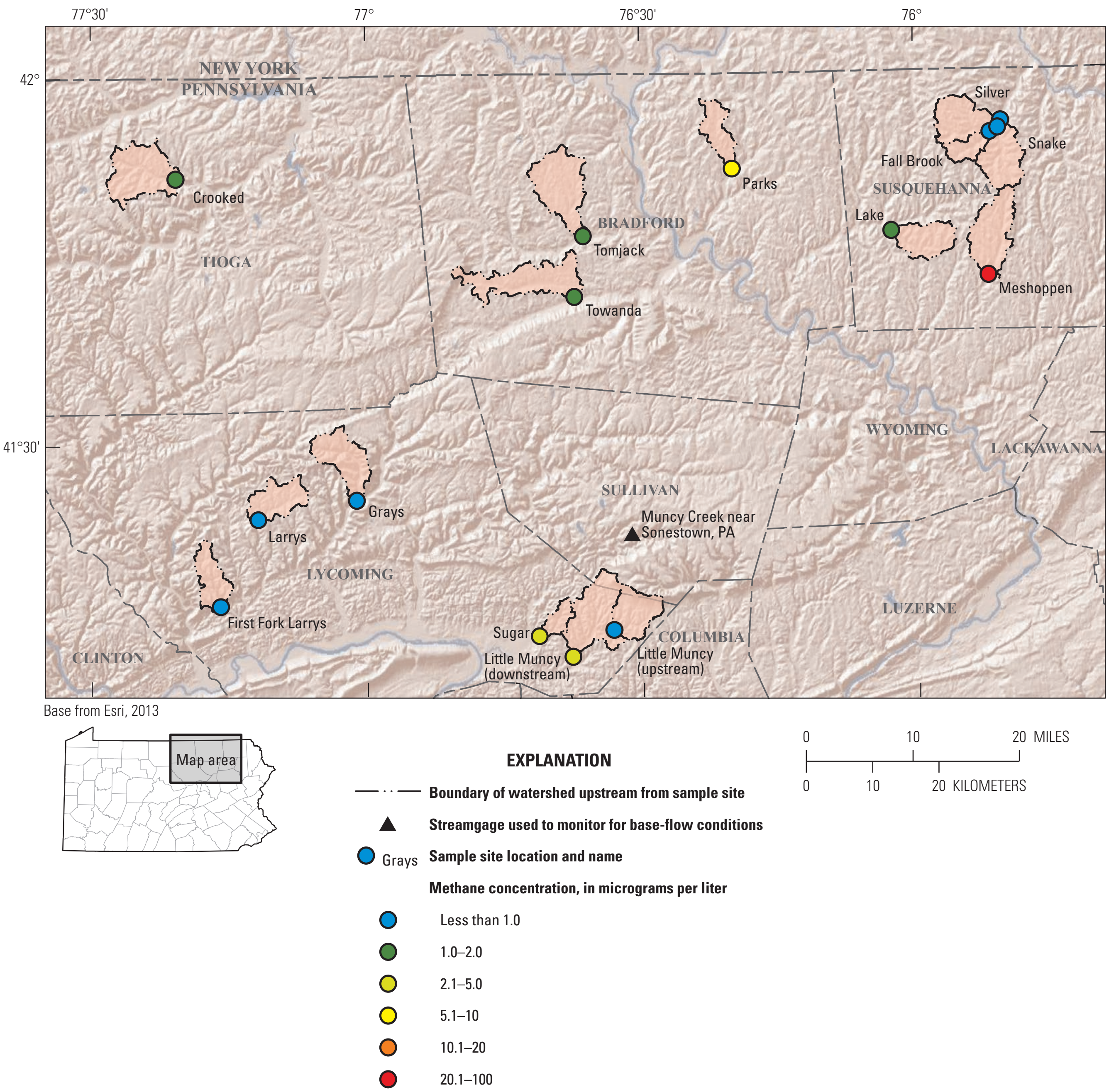


Figure 3. Locations of stream sampling sites and dissolved methane concentrations in samples collected from streams in northeastern Pennsylvania, May and June 2013. Values less than the minimum reporting limit of 1.0 microgram per liter are estimated.

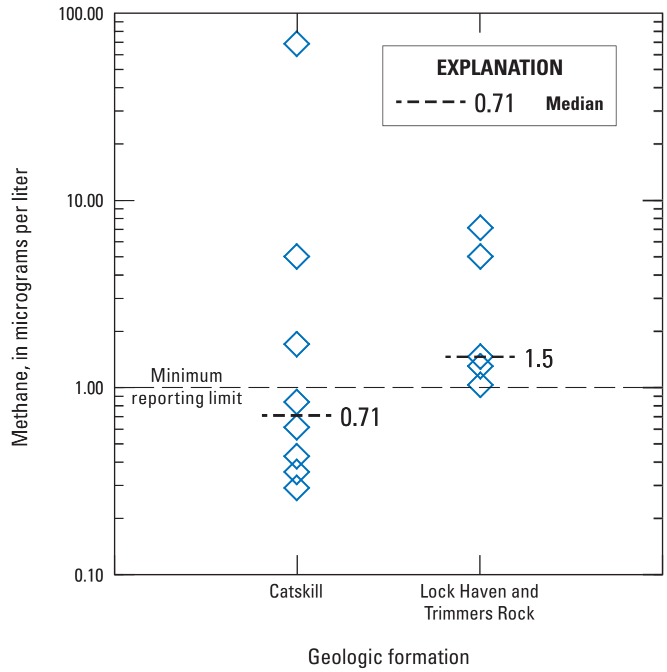


Figure 4. Dissolved methane concentrations, grouped by predominant geologic formation outcrop in the watershed, in samples collected from streams in northeastern Pennsylvania, May and June 2013. Methane concentration is the mean value of two samples from each site, analyzed by the U.S. Geological Survey Chlorofluorocarbon Laboratory. Values less than the minimum reporting limit of 1.0 microgram per liter are estimated.

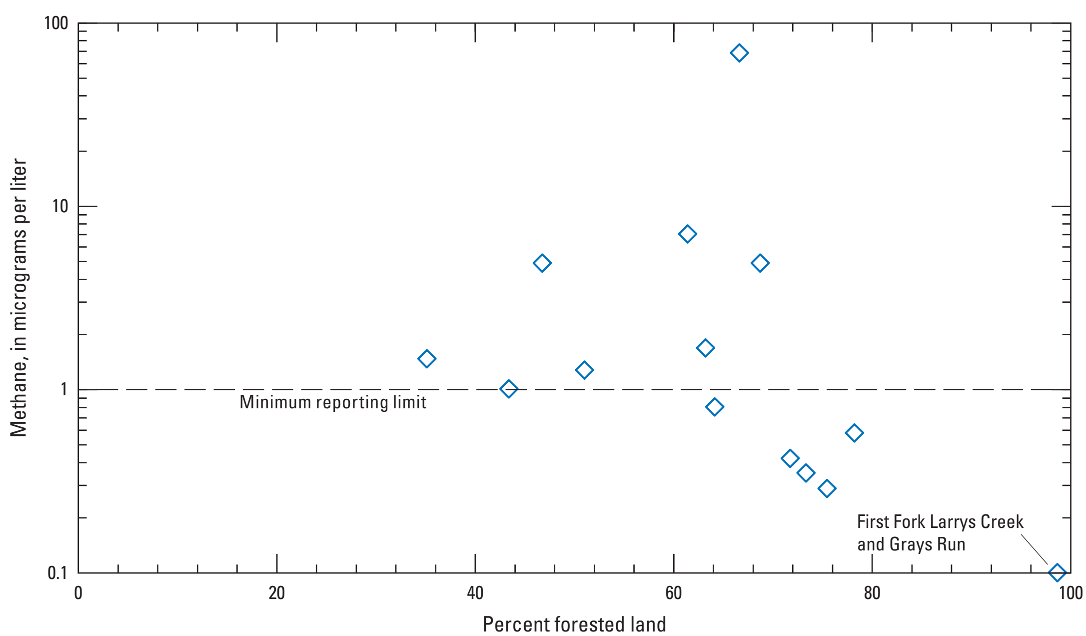


Figure 5. Relation of dissolved methane concentrations in samples collected from streams in northeastern Pennsylvania to the percentage of forested land (from Price and others, 2006) in the associated watershed. Methane concentration is the mean value of two samples from each site, analyzed by the U.S. Geological Survey Chlorofluorocarbon Laboratory. Values less than the minimum reporting limit of 1.0 microgram per liter are estimated.

relation could indicate a direct effect of forests on stream methane but probably involves other factors associated with forested lands, such as lower human population density and less agriculture.

The largest methane concentration (68.5 µg/L) occurred in Meshoppen Creek, which is in a watershed underlain by the Catskill Formation and has a basin slope (7.5 percent) and percentage of forested lands (about 67 percent) similar to the other sampled watersheds. The sample was collected at a site downstream from a swampy section of the stream, which could be a source of biogenic methane. The site is also downstream from an area of high gas-well density (table 1) where thermogenic methane has been found in groundwater (Osborn and others, 2011). The relation between stream methane and well-pad density for all samples is shown in figure 6.

Sugar Run Synoptic Sampling

During the reconnaissance sampling in May 2013, the USGS also conducted a stream sampling synoptic study along a 4-km reach of Sugar Run (fig. 7, table 2). This synoptic study included collection of samples for methane analysis and stream-discharge measurements at seven locations (six Sugar Run main-stem sites and one tributary). Stream methane during the May synoptic study ranged from below the minimum reporting limit of 1.0 µg/L to 19.6 µg/L (fig. 8, table 3, at end of report). On the basis of the high methane concentration (19.6 µg/L) found at Site 2 (3,160 m downstream) during May, a more detailed synoptic study of stream methane was conducted during lower flow conditions in June 2013 at five sites, approximately every 400 m along the lower part this reach (Sites 3, 2.5, 2, 1.5, and 1, located 2,450 to 4,000 m downstream, respectively; fig. 7*A*). Methane analysis of those samples showed concentrations of as much as 67 µg/L at Site 1.5 (3,520 m downstream). A third synoptic study was conducted at seven stream sites along Sugar Run in November 2013 to provide further spatial refinement of the higher stream methane between Site 1 and Site 2 (Sites 2, 1.8, 1.6, 1.5, 1.4, 1.2, and 1, located 3,160–4,000 m downstream, respectively; fig. 7*B*). During this synoptic study, stream methane was highest (29 µg/L) at Site 1.5.

During the June and November synoptics, shallow groundwater methane samples were also collected. Two temporary piezometers were installed in the streambed in the main channel flow during the June synoptic (fig. 7A). Groundwater from the piezometer upstream from Site 1.5 (Piezo 1.5 at 3,500 m downstream) had a methane concentration of 2,700 µg/L, whereas groundwater from the piezometer at Site 1 (Piezo 1 at 4,000 m downstream) had a methane concentration of 7.7 µg/L (table 3). The high stream methane at Site 1.5 was consistent with the high groundwater methane from Piezo 1.5 and in contrast to the lower concentration in groundwater at Piezo 1. In November, groundwater was

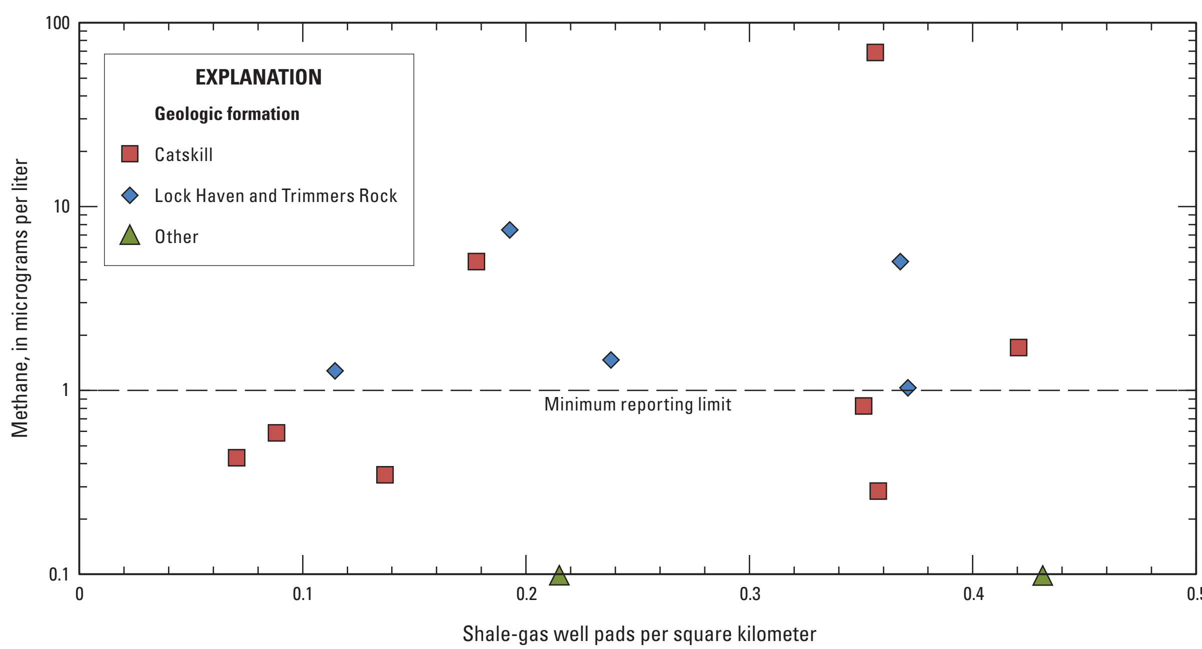


Figure 6. Relation of dissolved methane concentrations in samples collected from streams in northeastern Pennsylvania to shale-gas well-pad density in the associated watersheds, July 2013. Methane concentration is the mean value of two samples from each site, analyzed by the U.S. Geological Survey Chlorofluorocarbon Laboratory. Values less than the minimum reporting limit of 1.0 microgram per liter are estimated.

