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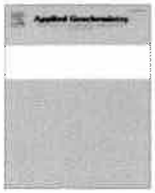

Carbon and hydrogen isotopic evidence for the origin of combustible gases in water-supply wells in north-central Pennsylvania

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ABSTRACT

The origin of the combustible gases in groundwater from glacial-outwash and fractured-bedrock aquifers was investigated in northern Tioga County, Pennsylvania. Thermogenic methane (CH_4) and ethane (C_2H_6) and microbial CH_4 were found. Microbial CH_4 is from natural *in situ* processes in the shale bedrock and occurs chiefly in the bedrock aquifer. The $\delta^{13}C$ values of CH_4 and C_2H_6 for the majority of thermogenic gases from water wells either matched or were between values for the samples of non-native storage-field gas from injection wells and the samples of gas from storage-field observation wells. Traces of C_2H_6 with microbial CH_4 and a range of C and H isotopic compositions of CH_4 indicate gases of different origins are mixing in sub-surface pathways; gas mixtures are present in groundwater. Pathways for gas migration and a specific source of the gases were not identified. Processes responsible for the presence of microbial gases in groundwater could be elucidated with further geochemical study.

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1. Introduction

Combustible gases in groundwater can occur naturally through *in situ* microbial processes or can result from migration of non-native gases into aquifers (Barker and Fritz, 1981; Keech and Gaber, 1982; Aravena et al., 1995; Chafin et al., 1996; Baldassare and Laughrey, 1997; Van Stempvoort et al., 2005). Methane in groundwater is a safety concern due to outgassing in water well and plumbing systems if the systems are not properly vented (Joyce, 1982; Swistock and Sharpe, 2006; Pennsylvania Department of Environmental Protection, 2008). Outgassing is related to gas solubility. In water exposed to one atmosphere pressure of pure CH_4, for example, CH_4 solubility is about 28 mg/L. A CH_4 concentration of 10 mg/L in groundwater is considered a warning level (Eltschlager et al., 2001, p. 40), indicating that there is the possibility of accumulation that could lead to a subsequent explosion.

In 2001, inspectors from the Bureau of Oil and Gas Management (BOGM) of the Pennsylvania Department of Environmental Protection (PADEP) noted outgassing bubbles of natural gas in well water during investigation of a complaint near Tioga Junction, Tioga County, north-central Pennsylvania. Water samples from selected household-supply wells had concentrations of dissolved CH_4 as high as 92 mg/L. PADEP expressed concern that the gas could be migrating from compromised (improperly plugged, leaking, or abandoned) gas wells, leaking gas-storage fields, or new uncontrolled pathways opened by some geologic process (such as a seismic event) that may have changed local permeability in the bedrock. By 2004, inspectors were taking action to plug abandoned gas wells. However, this did not solve the problem, and neither the origin nor the specific source of the natural gas in groundwater was known during PADEP's initial investigation.

This paper describes results of an expanded investigation by the US Geological Survey (USGS) and PADEP to determine the occurrence and origin of natural gas in groundwater in an area of about 130 km^2 near Tioga Junction, Pennsylvania, in the spring and summer of 2005. Stable and radioactive C isotope and stable H isotope composition of CH_4, stable C isotope composition of C_2H_6 and dissolved inorganic C, and stable H and O isotopic composition of water were used to constrain possible origins of the gases in groundwater.

1.1. Characteristics of microbial and thermogenic natural gases

Analyses of gas composition, stable isotopes, and the radioactive C isotope need to be employed to distinguish between microbial and thermogenic origins of natural gases, and thermogenic gases of native and non-native sources. As summarized by Osborn and McIntosh (2010), thermogenic gas has a greater proportion of higher chain hydrocarbons (ethane, propane, butane and pentane) relative to methane, than microbial gas, which dominantly contains CH_4 and CO_2. Schoell (1980) and Coleman (1994) noted that $\delta^{13}C_{CH_4}$ (CH_4 and C_2H_6 are shown as CH_4 and C_2H_6 in

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subscripts) < −64‰ and C_2H_6 concentration less than 0.5 mol% likely represent a purely microbial gas origin. With $\delta^{13}C_{CH_4}$ values more positive than −50‰, a thermogenic origin is most likely. It follows that a mixture of thermogenic and microbial gases is likely when $\delta^{13}C_{CH_4}$ values range from −64‰ up to about −50‰.

The −50‰ $\delta^{13}C_{CH_4}$ threshold value combined with the ratio of CH_4 concentration to the sum of concentrations of higher chain hydrocarbons (C_1/C_2^+) provides additional evidence of gas origin. A gas composition with $C_1/C_2^+ > 1000$ and $\delta^{13}C_{CH_4}$ value less than −50‰ generally indicates microbial gases, whereas $C_1/C_2^+ < 1000$ and $\delta^{13}C_{CH_4}$ value more positive than −50‰ generally indicates thermogenic gases (Bernard et al., 1976; Schoell, 1980; Whiticar and Faber, 1986). Taylor et al. (2000) showed that the $\delta^{13}C$ of C_2H_6 combined with C_1/C_2^+ can be used in a similar manner to assess gas origin. A gas concentration ratio less than 1000 and $\delta^{13}C_{C_2H_6}$ value more positive than −45‰ indicates thermogenic gases; a ratio more than 1000 and $\delta^{13}C_{C_2H_6}$ value < −45‰ indicates a microbial origin.

The ^{14}C content of CH_4 is also used to distinguish thermogenic from microbial gas. When plant material decomposes to CH_4, the CH_4 contains nearly the same concentration of ^{14}C (the radioactive C isotope, formed in the atmosphere) as the organic material from which it was formed. The half-life of ^{14}C is 5730 a, and ^{14}C content can be measured in organic materials that are less than about 50 ka old (Coleman et al., 1995). Microbial gas formed by buried peats covered by glaciers has measurable ^{14}C. Microbial CH_4 from landfills has ^{14}C similar to that of currently living materials. Thermogenic gases, however, are formed from organic materials that are millions of years old and do not contain measurable ^{14}C.

The isotope values of the different gases could be altered by microbial consumption of CH_4 and higher chain hydrocarbon or by simple diffusion. Therefore, to understand the origin of gases in aquifers, it is essential to study the isotopes of C in, and the H and O stable isotopes of, the associated water (Révész et al., 2009; Osborn and McIntosh, 2010).

1.2. Characteristics of waters associated with combustible natural gases

Microbial processes such as CH_4 production or CH_4 consumption by oxidation can impart unique isotopic signatures to gases and components of the associated waters. Using a combined gas and water approach is important for constraining the origin of natural gas in water wells.

Microbial CH_4 production by acetate fermentation results in C and H stable isotope signatures in associated waters that are different from microbial CH_4 produced by CO_2 reduction (Whiticar and Faber, 1986). There is an intra-molecular fractionation of the CH_3COOH molecule, the ^{13}C and ^{2}H isotopes are depleted in the methyl group, and the ^{13}C is enriched in the carboxyl group. As the CH_4 is produced ($CH_3COOH \rightarrow CH_4 + CO_2$) the $\delta^{13}C$ and $\delta^{2}H$ in the CH_4 are depleted, whereas the ^{13}C in the CO_2 is enriched (Martini et al., 1998). Production of CO_2 increases the alkalinity in associated waters and results in very positive $\delta^{13}C$ values of dissolved inorganic C (DIC) compared to the DIC in the background water. The $\delta^{2}H$ of water is enriched but usually is not detectable because the reaction consumes only one atom of H from the associated water (Whiticar and Faber, 1986).