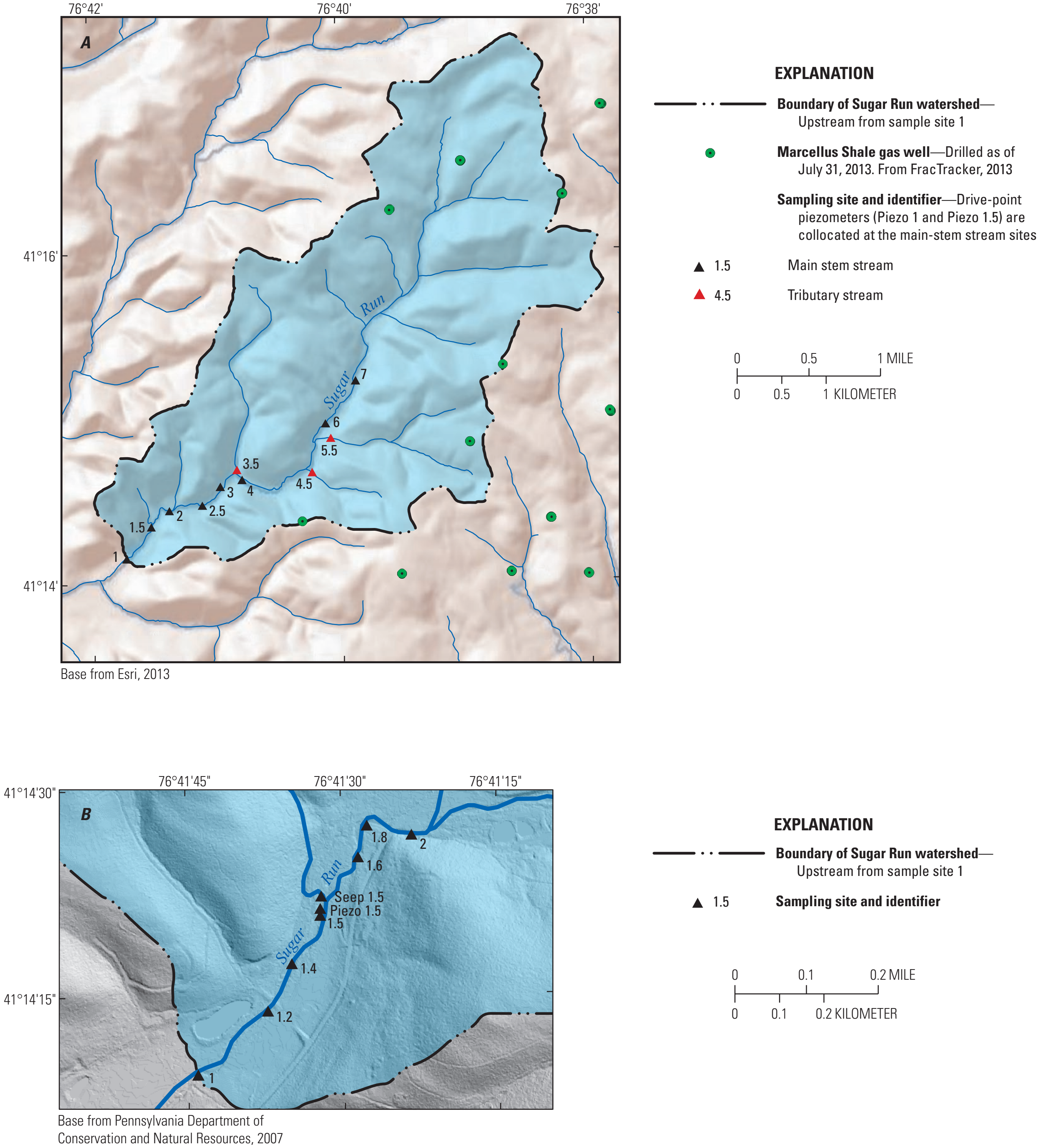


Figure 7. Location of sampling sites on Sugar Run, Lycoming County, Pennsylvania, sampled in *A*, May and June, and *B*, November 2013.

Table 2. Location and characteristics of the sampling sites along Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013.

[Map identifier can be used to locate sites on figure 7. Station number is a unique 9- or 15-digit number used by the U.S. Geological Survey to identify a stream or well site; dd, decimal degrees; km^2, square kilometers; m, meters; pizeo, water sample collected from drive point piezometer installed in streambed]

Map identifier	Station number	Site name	Longitude (dd)	Latitude, (dd)	Drainage area (km^2)	Distance downstream (m)
		May 21, 2013 samples				
Site 7	01552840	Sugar Run in Penn Township near Lairdsville, PA	41.25367	-76.66461	3.13	0
Site 6	01552845	Sugar Run near Lairdsville, PA	41.24936	-76.66872	3.46	620
Site 4	01552869	Sugar Run in Green Valley near Hughesville, PA	41.24378	-76.68000	4.71	2,100
Site 3	01552876	Sugar Run downstream unnamed trib near Hughesville, PA	41.24311	-76.68297	5.57	2,450
Site 2	01552878	Sugar Run in Penn Township near Hughesville, PA	41.24072	-76.68978	6.01	3,160
Site 1	01552880	Sugar Run near Hughesville, PA	41.23592	-76.69558	6.45	4,000
Tributary 5.5	01552855	Unnamed trib to Sugar Run near Lairdsville, PA	41.24789	-76.66808	0.66	910
Tributary 4.5	01552865	Unnamed trib to Sugar Run in Green Valley near Hughesville, PA	41.24444	-76.67061	0.25	1,250
Tributary 3.5	01552870	Unnamed trib to Sugar Run near Hughesville, PA	41.24478	-76.68067	0.80	2,200
		June 27, 2013 samples				
Site 3	01552876	Sugar Run downstream unnamed trib near Hughesville, PA	41.24311	-76.68297	5.57	2,450
Site 2.5	01552877	Sugar Run 2.5 downstream unnamed trib near Hughesville, PA	41.24122	-76.68536	5.64	2,770
Site 2	01552878	Sugar Run in Penn Township near Hughesville, PA	41.24072	-76.68978	6.01	3,160
Site 1.5	01552879	Sugar Run 1.5 near Hughesville, PA	41.23911	-76.69225	6.15	3,520
Site 1	01552880	Sugar Run near Hughesville, PA	41.23592	-76.69558	6.45	4,000
Piezo 1.5	411421076413201	LY 695	41.23911	-76.69225	6.15	3,500
Piezo 1	411409076414401	LY 694	41.23592	-76.69558	6.45	4,000
		November 12, 2013 samples				
Site 2	01552878	Sugar Run in Penn Township near Hughesville, PA	41.24072	-76.68978	6.01	3,160
Site 1.8	015528784	Sugar Run SIte 1.8 near Huhghesville, PA	41.24092	-76.69097	6.03	3,260
Site 1.6	015528786	Sugar Run Site 1.6 near Hughesville, PA	41.24028	-76.69122	6.05	3,350
Site 1.5	01552879	Sugar Run 1.5 near Hughesville, PA	41.23911	-76.69225	6.15	3,520
Site 1.4	015528793	Sugar Run Site 1.4 near Hughesville, PA	41.23814	-76.69303	6.18	3,650
Site 1.2	015528795	Sugar Run Site 1.2 near Hughesville, PA	41.23719	-76.69369	6.27	3,770
Site 1	01552880	Sugar Run near Hughesville, PA	41.23592	-76.69558	6.45	4,000
Piezo 1.5	411421076413201	LY 695	41.23925	-76.69558	6.15	3,500
Seep 1.5	411422076413201	LY SP10	41.23950	-76.69225	0.09	3,480

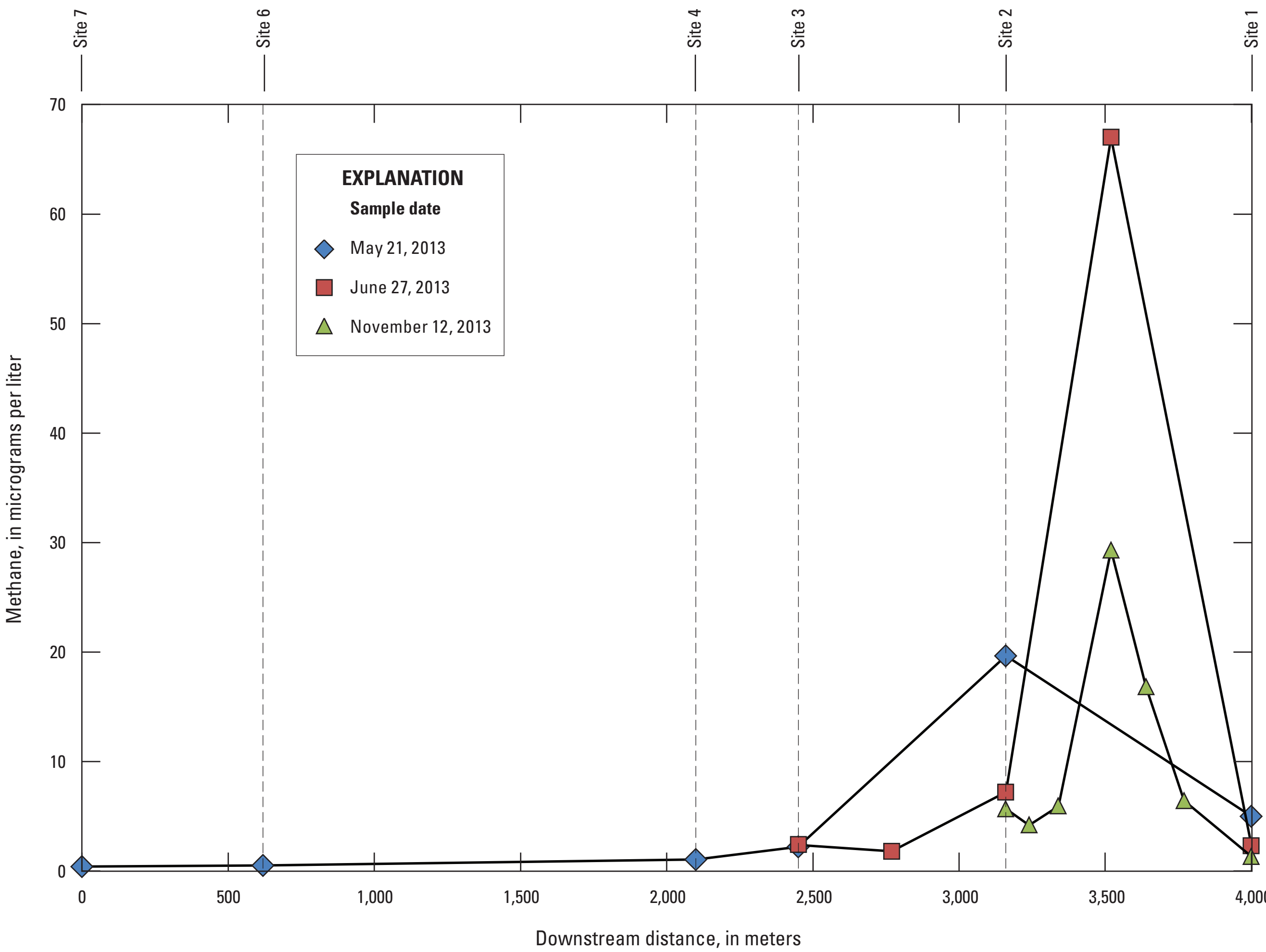


Figure 8. Dissolved methane concentrations in samples collected from Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013. Values less than the minimum reporting limit of 1.0 microgram per liter are estimated.

collected again at Piezo 1.5 and from a groundwater seep slightly upstream from the piezometer (Seep 1.5 at 3,480 m downstream; fig. 7*B*); groundwater methane concentrations of these samples were 4,600 µg/L and 2,300 µg/L, respectively.

Stream-discharge measurements in Sugar Run during base flow in May, June, and November 2013 are shown in figure 9. Measured stream discharge at the lower end of the study reach (Site 1) was about 0.10, 0.04, and 0.02 m^3/s, respectively. The measured-stream-discharge uncertainties range from about 3 to 7 percent (table 3). Although discharge increased by 0.05 m^3/s over the entire 4-km reach in May, 0.023 m^3/s of this gain came from tributary inflow, resulting in a total gain from groundwater inflow of about 0.028 m^3/s. During the June and November synoptic studies, there was less streamflow along the lower end of the study reach, and it was a slightly losing stream with net losses of 0.019 m^3/s from Site 3 to Site 1 in June and 0.017 m^3/s from Site 2 to Site 1 in November. Because no tributary inflow was observed, the small amount of stream gain (0.014 m^3/s between Site 2.5 and Site 2 in June; 0.011 m^3/s between Site 2 and Site 1.4 in November) was all attributed to groundwater inflow. The stream flows directly on bedrock at Site 3 and Site 2. Thus, it is possible that subsurface flow in the fluvial sediments was forced into the channel at those two locations, causing the measured flow to be greater at these locations. Downstream from Site 2, the streambed is on alluvium, so the gain measured between Sites 2 and 1.4 may have been from deeper regional groundwater discharge.

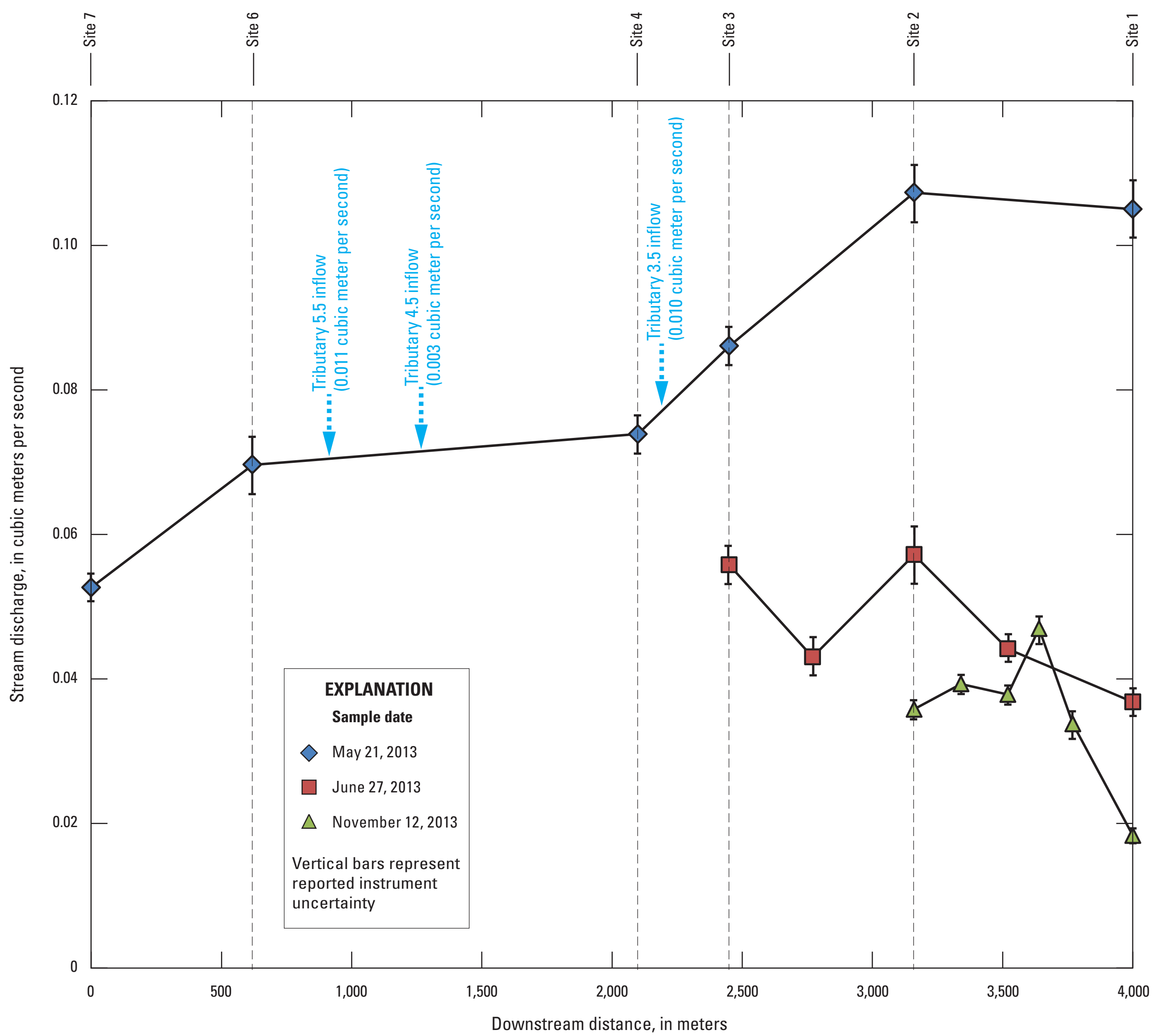


Figure 9. Flowmeter measurements of stream discharge and reported instrument uncertainty for Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013. No tributary inflow was observed during June or November.

Estimation of Methane Concentrations and Loads in Groundwater Discharge to Sugar Run

Stream methane concentrations along Sugar Run on May 21, June 27, and November 12, 2013, were simulated by the use of a one-dimensional (1-D) transport model. The purpose of the modeling was to estimate methane concentrations and loads in groundwater discharge to the stream. The data collected on each date were modeled separately.

Conditions on May 21, 2013

In order to simulate gas exchange with the 1-D methane transport model, a gas transfer velocity must be specified. The following empirical relation (Equation 1 in table 2 of Raymond and others, 2012) was used to derive a gas transfer velocity:

$$K_{600} = (VS)^{0.89} \times D^{0.54} \times 5037, \quad (2)$$

where

- K_{600} is gas transfer velocity in freshwater for a gas having a Schmidt number of 600 (carbon dioxide at 20 degrees Celsius (°C) or oxygen at 17.5 °C), in meters per day (m/d);
- V is stream velocity, in meters per second (m/s); and
- S is stream slope (unitless).

The uncertainty of the empirically derived gas transfer velocity estimated using this equation is assumed to be within ±50 percent. This is a conservative estimate based on the mean absolute difference between direct experimental results and empirically derived gas transfer velocity for six previously reported streams of about ±30 percent (table 4). Another empirical relation (Equation 7 in table 2 of Raymond and others, 2012) resulted in the same mean absolute difference of ±30 percent. On the basis of a mean stream depth of 0.15 m, a mean velocity of 0.151 m/s (from stream discharge measurements at the six sites along the study reach in May 2013; table 3) and a stream slope of 0.0426, the empirically derived K_{600} value was 20.3 m/d (table 4). In order to convert K_{600} to the gas transfer velocity for methane (K_{CH4}), the following equation was first used for determining the Schmidt number (SC_{CH4}) for methane (Wanninkhof and others, 1990; compiled in table 1 of Raymond and others, 2012):

$$SC_{CH4} = 1898 - 114.28(T) + 3.29(T^2) - 0.0391(T^3), \quad (3)$$

where

- T is temperature, in °C.

Assuming a stream temperature (T) based on the average of measurements from the six sampling sites (20.4 ±0.6 °C; 1σ), the resulting SC_{CH4} value was 604 ±17.5. This value was then used to convert K_{600} to K_{CH4} using a revised form of equation 2 in Jahne and others (1987),

$$K_{600} = K_{CH4}(600/SC_{CH4})^{-n}, \quad (4)$$

where

- n is the Schmidt number exponent, which can range from 0.5 to 1.0.

Following Wanninkhof and others (1990, equation 7) and Raymond and others (2012, equation 3), an n value of 0.5 was used. The resulting K_{CH4} value for Sugar Run on May 21, 2013, was 20.2 ±0.3 m/d. This is within the range of previously reported stream gas transfer velocities of 0.4 to 29 m/d (table 2 of Heilweil and others, 2013).

The Radin13 Excel-based 1-D stream transport model (Cook and others, 2003, 2006) was used to estimate groundwater methane concentrations and loads discharging into Sugar Run on May 21, 2013. The total length of the simulated stream reach was 4,000 m. Simulated stream width, depth, and groundwater inflow for each section of the study reach were based on stream discharge measurements (table 3). The groundwater inflow for each section was calculated by comparing discharge measurements at the upstream and downstream ends and accounting for any tributary inflow. Discharge measurements indicate that the section between Site 2 and Site 1 (3,160 to 4,000 m downstream) was a losing section (fig. 10), but initial model calibration indicated that some methane-laden groundwater inflow must be occurring upstream from Site 1 to match the stream methane of 5 µg/L at this location. Because the sparsely spaced discharge measurements only show the net gain or loss across an entire section, it is possible that any particular section is composed of gaining and losing subsections. Thus, the gain/loss profile shown in figure 10 was modified in the numerical model by adding a 50-m gaining section upstream from Site 1 with a groundwater inflow rate of 1.86 cubic meters per day per meter ($m^3/d/m$; the average of the other gaining reaches). To compensate for this additional gain of 93 m^3/d, the loss along the remainder of this section was increased by -93 m^3/d, resulting in a total simulated loss of -289 m^3/d.

During model calibration, the groundwater methane concentrations for the gaining reaches between Site 4 and Site 2 were varied from 8 to 3,200 µg/L, the range of concentrations in shallow groundwater samples collected in June and November, such that simulated stream methane concentrations matched measured concentrations (fig. 11). The minimum concentration of 8 µg/L was based on the measurement in groundwater from the piezometer at Site 1 (Piezo 1) in June 2013. The maximum concentration of 3,200 µg/L was based on the average of three measurements in groundwater collected near Site 1.5 (Piezo 1.5 in June and November 2013; Seep 1.5 in November 2013); methane in groundwater inflow from the

Table 4. Gas transfer velocity and other stream characteristics for Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013, and from other studies.

[1/d, per day; m/d, meters per day; %, percent; m, meters; m/s, meters per second; m^3/s, cubic meters per second; km, kilometers; °C, degrees Celsius; --, no data; CH_4, dissolved methane; ^4He, helium-4; ^{84}Kr, krypton-84; Kr, krypton; SF_6, sulfur hexaflouride; PA, Pennsylvania; UT, Utah; TN, Tennessee; NC, North Carolina]

Location	Gas	Measured gas-transfer velocity (m/d)	Measured gas-transfer coefficient (1/d)	[1]Measurement-derived K_{600} (m/d)	[2]Empirical method 1 K_{600} (m/d)	[2]Empirical method 1 K_{CH4} (m/d)	Difference between measurement-derived and empirical method 1 K_{600} (%)	[3]Empirical method 2 K_{600} (m/d)	Difference between measurement-derived and empirical method 2 K_{600} (%)
Sugar Run, PA, May 21, 2013	--	--	--	--	20.3	20.2	--	25.2	--
Sugar Run, PA, June 27, 2013	--	--	--	--	14.5	14.8	--	18.4	--
Sugar Run, PA, November 12, 2013	--	--	--	--	14.6	9.6	--	21.9	--
Nine-Mile Creek, UT	CH_4	4.5	37.5	5.0	5.8	--	-17.5	6.9	-38.9
Fischa, Austria	^4He	15.0	50.1	13.1	8.4	--	35.9	8.8	33.4
Fischa, Austria	^{84}Kr	7.0	23.3	9.0	8.4	--	6.4	8.8	2.6
Cockburn River, 0–10 km, Australia	SF_6	1.6	6.4	2.1	3.4	--	-57.4	3.8	-76.8
Cockburn River, 10–33 km, Australia	SF_6	1.6	2.1	2.1	7.1	--	-231.1	8.6	-301.8
West Fork Walker Branch, TN	SF_6	7.0	70.0	10.5	7.4	--	30.1	10.9	-3.3
West Bear Creek, NC, July 2012	Kr	1.6	5.3	1.4	0.8	--	42.0	1.2	14.2
						[4]Mean =	30		30

Location	Stream slope, *S* (unitless)	Stream depth, *D* (m)	Water temperature, *T* (°C)	Stream velocity, *V* (m/s)	Stream discharge, *Q* (m^3/s)	Reference
Sugar Run, PA, May 21, 2013	0.043	0.15	20.4	0.15	0.078	This study
Sugar Run, PA, June 27, 2013	0.043	0.10	21.2	0.14	0.047	This study
Sugar Run, PA, November 12, 2013	0.043	0.10	5.0	0.16	0.035	This study
Nine-Mile Creek, UT	0.007	0.12	16.5	0.26	0.12	Heilweil and others, 2013
Fischa, Austria	0.005	0.30	11.2	0.35	0.68	Stolp and others, 2010
Fischa, Austria	0.005	0.30	11.2	0.35	0.68	Stolp and others, 2010
Cockburn River, 0–10 km, Australia	0.003	0.25	17.6	0.24	0.41	Cook and others, 2006
Cockburn River, 10–33 km, Australia	0.003	0.75	17.6	0.29	0.58	Cook and others, 2006
West Fork Walker Branch, TN	0.038	0.10	13.5	0.07	0.02	Wanninkhof and others, 1990
West Bear Creek, NC, July 2012	0.003	0.30	24.9	0.05	0.095	D.K. Solomon, written commun., 2013

[1]Using a modified version of Jahne and others (1987) equation 2 and assuming $n = 0.5$.

[2]Using Equation 1 in Table 2 of Raymond and others (2012): $K_{600} = (VS)^{0.89} \times D^{0.54} \times 5037$.

[3]Using Equation 7 in Table 2 of Raymond and others (2012): $K_{600} = 4725 \times (VS)^{0.86} \times Q^{-0.14} \times D^{0.66}$.

[4]Mean of absolute values of differences and excluding Cockburn River 10–33 km, which is considered an outlier.

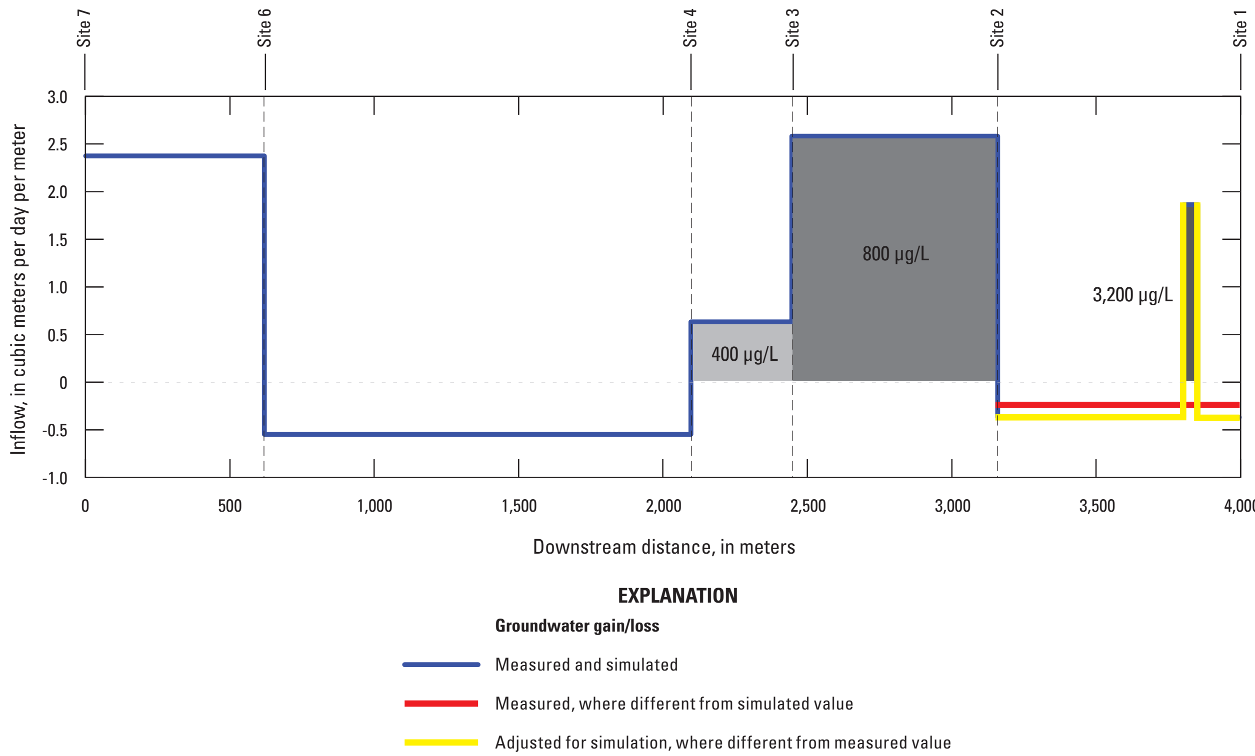


Figure 10. Measured and adjusted groundwater inflow to Sugar Run, Lycoming County, Pennsylvania, May 21, 2013, in relation to downstream distance. Corresponding groundwater methane concentrations, shown within the gray-fill areas, are based on a K_{CH4} value of 20.2 meters per day. (µg/L, micrograms per liter; K_{CH4}, gas transfer velocity for methane)

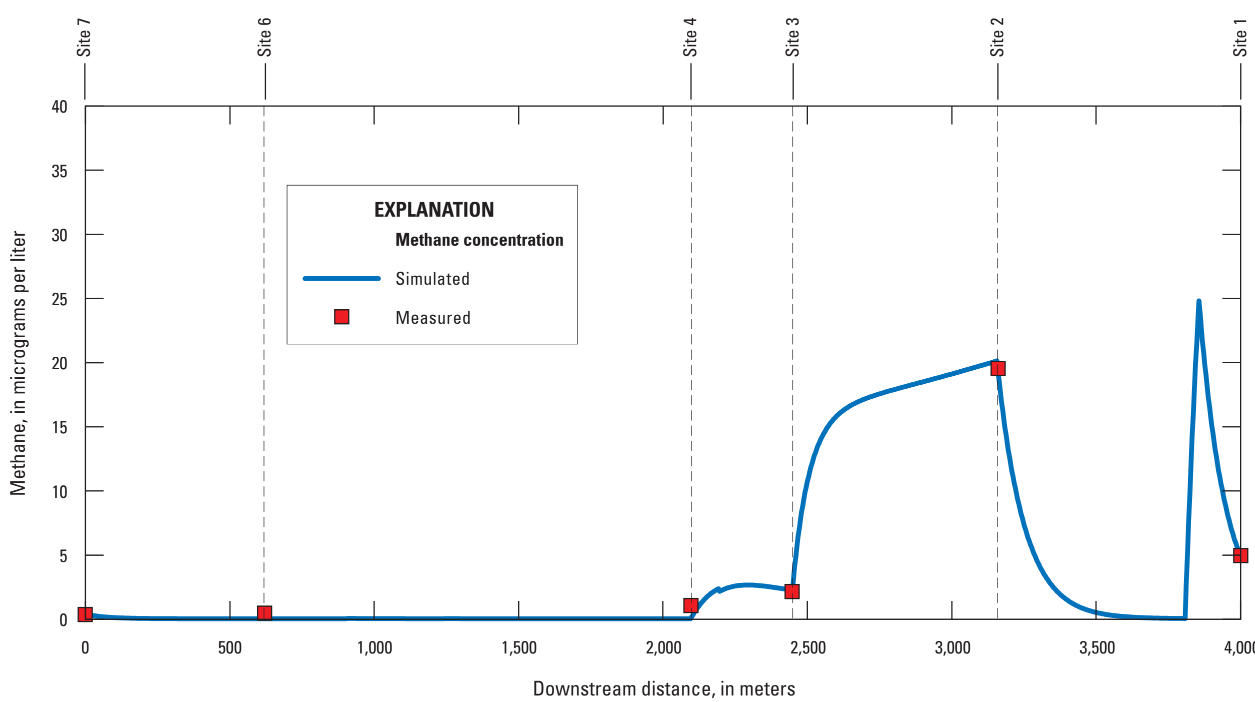


Figure 11. Measured and simulated methane concentrations in samples collected from Sugar Run, Lycoming County, Pennsylvania, May 21, 2013. Simulated concentrations were determined using K_{CH4} = 20.3 meters per day. (K_{CH4}, gas transfer velocity for methane)

additional simulated gaining reach upstream from Site 1 was held constant at this value. With this groundwater inflow methane concentration of 3,200 µg/L, the upstream location of this 50-m gaining reach was then varied between Site 2 and Site 1 in order to match the measured stream methane at Site 1. In the final calibrated model, the groundwater methane ranged from 400 to 3,200 µg/L, and the 50-m gaining reach is located 190 to 140 m upstream from Site 1 (3,810 to 3,860 m downstream). Figure 11 illustrates the possibility that a peak stream methane concentration of about 25 µg/L may have occurred upstream from Site 1 but may not have been observed because of the coarse sample spacing (800 m). Using the concentrations and groundwater inflow rates shown in figure 10, the methane load to the stream along the study reach was 1.9 kilograms per day (kg/d). This dissolved methane in Sugar Run was either consumed within the stream by oxidizing bacteria (methantropic activity) or released to the atmosphere by gas transfer (Guerin and others, 2006; Kemenes and others, 2007; Grinham and others, 2011; Moore and Knowles, 1990).

Sensitivity analyses of the May synoptic study model were conducted by varying the amount of groundwater inflow upstream from Site 1, the simulated gas transfer velocity (K_{CH4}), the methane concentration in groundwater inflow, and the location of the gaining reach upstream from Site 1. For the 50-m gaining subsection just upstream from Site 1, the effect of doubling the amount of groundwater inflow to 3.72 m^3/d/m was evaluated with the median gas transfer velocity of 20.6 m/d. In order to match measured stream methane at this location (5 µg/L), the methane load of groundwater inflow upstream from Site 1 had to be maintained by reducing groundwater methane by one-half (from 600 µg/L to 300 µg/L). This indicates that stream methane is sensitive to the total load (product of groundwater inflow and methane concentration) coming into the stream. Unless precise groundwater-inflow quantities and methane concentrations are known, the same methane load can be arrived at either with higher groundwater methane concentrations and lower inflow rates or with lower groundwater methane concentrations and higher inflow rates.

Because of the estimated ±50 percent uncertainty in the empirically derived K_{CH4} (20.2 m/d), a range of values was tested. Reducing K_{CH4} by 50 percent (10.1 m/d) while maintaining the same methane load (1.9 kg/d) resulted in simulated stream methane concentrations that were generally too high (fig. 12*A*) because the methane in the groundwater inflow dissipates less readily into the atmosphere. In order to match measured stream methane using a lower K_{CH4}, the methane concentration of groundwater inflow was reduced to the minimum measured shallow groundwater methane concentration (2,300 µg/L), and the 50-m gaining reach was moved upstream to 290 to 240 m upstream from Site 1 (3,710 to 3,760 m downstream), resulting in a total methane load to the stream in the study reach of 1.0 kg/d. In contrast, to match measured stream methane using a higher K_{CH4} (30.3 m/d), the groundwater methane was increased to the maximum measured methane in shallow groundwater (4,600 µg/L), and the 50-m reach was moved downstream to 150 to 100 m upstream from Site 1 (3,850 to 3,900 m downstream), resulting in a total methane load of 2.6 kg/d. In summary, varying K_{CH4}, groundwater methane, and the location of the gaining reach upstream from Site 1 produced a range in total methane load for the May synoptic sampling of 1.0 to 2.6 kg/d.

Conditions on June 27, 2013

Similar to the May 21, 2013, calculations, the K_{600} value for the Sugar Run stream conditions on June 27, 2013, was estimated using equation 2. Based on the stream slope of 0.0426 and the average depth and stream velocity (D = 0.095 m, V = 0.137 m/s) from discharge measurements at five sites (table 3), the resulting empirically derived K_{600} value was 14.5 m/d (table 4). With a mean stream temperature (T) based on the average of measurements at these five sampling sites (21.2 °C ±1.0 °C; 1σ), equation 3 was used to convert the K_{600} value to K_{CH4} = 14.8 ±0.3 m/d. This conforms to expectations of decreased gas transfer at lower flow regimes, primarily because there is less turbulence at lower velocities. Although the accompanying decrease in stream depth is an offsetting factor (gas transfer occurs more readily in shallower streams), this parameter is of less importance than stream velocity.

Initial model calibration indicated that the elevated stream methane of 7.2 µg/L at Site 2 (3,160 m downstream) and 67 µg/L at Site 1.5 (3,520 m downstream) was caused by methane-laden groundwater inflow entering upstream from both locations. Discharge measurements indicate that the section from Site 2.5 to Site 2 (2,770 to 3,160 m downstream) was a gaining section, whereas the section from Site 2 to Site 1.5 (3,160 to 3,520 m downstream) was a losing section (fig. 13). However, because these stream discharge measurements were not closely spaced (only about every 400 m), there is the possibility that some groundwater inflow was occurring along parts of this losing section. Therefore, the gain/loss profile was modified in the numerical model by adding a 50-m gaining section upstream from Site 1.5 using the same inflow rate (3.14 m^3/d/m) as the gaining section between Site 2.5 and Site 2, resulting in a total inflow of 157 m^3/d. During model calibration, the upstream location of this 50-m gaining reach was varied between Site 2 and Site 1.5 while maintaining a groundwater inflow methane concentration of 3,200 µg/L in order to match the measured stream methane at Site 1.5. Using the empirically derived K_{CH4} = 14.8 m/d with the gaining reach located 70 to 20 m upstream from Site 1.5 (3,450 to 3,500 m downstream) resulted in the best match to the measured stream methane. This indicates that the maximum stream methane may have been about 90 µg/L just upstream from Site 1.5 (fig. 14). The groundwater inflow along this 50-m gaining section was offset by an additional 157 m^3/d of loss to groundwater in the upper and lower parts of this section (3,160 to 3,450 and 3,500 to 3,520 m downstream, respectively) to maintain the same total net loss of 1,640 m^3/d between Site 2 and Site 1.5. Simulated stream methane at Site 1 (4,000 m

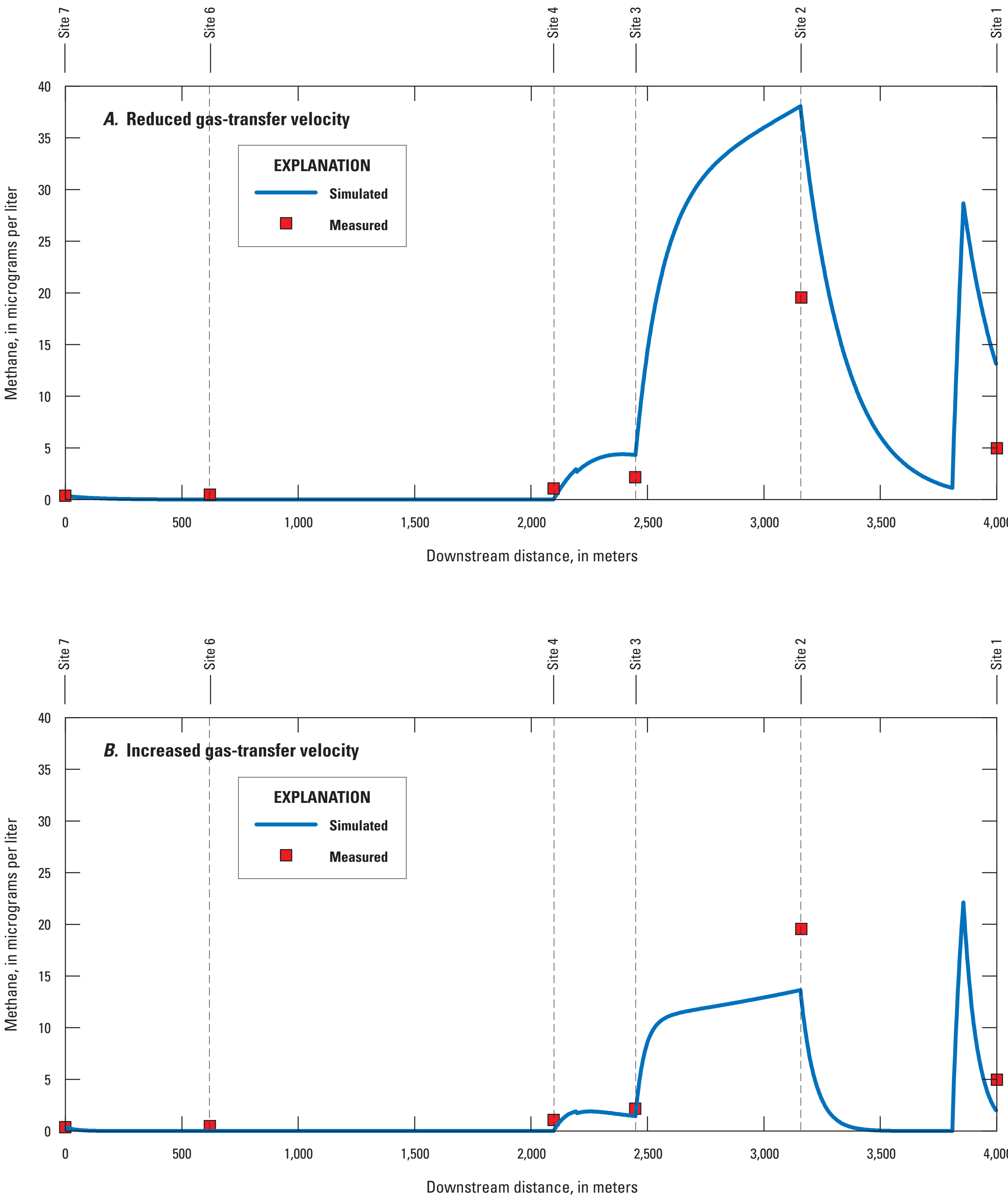


Figure 12. Measured and simulated methane concentrations in samples collected from Sugar Run, Lycoming County, Pennsylvania, May 21, 2013. Simulated concentrations were determined using *A*, reduced gas transfer velocity K_{CH4} = 10.1 meters per day and *B*, increased gas transfer velocity K_{CH4} = 30.3 meters per day.

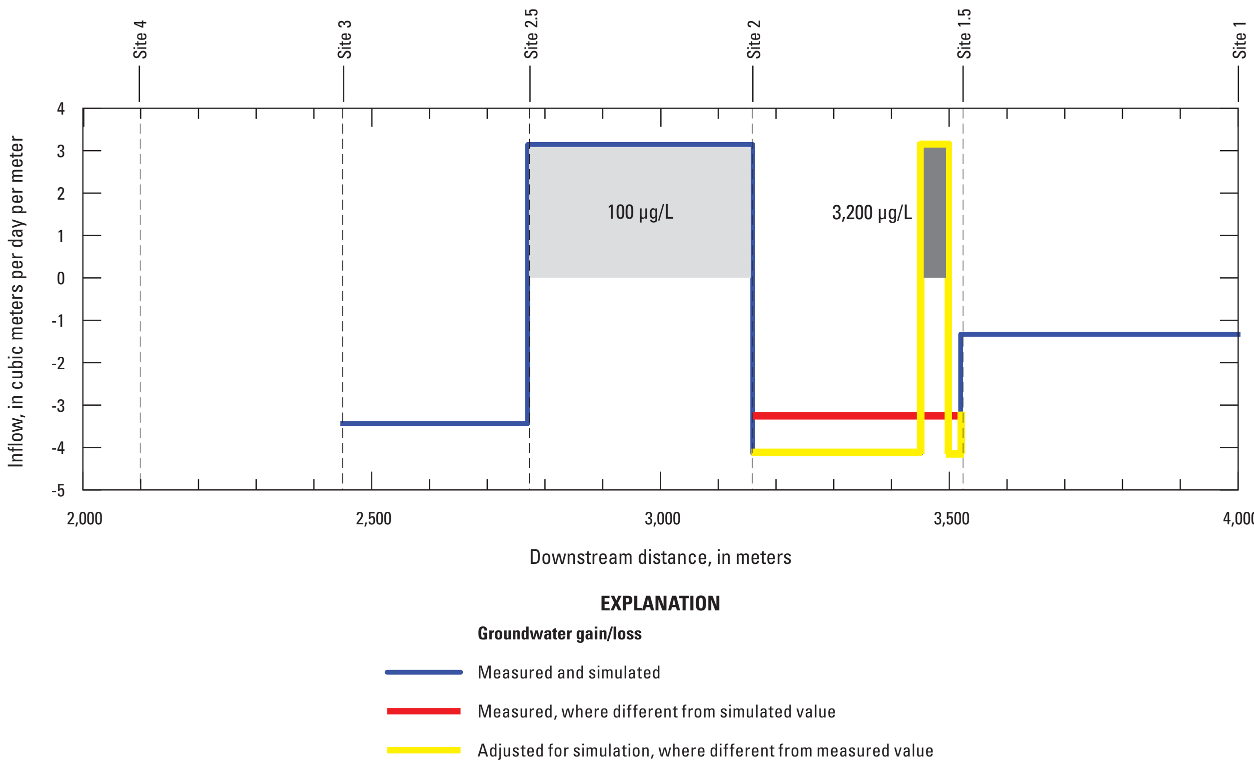


Figure 13. Measured and adjusted groundwater inflow to Sugar Run, Lycoming County, Pennsylvania, June 27, 2013, in relation to downstream distance. Corresponding groundwater methane concentrations, shown within the gray-fill areas, are based on a K_{CH4} value of 14.8 meters per day and a 50-meter gaining reach upstream from Site 1.5 (µg/L, micrograms per liter).

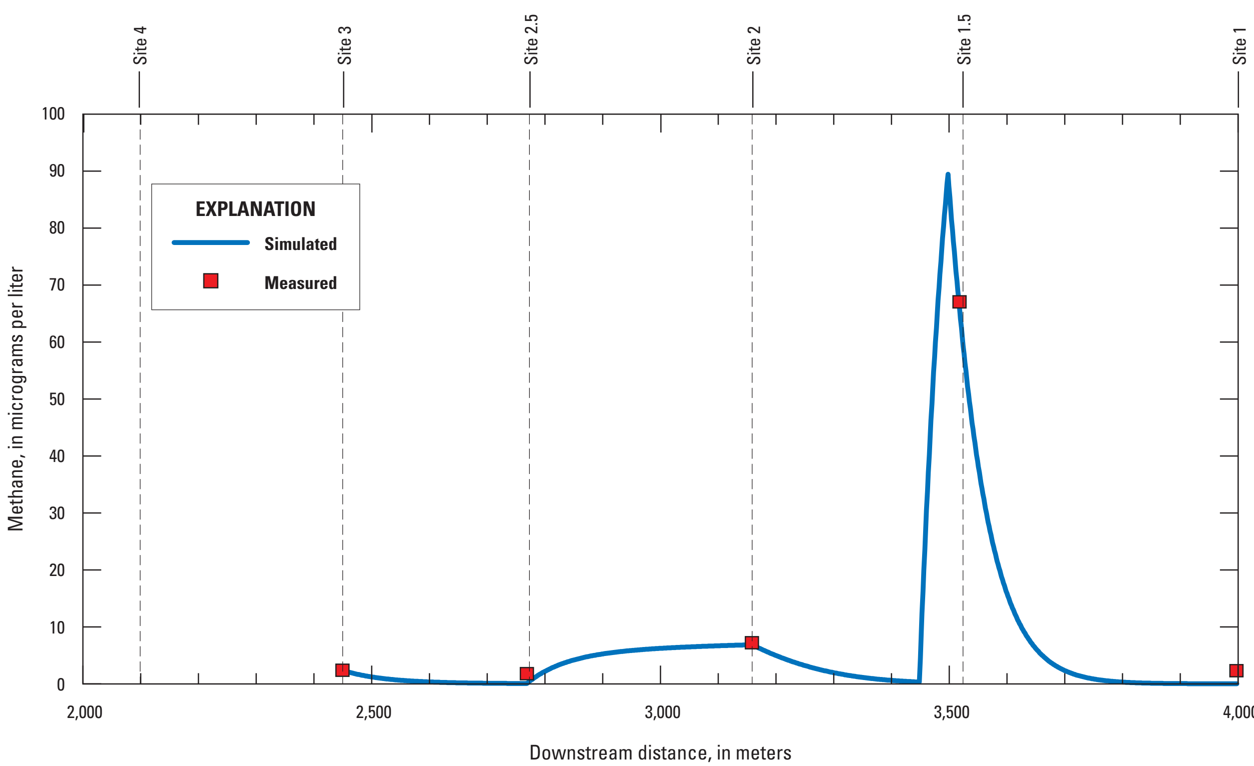


Figure 14. Measured and simulated methane concentrations in samples collected from Sugar Run, Lycoming County, Pennsylvania, June 27, 2013. Simulated concentrations were determined using K_{CH4} = 14.8 meters per day and a 50-meter gaining reach 150 to 100 meters upstream from Site 1.5.

downstream), however, was less than measured stream methane (2.3 µg/L) because no groundwater inflow was simulated upstream from this location. There may have been low levels of methane input along this and other sections of the stream (either from small amounts of methane-laden groundwater or from other sources such as in-stream biological production) that were not simulated in this study. The estimated total methane load to the stream on June 27, calculated by multiplying the groundwater inflow rates along these gaining sections by their respective groundwater methane concentrations, was 0.62 kg/d.

Sensitivity analyses of the June synoptic study model were conducted by varying length and location of the gaining reach upstream from Site 1.5, K_{CH4}, and groundwater methane concentrations. As an alternative to the 50-m gaining reach upstream from Site 1.5, two other lengths were simulated: 10 m and 100 m. The amount of groundwater inflow along both of these alternative reach lengths was kept constant at 157 m^3/d, resulting in groundwater inflow rates of 15.7 and 1.57 m^3/d/m for the 10- and 100-m reaches, respectively. As with the above simulation of the June synoptic study (K_{CH4} = 14.8 m/d; 50-m long gaining reach upstream from Site 1.5), groundwater methane was held constant at the average of the three measured values (3,200 µg/L) for the two alternative gaining reach lengths.

Simulating the shorter (10-m) gaining reach and K_{CH4} = 14.8 m/d, a reasonable model fit could be achieved only if this reach was located 50 to 40 m upstream from Site 1.5 (3,470 to 3,480 m downstream) and groundwater methane of the upper gaining reach (2,770 to 3,160 m) was increased to 110 µg/L, causing an increase in the total methane load to 0.64 kg/d. Alternative simulations varying K_{CH4} for this shorter reach (±50% of the empirically derived value of 14.8 m/d) also were conducted. If K_{CH4} is decreased to 7.4 m/d, the 10-m gaining reach can be moved to 100 to 90 m upstream from Site 1.5 (3,420 to 3,410 m downstream) to match the measured stream methane at Site 1.5, but groundwater methane of the upper gaining reach (2,770 to 3,160 m) had to be decreased from 110 to 70 µg/L, reducing the total methane load to 0.59 kg/d. When K_{CH4} was increased to 22.1 m/d, the 10-m gaining reach was moved 30 to 20 m upstream from Site 1.5 (3,490 to 3,500 m downstream) to match measured stream methane at Site 1.5, but groundwater methane of the upper gaining reach had to be increased from 110 to 150 µg/L, increasing the total methane load to 0.69 kg/d.

Simulating a longer (100-m) gaining reach and K_{CH4} = 14.8 m/d, a reasonable model fit could be achieved only if this reach was located 100 to 0 m upstream from Site 1.5 (3,420 to 3,520 m downstream) and the groundwater methane for the upper gaining reach (2,770 to 3,160 m) was held at 110 µg/L; this resulted in a total simulated methane load of 0.64 kg/d. Alternative simulations were also conducted by varying K_{CH4} (±50% of the empirically derived value of 14.8 m/d) for this longer reach. When K_{CH4} was decreased to 7.4 m/d, the 100-m gaining reach was moved to 150 to 50 m upstream from Site 1.5 (3,370 to 3,470 m downstream) to match the measured stream methane at Site 1.5; because groundwater methane of the upper gaining reach (2,770 to 3,160 m) had to be decreased from 110 to 70 µg/L, the total simulated methane load was reduced to 0.59 kg/d. No reasonable model fit could be achieved using K_{CH4} = 22.1 m/d with a 100-m gaining reach upstream from Site 1.5.

Keeping the length of the gaining reach upstream from Site 1.5 constant at 50 m, K_{CH4} was decreased to 7.4 m/d and increased to 22.1 m/d. The results of varying K_{CH4} were similar to those for the May synoptic study; the measured stream methane could not be matched (particularly the value of 67 µg/L at Site 1.5) using either the smaller or larger K_{CH4} values unless the amount and location of groundwater inflow was modified. In order to match measured stream methane using the smaller K_{CH4} value, groundwater methane was reduced to the minimum measured methane concentration in shallow groundwater (2,300 µg/L), and the 50-m gaining reach was moved upstream to 70 to 20 m upstream from Site 1.5 (3,450 to 3,500 m downstream), resulting in a total methane load to the stream of 0.4 kg/d. To match measured stream methane using the larger K_{CH4} value, the groundwater methane was increased to the maximum methane concentration measured in shallow groundwater (2,300 µg/L), and the 50-m gaining reach was moved upstream to 80 to 30 m upstream from Site 1.5 (to 3,480 to 3,530 m downstream); this resulted in a total methane load to the stream of 1.0 kg/d. In summary, varying both the length of the gaining reach upstream from Site 1.5 and K_{CH4} produced a range in estimated total methane load for the June synoptic study of 0.4 to 1.0 m/d.

Conditions on November 12, 2013

Similar to the May and June 2013 calculations, the K_{600} value for the Sugar Run stream conditions on November 12, 2013, was estimated using equation 2, based on the stream slope of 0.0426 and the average of discharge measurements from six stations from Site 1 to Site 2 (D = 0.099 m, V = 0.155 m/s), resulting in an empirically derived K_{600} value of 14.6 m/d (table 4). With a mean stream temperature (T) based on the average of measurements from the six sampling sites (5.0 ±0.1 °C; 1σ), equation 3 was used to convert the K_{600} value to a K_{CH4} value for Sugar Run on June 27, 2013, of 9.57 ±0.03 m/d. Although the streamflow characteristics were similar during May and June, the large decrease in K_{CH4} in November was mostly due to the much cooler water in November because of methane's increased solubility at cooler temperatures.

Similar to the June synoptic study, in order to match the November measured peak stream methane of 28 µg/L at Site 1.5, it was necessary to add a short gaining subsection upstream from Site 1.5 (fig. 15). The gain/loss profile was modified in the numerical model by adding a 50-m gaining section using a mean weighted inflow rate of 3.3 m^3/d/m (based on the two gaining sections—Site 2 to Site 1.6 and Site 1.5 to Site 1.4), resulting in a total inflow of 165 m^3/d. A good match between measured and simulated stream methane

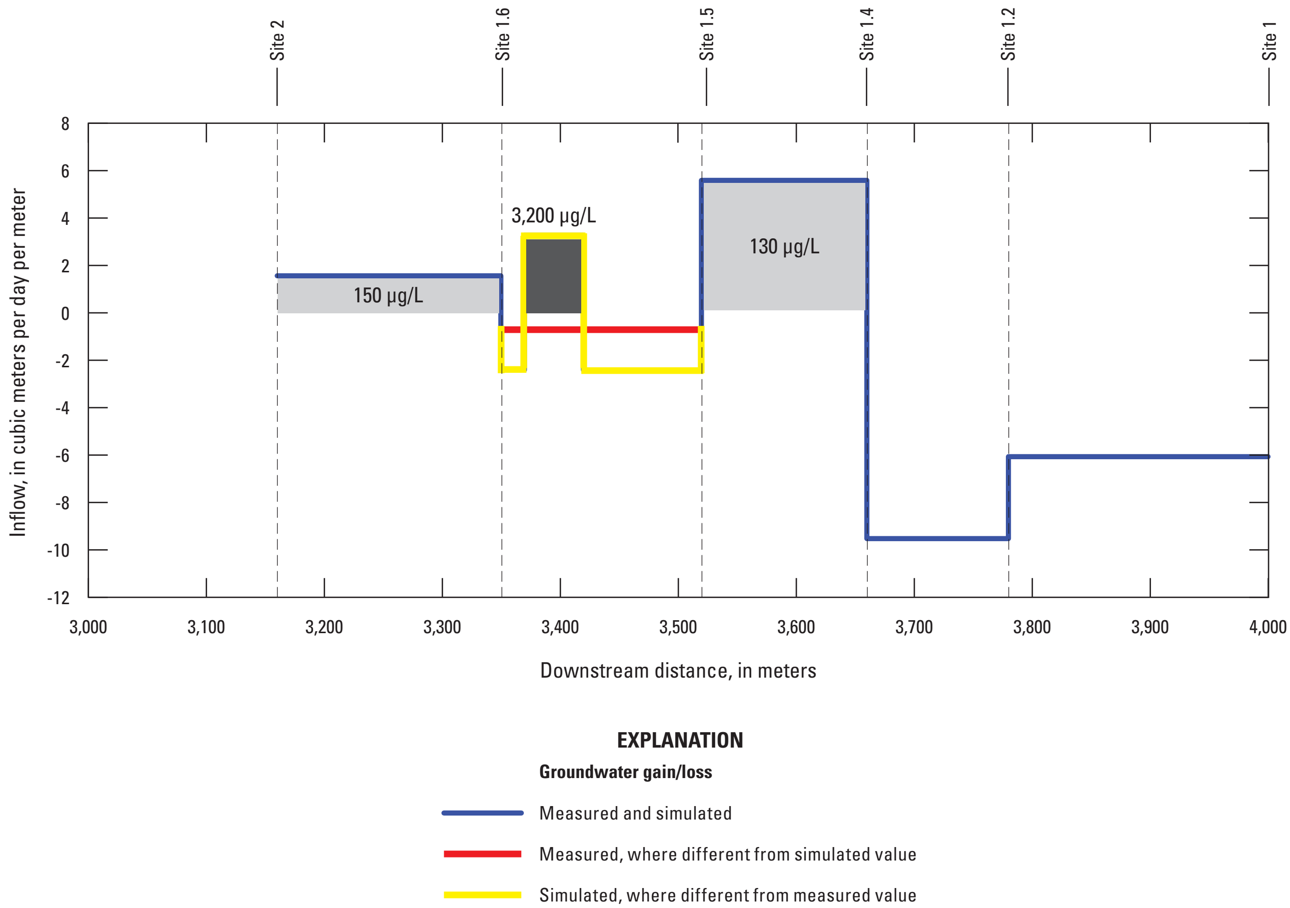


Figure 15. Measured and adjusted groundwater inflow to Sugar Run, Lycoming County, Pennsylvania, November 12, 2013, in relation to downstream distance. Corresponding methane concentrations, shown within the gray-fill areas, are based on a K_{CH4} value of 14.4 meters per day and a 50-meter gaining reach upstream from Site 1.5. (µg/L, micrograms per liter; K_{CH4}, gas transfer velocity for methane)

could not be achieved using K_{CH4} = 9.6 m/d while maintaining the groundwater methane concentration of 3,200 µg/L. Using K_{CH4} = 14.4 m/d and a 50-m gaining reach located 150 to 100 m upstream from Site 1.5 (3,370 to 3,420 m downstream), however, provided a good match to the measured stream methane of 28 µg/L (fig. 16). This location was just upstream of observed groundwater seeps above Site 1.5. This additional gain of 165 m^3/d was offset by increasing the loss in the other parts of the section between Site 1.6 and Site 1.5 by the same amount (increasing the loss from -124 m^3/d to -289 m^3/d by assigning a groundwater inflow rate of -2.4 m^3/d/m). These results indicated that the actual stream methane was likely much higher (up to 110 µg/L) between Site 1.6 and Site 1.5. Estimated groundwater methane in inflow to the upper part of the reach (3,160 to 3,350 m downstream) and lower part of the reach (3,520 to 3,660 m downstream) were 150 and 130 µg/L, respectively, resulting in an estimated total methane load of 0.67 kg/d.

Sensitivity analyses of the November synoptic study model were conducted by varying length and location of the gaining reach upstream from Site 1.5, K_{CH4}, and groundwater methane. As an alternative to the 50-m gaining reach upstream from Site 1.5, two other lengths were simulated: 10 m and 100 m. The amount of groundwater inflow along these alternative reaches was kept constant at 165 m^3/d, resulting in groundwater inflow rates of 16.5 and 1.65 m^3/d/m for the 10- and 100-m reaches, respectively. As with the above simulation of the November synoptic sampling (K_{CH4} = 14.4 m/d; 50-m long gaining reach 150 to 100 m upstream from Site 1.5), groundwater methane was held constant at 3,200 µg/L for the shorter and longer gaining reaches upstream from Site 1.5.

By reducing the length of the gaining reach upstream from Site 1.5 from 50 m to 10 m, and using a K_{CH4} value of 9.6 m/d, the simulated concentrations were similar to measured stream methane when the gaining reach was 170 to 160 m upstream from Site 1.5 (3,420 to 3,410 m downstream). This is in contrast to the findings (above) showing that measured stream methane could not be matched by simulating a 50-m gaining reach using K_{CH4} = 9.6 m/d. For this alternative simulation, groundwater methane in the upper and lower gaining reaches was decreased to 100 and 20 µg/L, respectively, reducing the total methane load to 0.57 kg/d. Using the

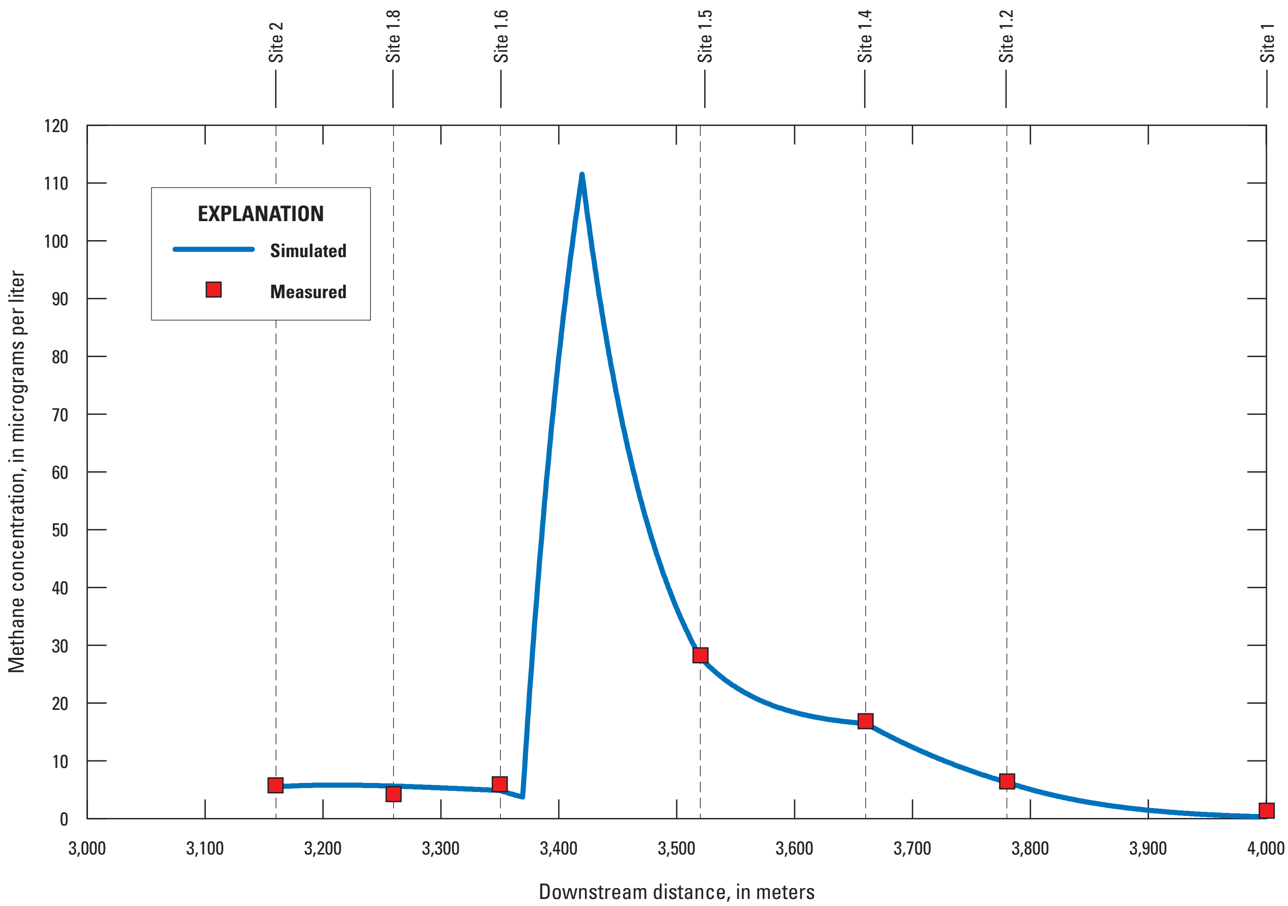


Figure 16. Measured and simulated methane concentrations in samples collected from Sugar Run, Lycoming County, Pennsylvania, November 12, 2013. Simulated concentrations were determined using K_{CH4} = 14.4 meters per day and a 50-meter gaining reach 150 to 100 meters upstream from Site 1.5. (K_{CH4}, gas transfer velocity for methane)

maximum K_{CH4} value of 14.4 m/d, a reasonable model fit was achieved by locating the 10-m gaining reach 130 to 120 m upstream from Site 1.5 (3,390 m to 3,400 m downstream). This simulation used the same groundwater methane for the upper (3,160 to 3,350 m) and lower (3,520 to 3,660 m) gaining reaches of 150 and 20 µg/L, respectively, resulting in the same total simulated methane load of 0.67 kg/d. No reasonable model fit could be attained for the shorter (10-m) gaining reach when the K_{CH4} was decreased to 4.8 m/d.

By simulating a longer (100-m) gaining reach upstream from Site 1.5 with K_{CH4} = 14.4 m/d, a reasonable model fit was achieved by moving this reach to 170 to 70 m upstream from Site 1.5 (3,350 to 3,450 m downstream). The groundwater methane of the upper gaining reach (150 µg/L) was the same as that for the 50-m gaining reach (3,520 to 3,660 m), but the groundwater methane concentration for the lower gaining reach was reduced to 100 µg/L, resulting in a total methane load of 0.65 kg/d. A reasonable match to stream methane could not be achieved when K_{CH4} was decreased to less than 14.4 m/d with a 100-m gaining reach upstream from Site 1.5.

While keeping the length of gaining reach upstream from Site 1.5 constant at 50 m, K_{CH4} was decreased to 4.8 m/d and increased to 14.4 m/d, groundwater methane was varied within the range of measured values (2,300 to 4,600 µg/L), and the location of the 50-m gaining reach upstream from Site 1.5 was varied. No match to measured stream methane concentrations could be obtained using the smaller K_{CH4} value of 4.8 m/d. The empirically derived value of 9.6 m/d, however, produced a good fit to measured stream methane by reducing groundwater methane to the minimum concentration measured in shallow groundwater (2,300 µg/L at Seep 1.5 on November 12, 2013) and by moving the 50-m gaining reach to 170 to 120 m upstream from Site 1.5 (3,350 to 3,400 m downstream); these values resulted in a total methane load to the stream of 0.5 kg/d. To match measured stream methane using the larger K_{CH4} value of 14.4 m/d, groundwater methane was increased to the maximum concentration measured in shallow groundwater (4,600 µg/L at Piezo 1.5 on November 12, 2013), and the 50-m gaining reach was moved 160 to 110 m upstream from Site 1.5 (3,360 to 3,410 m downstream); these values resulted in a total methane load of 0.9 kg/d. In summary, varying K_{CH4}, along with the length and location of the gaining reach upstream from Site 1.5, produced a range in total estimated methane load for the November synoptic study of 0.5 to 0.9 m/d.

Estimating Methane Loads in Groundwater Discharge

This study shows the utility of both reconnaissance stream methane sampling and detailed synoptic studies for locating and estimating methane loads in groundwater discharge. For the May 2013 synoptic study of Sugar Run, the higher streamflow and coarser sample spacing of about 800 m resulted in a large value for, and uncertainty in, the estimated total methane load (1.8 ±0.8 kg/d; fig. 17). Because most (about 84 percent) of the methane load for the May synoptic study entered along the lower reach between Site 3 and Site 1, the June and November synoptic studies focused on this downstream area. Simulation results from the June synoptic study indicate that by increasing sample spacing to about 400 m, along with the lower base-flow conditions, total methane load and uncertainty were reduced to 0.7 ±0.3 kg/d. Simulation of the November synoptic study with an even finer spacing (about every 200 m) during even lower base-flow conditions resulted in the same estimated total methane load of 0.7 kg/d as June, but uncertainty decreased to ±0.2 kg/d. Assuming the methane concentration in groundwater inflow to Sugar Run was constant, the larger methane load in May indicated that the amount of base flow (groundwater inflow) varied seasonally with stream discharge. Such variability of base flow has been reported in several other hydrograph separation studies (Kennedy and others, 1986; McDonnell and others, 1990; Risser and others, 2009; Sanford and others, 2012, appendix 1).

Optimal sample spacing for capturing stream methane peaks (and reducing uncertainty in estimated methane load) depends on the gas transfer velocity and amount of groundwater inflow relative to stream discharge (Stolp and others, 2010). Finer resolution sampling is necessary for streams with high gas transfer velocity and small rates of groundwater inflow. The simulations in this study showed that even as sample spacing was refined (from 800 m during May to 400 m during June to 200 m during November), the peak in stream methane immediately downstream from groundwater inflow sources may not have been entirely captured. Closer spacing of sampling sites (perhaps every 100 m) for streams such as Sugar Run would further reduce uncertainty in the estimated methane concentration and total methane load in groundwater inflow. A minimum downstream distance from the location of groundwater inflow, however, is needed to ensure that methane-laden groundwater entering the stream is well-mixed at the sampling location. This minimum distance would vary with stream conditions and characteristics.

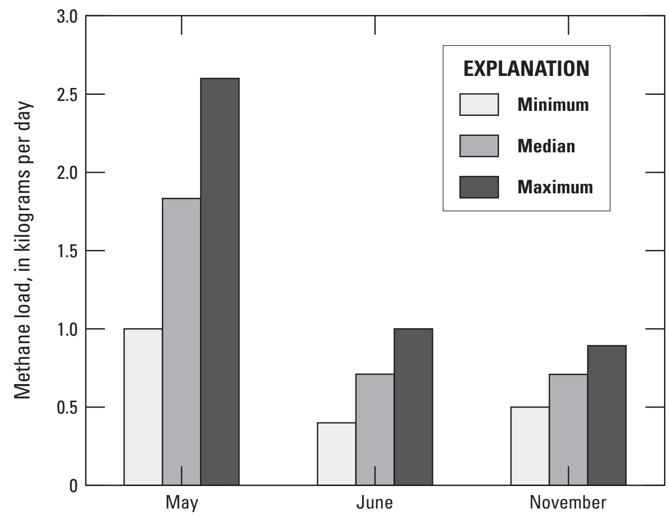


Figure 17. Minimum, median, and maximum estimated methane loads in groundwater discharge to Sugar Run, Lycoming County, Pennsylvania, during the May, June, and November 2013 synoptic sampling studies.

Evaluation of Uncertainty

Uncertainty in the estimation of methane concentration in groundwater (C_{gw} of equation 1) is governed by uncertainty in stream methane concentration (C), gas transfer velocity (K_{CH4}), and groundwater inflow rate (I). For stream methane concentration, the laboratory analytical precision was estimated to be ±0.5 µg/L. Replicate values, which are listed in tables 1 and 3, incorporate laboratory analytical precision and field variability caused by in-situ variability and sampling procedures. The differences in replicate values were generally less than 20 percent for methane concentrations of less than 3 µg/L and less than 10 percent for concentrations greater than 3 µg/L. Reaches with higher stream methane concentrations generally had higher groundwater methane loads; this indicates that analytical precision and sampling variability of the methane concentration did not introduce large uncertainty into the estimated methane load from groundwater.

For gas transfer velocity, sensitivity analysis indicates that the use of empirical estimates introduces much uncertainty, particularly when the location of groundwater inflow is poorly constrained, as was the case with the Sugar Run synoptic study in May 2013. Introduced gas tracers are one possible means for reducing uncertainty in gas transfer velocity (Cook and others, 2006; Stolp and others, 2010; Heilweil and others, 2013). Much closer sample spacing can also constrain the range of possible values, as shown by the reduction in the range of estimated K_{CH4} with increased sample spacing during the consecutive synoptic studies of Sugar Run: the range of empirically derived gas transfer velocities declined from May (10.1 to 30.3 m/d) to June (9.6 to 22.0 m/d) to November (4.8 to 14.4 m/d). In addition to the temporal variability in gas transfer velocity with changing stream conditions, it is recognized that gas transfer velocity is likely not constant for an entire stream reach but will vary on the basis of stream velocity, water depth, water temperature, wind shear, and turbulence. Also, the gas transfer velocity used in the 1-D transport modeling was an apparent value that included any possible gas loss caused by microbial degradation. The fraction of overall gas loss caused by this mechanism could not be evaluated within the scope of this study.

For groundwater inflow rate, an important limitation of all three Sugar Run synoptic studies was the uncertainty associated with stream discharge. The discharge measurements generally had an instrument uncertainty of about 4 to 7 percent (table 3). Replicate sample measurements at Site 1 on November 12 were 0.66 and 0.76 ft^3/s. This indicated an overall error in the stream discharge measurement (instrument precision and sampling error) of about 15 percent. Because relative uncertainty is additive when calculating the product of two numbers, combining the ±15 percent uncertainty in groundwater inflow (derived from stream discharge measurements) with the ±50 percent uncertainty in the methane concentration in groundwater inflow (2,300 to 4,600 µg/L) indicated an overall uncertainty in methane load of ±65 percent, which was similar to the range in estimated loads for the three synoptic studies. The uncertainty associated with inflows could have been further minimized by using an average of multiple flow measurements at each site. Estimates of groundwater inflow could be further refined with conservative-ion stream injection and use of the stream-dilution method (Kilpatrick and Cobb, 1985) to provide more precise inflow quantities.

In summary, gas transfer velocity and the amount and location of groundwater inflow were the largest sources of uncertainty associated with methane loads calculated for Sugar Run. Such uncertainty could be reduced by closer sampling site spacing, a more-accurate determination of the amount and location of groundwater inflow using the conservative-ion dilution method, and in-situ gas injection experiments to quantify gas transfer velocity.

Limitations

The relations between stream methane and geology, percent forested land, and shale-gas well-pad density shown in figures 4 through 6 were only an initial attempt to assess potential causes for higher stream methane from the limited reconnaissance dataset. If additional stream methane data are collected, a more robust multi-variate approach (such as principal component analysis and regression methods for censored data) could be used to more fully investigate these relations.

Although the stream methane monitoring approach was successfully used in this study to identify a stream receiving methane from groundwater inflow and estimate methane loads, further geochemical characterization is needed to determine the source of methane in groundwater. Furthermore, without baseline stream methane measured prior to unconventional shale gas extraction in the watershed, it cannot be determined whether these methane fluxes were related to shale-gas development activities. Ideally, this type of stream monitoring study would begin prior to shale-gas development in order to establish seasonal and annual variability in baseline groundwater quality prior to development.

It is important to recognize that the stream methane monitoring approach does not provide information on spatial distribution of methane concentrations in groundwater within the aquifer, which may be highly variable in fractured-rock aquifers such as those in northeastern Pennsylvania. The method provides a flow-weighted integrated estimate of methane concentrations in groundwater discharging to a stream. It cannot be used to predict whether methane migration, either along natural pathways or induced by shale-gas development, may affect a particular groundwater well.

Considerations for Future Work

On the basis of these preliminary results at Sugar Run, future work could be conducted to (1) identify sources of the groundwater methane (thermogenic versus biogenic) with geochemical fingerprinting, (2) more accurately quantify gas transfer velocity and potential loss resulting from microbial activity with gas injections into the stream, and (3) more accurately quantify the amount and locations of groundwater discharge with conservative-ion stream injections. These latter two activities would enable more precise determination of methane concentrations and loads in groundwater discharging to the stream. Additional work could also include continued stream monitoring to evaluate seasonal and year-to-year temporal changes in methane concentrations and loads in groundwater discharge. Such long-term stream methane monitoring may be useful for evaluating trends in, and potential effects of natural gas development on groundwater quality.

Summary

This report describes stream methane monitoring in northeastern Pennsylvania, an area undergoing extensive shale-gas development in the Marcellus Formation. A preliminary reconnaissance of methane in 15 small streams showed that four streams had methane concentrations greater than or equal to 5 micrograms per liter (µg/L; Sugar Run, Little Muncy Creek, Parks Creek, and Meshoppen Creek). A stream monitoring and modeling approach was used to estimate methane concentrations and loads in groundwater discharge to Sugar Run. Three synoptic sampling studies were conducted (May 21, June 27, and November 12, 2013) involving measurements of stream discharge, stream methane, and groundwater methane in samples collected from in-stream piezometers and a seep. The results show seasonal variability in stream discharge, groundwater inflow, and streamwater methane concentrations. Streamflow and groundwater discharge were higher in May than during the synoptic studies in June and November. Measured stream methane in May (maximum

19.6 µg/L) was less than in June (maximum 67 µg/L) and November (maximum 29 µg/L). The lower stream methane identified in May could have been caused by dilution of groundwater methane by higher streamflow conditions or by the larger sample spacing (compared with June and November), which would have reduced the ability to accurately identify peak stream-methane concentrations.

A one-dimensional (1-D) stream-methane transport model was used to estimate the methane concentration and load in groundwater discharging to Sugar Run during each of the three synoptic studies. Because no gas injection was conducted to directly measure gas transfer velocity, a range of values was estimated empirically on the basis of the stream conditions during each synoptic study. The rates of groundwater inflow were determined for subsections of each study reach by comparing upstream/downstream flowmeter discharge measurements (and accounting for any tributary surface-water flow). Estimated methane concentrations in groundwater were constrained by measured concentrations in samples from piezometers and a seep (8 to 4,600 µg/L). The modeling results indicate that estimated groundwater methane concentrations are sensitive to the stream methane concentrations, the amount of groundwater inflow, the length and upstream location of gaining reaches, and the gas transfer velocity. Gas transfer velocities, based on empirical relations, that provided reasonable fits to observed data were 10.1 to 30.3 meters per day (m/d) for the May synoptic study, 7.4 to 22.1 m/d for the June synoptic study, and 9.6 to 14.4 m/d for the November synoptic study. The estimated total methane load discharging to Sugar Run during the May, June, and November 2013 synoptic studies was 1.8 ±0.8 kilograms per day (kg/d), 0.7 ±0.3 kg/d, and 0.7 ±0.2 kg/d, respectively.

This study illustrates the feasibility of the stream methane method for estimating methane concentrations and loads in groundwater discharge to streams. The results show that a reconnaissance sampling study can be used to identify streams potentially receiving methane-laden groundwater discharge. Subsequent more detailed stream- and shallow groundwater-methane sampling, along with discharge measurements in one stream (Sugar Run) during base-flow conditions, coupled with 1-D stream transport modeling, resulted in estimates of methane concentrations and loads in groundwater discharge to the stream. Repeat synoptic sampling studies along this stream during different seasons gave consistent results for two low base-flow periods but larger methane loads during higher base-flow conditions. This suggests that the method can be used to assess seasonal variations in groundwater methane discharging to streams. For high-gradient streams such as Sugar Run that have large gas transfer velocities and a relatively small amount of groundwater inflow, synoptic sampling at closely spaced intervals (perhaps every 100 m downstream) may be required to adequately capture peak stream methane. Alternatively, if the gas transfer velocity of a stream is low and it receives a large fraction of its total flow from groundwater inflow, distances between sampling sites could be larger.

References Cited

Berg, T.M., Edmunds, W.E., Geyer, A.R., and others, comps., 1980, Geologic map of Pennsylvania (2d ed.): Pennsylvania Geological Survey, 4th ser., Map 1, 3 sheets, scale 1:250.000.

Boyer, E.W., Swistock, B.R., Clark, James, Madden, Mark, and Rizzo, D.E., 2011, The impact of Marcellus gas drilling on rural drinking water supplies: The Center for Rural Pennsylvania, Harrisburg, Pa., 28 p.

Brantley, S.L., Yoxtheimer, D., Arjmand, S., Grieve, P., Vidic, R., Pollak, J., Llewellyn, G.T., Abad, J., and Simon, C., 2014, Water resource impacts during unconventional shale gas development: The Pennsylvania experience: International Journal of Coal Geology, v. 126, no. 1, p. 140–156.

Breen, K.J., Révész,, K., Baldassare, F.J., and McAuley, S.D., 2007, Natural gases in ground water near Tioga Junction, Tioga County, north-central Pennsylvania—Occurrence and use of isotopes to determine origins, 2005: U.S. Geological Survey Scientific Investigations Report 2007–5085, 65 p., at *http://pubs.usgs.gov/sir/2007/5085/*.

Cook, P.G., Favreau, G., Dighton, J.C., and Tickell, S., 2003, Determining natural groundwater influx to a tropical river using radon, chlorofluorocarbons and ionic environmental tracers: Journal of Hydrology, v. 277, no. 1–2, p. 74–88.

Cook, P.G., Lamontagne, S., Berhane, D., and Clark, J.F., 2006, Quantifying groundwater discharge to Cockburn River, southeastern Australia, using dissolved gas tracers ^{222}Rn and SF_6: Water Resources Research, v. 42, no. 10, 12 p., DOI: 10.1029/2006WR004921.

Dammel, J.A., Beilicki, J.M., Pollak, M.F., and Wilson, E.J., 2011, A tale of two technologies: Hydraulic fracturing and geologic carbon sequestration: Environmental Science and Technology, v. 45, p. 5075–5076, *http://dx.doi.org/10.1021/es201403c*.

DiGiulio, D.C., Wilken, R.T., Miller, C., and Oberley, G., 2011 (Draft), Investigation of ground water contamination near Pavillion, Wyoming: Environmental Protection Agency Report 600/R-00/000, 43 p.

Esri, 2013, World shaded relief: Esri ArcGIS Map Service, accessed March 6, 2014, at *http://services.arcgisonline.com/arcgis/*.

FracTracker, 2013, PA unconventional drilled wells (1-1-2000 through 7-20-2013), accessed September 19, 2013, at *http://www.fractracker.org/downloads/*.

Grinham, A., Dunbabin, M., Gale, D., and Udy, J., 2011, Quantification of ebullitive and diffusive methane release to atmosphere from a water storage: Atmospheric Environment, v. 45, no. 39, p. 7166–7173.

Guérin, F., Abril, G., Richard, S., Burban, B., Reynouard, C., Seyler, P., and Delmas, R., 2006, Methane and carbon dioxide emissions from tropical reservoirs: Significance of downstream rivers: Geophysical Research Letters, v. 33, no. 21, 6 p., L21407, doi:10.1029/2006GL027929.

Heilweil, V.M., Stolp, B.J., Kimball, B.A., Susong, D.D., Marston, T.M., and Gardner, P.M., 2013, A stream-based methane monitoring approach for evaluating groundwater impacts associated with unconventional gas development: Groundwater, v. 51, no. 4 , p. 511–524, doi: 10.1111/gwat.12079. (Erratum published on p. 809 of Issue 5 (doi: 10.1111/gwat.12103) adding R.C. Rowland as a co-author)

Jackson, R.B., Vengosh, A., Darrah, T.H., Warner, N.R., Down, A., Poreda, R.J., Osborn, S.G., Zhao, K., and Karr, J.D., 2013, Increased stray gas abundance in a subset of drinking water wells near Marcellus shale gas extraction: Proceedings of the National Academy of Sciences, 6 p., doi: 10.1073/pnas.1221635110.

Jähne, B., Heinz, G., and Dietrich, W., 1987, Measurement of the diffusion coefficients of sparingly soluble gases in water: Journal of Geophysical Research: Oceans, v. 92, no. C10, p. 10767–10776.

Kappel, W.M., Williams, J.H., and Szabo, Z., 2013, Water resources and shale gas/oil production in the Appalachian Basin—Critical issues and evolving developments: U.S. Geological Survey Open-File Report 2013–1137, 12 p., *http://pubs.usgs.gov/of/2013/1137/*.

Kargbo, D.M., Wilhelm, R.G., and Campbell, D.J., 2010, Natural gas plays in the Marcellus Shale: Challenges and potential opportunities: Environmental Science and Technology, v. 44, no. 15, p. 5679‒5684.

Kemenes, A., Forsberg, B.R., and Melack, J.M., 2007, Methane release below a tropical hydroelectric dam: Geophysical Research Letters, v. 34, no. 12, 5 p., L12809, doi: 10.1029/2007GS029479.

Kennedy, V.C., Kendall, C., Zellweger, G.W., Wyerman, T.A., and Avanzino, R.J., 1986, Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River basin, California: Journal of Hydrology, v. 84, no. 1-2, p. 107–140.

Kilpatrick, F.A., and Cobb, E.D., 1985, Measurement of discharge using tracers: U.S. Geological Survey Techniques of Water-Resources Investigations, book 3, chap. A16, 52 p., *http://pubs.usgs.gov/twri/twri3-a16/*.

Linsley, R.K., Jr., Kohler, M.A., and Paulhus, J.L.H., 1975, Hydrology for engineers (2d ed.): New York, McGraw-Hill, 482 p.

Lytle, W.S., 1963, Underground gas storage in Pennsylvania: Pennsylvania Geological Survey, 4th ser., Mineral Resource Report M46.

McDonnell, J.J., Bonell, M., Stewart, M.K., and Pearce, A.J., 1990, Deuterium variations in storm rainfall: Implications for stream hydrograph separation: Water Resources Research, v. 26, no. 3, p. 455–458.

Marcellus Center for Outreach and Research (MCOR), 2014, Depth of Marcellus Shale base: The Pennsylvania State University Marcellus Center for Outreach and Research, accessed February 8, 2014, at *http://www.marcellus.psu.edu/images/Marcellus_Depth.gif*.

Molofsky, L.J., Connor, J.A., Wylie, A.S., Wagner, Tom, and Farhat, S.K., 2013, Evaluation of methane sources in groundwater in northeastern Pennsylvania: Groundwater, v. 51, no. 3, p. 333–349.

Moore, T.R., and Knowles, R., 1990, Methane emissions from fen, bog and swamp peatlands in Quebec: Biogeochemistry, v. 11, p. 45–61.

Nicot, J.-P., and Scanlon, B.R., 2012, Water use for shale-gas production in Texas, U.S.: Environmental Science and Technology, v. 46, no. 6, p. 3580–3586, *http://dx.doi.org/10.1021/es204602t*.

Osborn, S.G., Vengosh, A., 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, v. 108, no. 20, p. 8172–8176.

Pennsylvania Department of Conservation and Natural Resources, 2007, LAS Files (LiDAR Data of Pennsylvania); PAMAP Program, PA Department of Conservation and Natural Resources, Bureau of Topographic and Geologic Survey, accessed March 6, 2014, from the Pennsylvania Spatial Data Access (PASDA), at *http://maps.psiee.psu.edu/ImageryNavigator/*.

Pelley, J., 2003, Does hydraulic fracturing harm groundwater?: Environmental Science and Technology, v. 37, no. 1, p. 11A–12A, DOI: 10.1021/es032338+.

Pettyjohn, W.A., and Henning, R., 1979, Preliminary estimate of ground-water recharge rates, related streamflow and water quality in Ohio: Ohio State University Water Resources Center Project Completion Report Number 552, 241 p.

Price, C.V., Nakagaki, N., Hitt, K.J., and Clawges, R.C., 2006, Enhanced Historical Land-Use and Land-Cover Data Sets of the U.S. Geological Survey: U.S. Geological Survey Digital Data Series 240 [digital data set], *http://pubs.usgs.gov/ds/2006/240/*.

Raymond, P.A., Zappa, C.J., Butman, D., Bott, T.L., Potter, J., Mulholland, P., Laursen, A.E., McDowell, W.H., and Newbold, D., 2012, Scaling the gas transfer velocity and hydraulic geometry in streams and small rivers: Limnology and Oceanography: Fluids and Environments, v. 2, p. 41–53, DOI: 10.1215/21573689-1597669.

Renner, R., 2009, Spate of gas drilling leaks raises Marcellus concerns: Environmental Science and Technology, v. 43, no. 20, p. 75–99.

Risser, D.W., Gburek, W.J., and Folmar, G.J., 2009, Comparison of recharge estimates at a small watershed in east-central Pennsylvania, USA: Hydrogeology Journal, v. 17, no. 2, p. 287–298.

Roland, M.A., and Stuckey, M.H., 2008, Regression equations for estimating flood flows at selected recurrence intervals for ungaged streams in Pennsylvania: U.S. Geological Survey Scientific Investigations Report 2008–5102, 57 p., *http://pubs.usgs.gov/sir/2008/5102/*.

Sanford, W.E., Nelms, D.L., Pope, J.P., and Selnick, D.L., 2012, Quantifying components of the hydrologic cycle in Virginia using chemical hydrograph separation and multiple regression analysis: U.S. Geological Survey Scientific Investigations Report 2011–5198, 152 p., *http://pubs.usgs.gov/sir/2011/5198/*.

Schnoor, J.L., 2012, Shale gas and hydrofracturing: Environmental Science and Technology, v. 46, no. 9, p. 4686.

Sloto, R.A., 2013, Baseline groundwater quality from 20 domestic wells in Sullivan County, Pennsylvania, 2012: U.S. Geological Survey Scientific Investigations Report 2013–5085, 27 p., *http://pubs.usgs.gov/sir/2013/5085/*.

Sloto, R.A., and Crouse, M.Y., 1996, HYSEP: A computer program for streamflow hydrograph separation and analysis: U.S. Geological Survey Water-Resources Investigations Report 96–4040, 46 p., *http://pubs.er.usgs.gov/publication/wri964040*.)

Stolp, B.J., Solomon, D.K., Suckow, A., Vitvar, T., Rank, D., Aggarwal, P.K., and Han, L.F., 2010, Age dating base flow at springs and gaining streams using helium-3 and tritium: Fischa-Dagnitz system, southern Vienna Basin, Austria: Water Resources Research, v. 46, no. 7, 13 p., doi:10.1029/2009WR008006.

Van Stempvoort, D., Maathuis, H., Jaworski, E., Mayer, B., and Rich, K., 2005, Oxidation of fugitive methane in ground water linked to bacterial sulfate reduction: Ground Water, v. 43, no. 2, p. 187–199.

Vidic, R.D., Brantley, S.L., Vandenbossche, J.M., Yoxtheimer, D., and Abad, J.D., 2013, Impact of shale gas development on regional water quality: Science, v. 340, no. 6134, DOI:10.1126/science.1235009.

Wanninkhof, R., Mulholland, P.J., and Elwood, J.W., 1990, Gas exchange rates for a first-order stream determined with deliberate and natural tracers: Water Resources Research v. 26, no. 7, p. 1621–1630.

Table 1. Stream sampling sites for a reconnaissance survey in northeastern Pennsylvania, including water-quality characteristics and measured concentrations of methane in samples collected during May and June, 2013

[Station number is a unique 9-digit number used by the U.S. Geological Survey (USGS) to identify a stream site; dd, decimal degrees; NAD 83, North American Datum of 1983; km^2, square kilometers; %, percent; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; --, no data; CH_4, dissolved methane; µg/L, micrograms per liter; PA, Pennsylvania]

Site name	Station number	Longitude (dd) (NAD 83)	Latitude (dd) (NAD 83)	County	[1]Density of Marcellus gas wells (pads per km^2)	Drainage area (km^2)	[2]Outcropping geologic formation	[3]Percent of forested land	Mean topographic slope (%)	Temperature (°C)
Sugar Run near Hughesville, PA	01552880	41.23592	-76.69558	Lycoming	0.18	16.7	Lock Haven and Trimmers Rock	46.8	10.4	19.5
Grays Run near Fields Station, PA	01549990	41.42364	-77.02261	Lycoming	0.21	51.2	Other	98.8	13.3	12.7
Little Muncy Creek upstream (near Biggerstown, PA)	01552975	41.24269	-76.56092	Lycoming	0.07	42.6	Catskill	71.7	8.5	16.4
Crooked Creek near Shortsville, PA	01518350	41.86297	-77.34617	Tioga	0.11	69.9	Lock Haven and Trimmers Rock	51.1	8.2	20.0
West Branch Towanda Creek at West Franklin, PA	01531903	41.69714	-76.62347	Bradford	0.24	71.4	Lock Haven and Trimmers Rock	35.1	5.6	24.3
Larrys Creek near White Pine, PA	01549781	41.39853	-77.20044	Lycoming	0.35	39.9	Catskill	64.3	7	20.5
Tomjack Creek at Burlington, PA	01531430	41.78003	-76.60644	Bradford	0.37	70.1	Lock Haven and Trimmers Rock	43.5	5.8	26.3
Parks Creek near Rome, PA	01532570	41.86794	-76.33331	Bradford	0.19	31.1	Lock Haven and Trimmers Rock	61.3	6.8	23.5
First Fork Larrys Creek near Salladasburg, PA	01549786	41.28017	-77.27022	Lycoming	0.43	34.8	Other	98.6	10.1	14.9
Fall Brook near Franklin Forks, PA	01502777	41.91172	-75.86289	Susquehanna	0.36	19.6	Catskill	75.6	8	18.5
Snake Creek near Franklin Forks, PA	01502782	41.92745	-75.84289	Susquehanna	0.14	116.9	Catskill	73.4	7.8	20.9
Silver Creek at Franklin Forks, PA	01502779	41.91772	-75.84803	Susquehanna	0.09	68.0	Catskill	78.1	7.7	21.0
Meshoppen Creek at Parkvale, PA	01533290	41.71744	-75.87075	Susquehanna	0.36	61.8	Catskill	66.5	7.5	24.4
Lake Creek near Lawton, PA	01532780	41.78008	-76.04536	Lycoming	0.42	40.5	Catskill	63.2	7.5	24.5
Little Muncy Creek downstream (near Frenchtown, PA)	01553002	41.20731	-76.63533	Lycoming	0.37	112.5	Catskill	68.6	9.4	22.9

Table 1. Stream sampling sites for a reconnaissance survey in northeastern Pennsylvania, including water-quality characteristics and measured concentrations of methane in samples collected during May and June, 2013—Continued

[Station number is a unique 9-digit number used by the U.S. Geological Survey (USGS) to identify a stream site; dd, decimal degrees; NAD 83, North American Datum of 1983; km², square kilometers; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; --, no data; CH_4, dissolved methane; µg/L, micrograms per liter; PA, Pennsylvania]

Site name	Station number	Date sample collected	Specific conductance (µS/cm)	pH (standard units)	Dissolved oxygen (% saturation)	[4]USGS CH_4 (µg/L)	USGS CH_4 replicate A (µg/L)	USGS CH_4 replicate B (µg/L)	USGS laboratory (% difference)	Isotech CH_4 (µg/L)
Sugar Run near Hughesville, PA	01552880	5/21/2013	111	7.2	--	5.0	4.98	4.96	0.4	--
Grays Run near Fields Station, PA	01549990	5/22/2013	35	6.5	--	0.0	0.00	0.00	--	0.2
Little Muncy Creek upstream (near Biggerstown, PA)	01552975	5/22/2013	82	7.6	106	0.4	0.40	0.47	--	0.6
Crooked Creek near Shortsville, PA	01518350	5/22/2013	178	8.3	--	1.3	1.15	1.44	20.1	1.3
West Branch Towanda Creek at West Franklin, PA	01531903	5/22/2013	202	7.7	102	1.5	1.47	1.45	1.4	1.6
Larrys Creek near White Pine, PA	01549781	5/22/2013	80	7.7	--	0.8	0.83	0.81	2.5	1.1
Tomjack Creek at Burlington, PA	01531430	5/22/2013	207	8.4	113	1.0	1.06	1.00	6.0	1.4
Parks Creek near Rome, PA	01532570	5/22/2013	119	7.3	95	7.3	7.21	7.31	1.4	6
First Fork Larrys Creek near Salladasburg, PA	01549786	5/22/2013	41	6.4	--	0.0	0.00	0.06	--	0.4
Fall Brook near Franklin Forks, PA	01502777	6/26/2013	107	7.6	96	0.3	0.31	0.27	--	--
Snake Creek near Franklin Forks, PA	01502782	6/26/2013	106	7.9	108	0.4	0.31	0.39	--	--
Silver Creek at Franklin Forks, PA	01502779	6/26/2013	95	7.4	105	0.6	0.62	0.58	6.9	--
Meshoppen Creek at Parkvale, PA	01533290	6/26/2013	124	6.8	80	68.5	69.2	67.9	1.9	--
Lake Creek near Lawton, PA	01532780	6/26/2013	110	7.2	86	1.7	1.78	1.62	9.9	--
Little Muncy Creek downstream (near Frenchtown, PA)	01553002	6/26/2013	103	7.4	99	5.0	4.99	5.04	1.0	--

[1]Location of drill pads determined from dataset downloaded from FracTracker (2013).

[2]Bedrock formation at land surface covering more than 50 percent of the watershed upstream from the sampling site. Neither Catskill or Lock Haven and Trimmers Rock Formations covered more than 50 percent for "Other" locations.

[3]Based on Price and others (2006).

[4]Methane is reported as the mean value of the two replicate samples. Values less than 1 µg/L (the minimum reporting limit) are estimated.

Table 3. Streamflow, field water-quality parameters, and dissolved methane concentrations in streamwater and shallow groundwater at Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013.

[Map identifier can be used to locate sites on figure 7; dd; decimal degree; m, meter; m/s, meters per second; m^3/s, cubic meters per second; %, percent; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; --, no data; CH_4, dissolved methane; mg/L, micrograms per liter; Values less than 1 µg/L (the minimum reporting limit) are estimated]

Map identifier	Site name	Latitude (dd)	Longitude (dd)	Mean depth (m)	Width (m)	Mean velocity (m/s)	Flow (m^3/s)	Flow uncertainty (%)	Temperature (°C)
		May 21, 2013, samples							
Site 7	Sugar Run in Penn Township near Lairdsville, PA	41.25367	-76.66461	0.169	3.05	0.10	0.053	4.1	20.1
Site 6	Sugar Run near Lairdsville, PA	41.24936	-76.66872	0.124	3.05	0.18	0.070	6.4	20.2
Site 4	Sugar Run in Green Valley near Hughesville, PA	41.24378	-76.68000	0.239	2.90	0.11	0.074	3.9	20.9
Site 3	Sugar Run downstream unnamed trib near Hughesville, PA	41.24311	-76.68297	0.069	6.10	0.21	0.086	3.0	21.0
Site 2	Sugar Run in Penn Township near Hughesville, PA	41.24072	-76.68978	0.144	4.80	0.16	0.107	3.9	21.0
Site 1	Sugar Run near Hughesville, PA	41.23592	-76.69558	0.087	4.27	0.28	0.105	4.2	19.5
Tributary 5.5	Unnamed trib to Sugar Run near Lairdsville, PA	41.24789	-76.66808	--	--	--	0.011	14.2	20.0
Tributary 4.5	Unnamed trib to Sugar Run in Green Valley near Hughesville, PA	41.24444	-76.67061	--	--	--	0.002	18.1	17.1
Tributary 3.5	Unnamed trib to Sugar Run near Hughesville, PA	41.24478	-76.68067	--	--	--	0.009	15.0	--
		June 27, 2013, samples							
Site 3	Sugar Run downstream unnamed trib near Hughesville, PA	41.243111	-76.68297	0.087	4.57	0.14	0.056	5.0	21.5
Site 2.5	Sugar Run 2.5 downstream unnamed trib near Hughesville, PA	41.241222	-76.68536	0.153	3.05	0.09	0.043	7.2	22.0
Site 2	Sugar Run in Penn Township near Hughesville, PA	41.240722	-76.68978	0.093	2.74	0.22	0.057	7.2	22.1
Site 1.5	Sugar Run 1.5 near Hughesville, PA	41.239111	-76.69225	0.076	4.72	0.12	0.044	5.1	21.1
Site 1	Sugar Run near Hughesville, PA	41.235917	-76.69558	0.066	5.18	0.11	0.037	5.0	19.5
Piezo 1.5	LY 695	41.239111	-76.69225	--	--	--	--	--	21.4
Piezo 1	LY 694	41.235917	-76.69558	--	--	--	--	--	--
		November 12, 2013, samples							
Site 2	Sugar Run near Hughesville, PA	41.240722	-76.68978	0.09	2.38	0.16	0.036	4.6	5.0
Site 1.8	Sugar Run near Hughesville, PA	41.240920	-76.69097	--	--	--	--	--	5.0
Site 1.6	Sugar Run near Hughesville, PA	41.240280	-76.69122	0.17	3.72	0.06	0.039	3.8	5.1
Site 1.5	Sugar Run near Hughesville, PA	41.239111	-76.69225	0.11	3.17	0.11	0.038	3.7	4.9
Site 1.4	Sugar Run near Hughesville, PA	41.238140	-76.69303	0.08	2.38	0.25	0.047	4.5	4.8
Site 1.2	Sugar Run near Hughesville, PA	41.237190	-76.69369	0.08	1.58	0.26	0.034	6.7	4.8
Site 1	Sugar Run near Hughesville, PA	41.235917	-76.69558	0.06	3.72	0.09	0.018	5.6	5.1
Piezo 1.5	LY 695	41.239250	-76.69225	--	--	--	--	--	9.8
Seep 1.5	LYSP 10	41.239500	-76.69222	--	--	--	--	--	9.8

Table 3. Streamflow, field water-quality parameters, and dissolved methane concentrations in streamwater and shallow groundwater at Sugar Run, Lycoming County, Pennsylvania, May 21, June 27, and November 12, 2013.—Continued

[Map identifier can be used to locate sites on figure 7; dd; decimal degree; m, meter; m/s, meters per second; m^3/s, cubic meters per second; %, percent; °C, degrees Celsius; µS/cm, microsiemens per centimeter at 25 °C; --, no data; CH_4, dissolved methane; mg/L, micrograms per liter; Values less than 1 µg/L (the minimum reporting limit) are estimated]

Map identifier	Site name	Specific conductance (µS/cm)	pH (standard units)	Dissolved oxygen (% saturation)	[1]CH_4 (µg/L)	USGS CH_4 replicate A (µg/L)	USGS CH_4 replicate B (µg/L)	USGS laboratory (% difference)
		May 21, 2013, samples						
Site 7	Sugar Run in Penn Township near Lairdsville, PA	118	7.51	--	0.4	0.40	0.44	--
Site 6	Sugar Run near Lairdsville, PA	118	7.46	--	0.5	0.47	--	--
Site 4	Sugar Run in Green Valley near Hughesville, PA	113	7.60	--	1.1	1.13	0.98	15.3
Site 3	Sugar Run downstream unnamed trib near Hughesville, PA	112	7.71	--	2.2	2.40	2.10	14.3
Site 2	Sugar Run in Penn Township near Hughesville, PA	111	7.48	--	20	19.81	19.46	1.8
Site 1	Sugar Run near Hughesville, PA	111	7.15	--	5.0	4.98	4.96	0.4
Tributary 5.5	Unnamed trib to Sugar Run near Lairdsville, PA	107	7.15	--	0.2	0.23	0.19	--
Tributary 4.5	Unnamed trib to Sugar Run in Green Valley near Hughesville, PA	67	7.17	--	--	--	--	--
Tributary 3.5	Unnamed trib to Sugar Run near Hughesville, PA	--	--	--	--	--	--	--
		June 27, 2013, samples						
Site 3	Sugar Run downstream unnamed trib near Hughesville, PA	138	7.51	98	2.4	2.48	2.34	6.0
Site 2.5	Sugar Run 2.5 downstream unnamed trib near Hughesville, PA	138	7.67	98	1.8	1.83	1.87	2.1
Site 2	Sugar Run in Penn Township near Hughesville, PA	136	7.66	99	7.2	7.44	6.97	6.7
Site 1.5	Sugar Run 1.5 near Hughesville, PA	136	7.53	97	67	68.1	65.2	4.4
Site 1	Sugar Run near Hughesville, PA	136	7.25	87	2.3	2.33	2.42	3.7
Piezo 1.5	LY 695	162	7.52	68	2,700	2,612	2,856	8.5
Piezo 1	LY 694	--	--	--	7.7	7.48	7.88	5.1
		November 12, 2013, samples						
Site 2	Sugar Run in Penn Township near Hughesville, PA	154	7.62	119	5.7	--	--	--
Site 1.8	Sugar Run Site 1.8 near Hughesville, PA	155	7.64	121	4.2	--	--	--
Site 1.6	Sugar Run Site 1.6 near Hughesville, PA	156	7.71	114	5.9	--	--	--
Site 1.5	Sugar Run 1.5 near Hughesville, PA	154	7.58	114	29	--	--	--
Site 1.4	Sugar Run Site 1.4 near Hughesville, PA	155	7.59	112	17	--	--	--
Site 1.2	Sugar Run Site 1.2 near Hughesville, PA	155	7.68	113	6.4	--	--	--
Site 1	Sugar Run near Hughesville, PA	156	7.63	106	1.3	--	--	--
Piezo 1.5	LY 695	226	8.03	68	4,600	--	--	--
Seep 1.5	LYSP 10	62	5.77	20	2,300	--	--	--

[1]Methane results as reported by the U.S. Geological Survey for the May 21 and June 27th samples (averages of replicate values; values less than the minimum reporting limit of 1 µg/L are estimated, and samples collected on November 12 were analyzed by Pennsylvania State University.

For additional information:
Director
U.S. Geological Survey
215 Limekiln Road
New Cumberland, PA 17070

http://pa.water.usgs.gov/

Document prepared by the West Trenton Publishing Service Center

Heilweil and others—**Estimation of Methane Concentrations and Loads in Groundwater Discharge to Sugar Run, Lycoming County, Pa.**—Open-File Report 2014–1126

ISSN 2331-1258 (online)

http://dx.doi.org/10.3133/ofr20141126