Production of CH_4 by microbial CO_2 reduction ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) results in a decrease in the CO_2 concentration with an increasing ^{13}C enrichment, consequently a decrease in the alkalinity concentration, with an enriched ^{13}C value in the DIC. Both the C and H isotopes of CH_4 are depleted, however, the $\delta^{2}H$ is less depleted than in CH_4 produced by acetate fermentation, because 3H atoms are consumed from the associated water rather than from the organic compound. Consequently, the ^{2}H enrichment of water could be detectable.

The secondary reactions of natural gases, such as oxidation and diffusion, (Prinzhofer and Huc, 1995; Prinzhofer and Pernaton, 1997; Whiticar, 1999) also alter the isotopes of DIC in the associated water, and the stable isotopes of CH_4. Oxidation of CH_4 ($2CH_4 + 4O_2 \rightarrow 2CO_2 + 4H_2O$), results in ^{13}C enrichment of the remaining CH_4 reservoir; and ^{13}C depletion in the product CO_2 (Rayleigh distillation; Clark and Fritz, 1997). Consequently, the alkalinity concentration increases and the ^{13}C in DIC are depleted.

Diffusion of CH_4 does not change the concentration and the $\delta^{13}C$ value of DIC in the associated water; however, it produces depleted ^{13}C and ^{2}H in the diffused CH_4 and enriched ^{13}C and ^{2}H in the CH_4 reservoir that remains behind.

2. Study area and possible sources of combustible gas

2.1. Geological setting, extraction of natural gas, and gas storage

The study area in northeastern Tioga County north of Mansfield (Fig. 1) includes the Tioga River valley and adjacent uplands about 6.5 km east and west of the valley (Fig. 2). Eastern Tioga County straddles glaciated and non-glaciated areas of the Appalachian Plateaus Physiographic Province (Sevon, 2000). The geology of the study area is described in Fuller and Alden (1903), Cathcart and Myers (1934), Lytle (1963), Luce and Edmunds (1981), Williams et al. (1998), Harper (1999), and is summarized in Breen et al. (2007). The Sabinsville anticline (Fuller and Alden, 1903, p. 5) is the main structural feature and trends NE through the study area

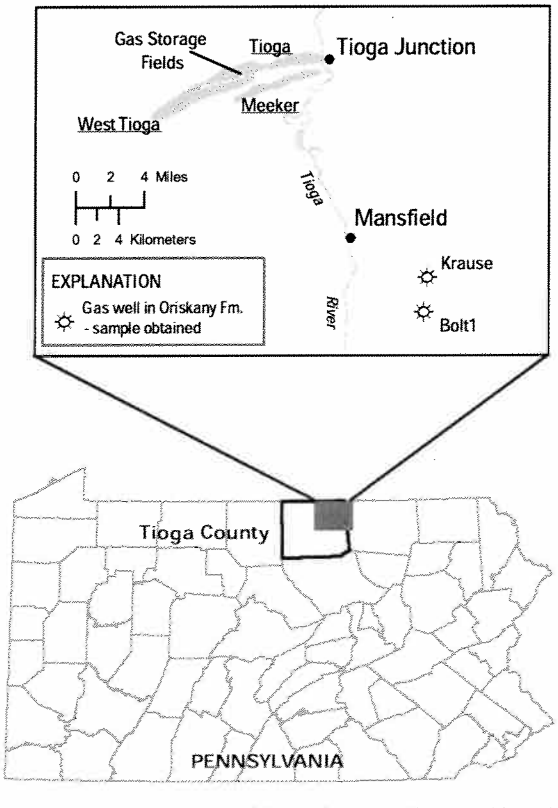

Fig. 1. Study area along the Tioga River valley in northeastern Tioga County, Pennsylvania, showing three gas-storage fields and the Krause and Bolt1 gas-wells sampled to characterize native natural gas in the Oriskany Sandstone Formation (Fm.). Gas-storage-field boundaries from Lytle (1963) and Consolidated Gas Supply Corporation (1970).

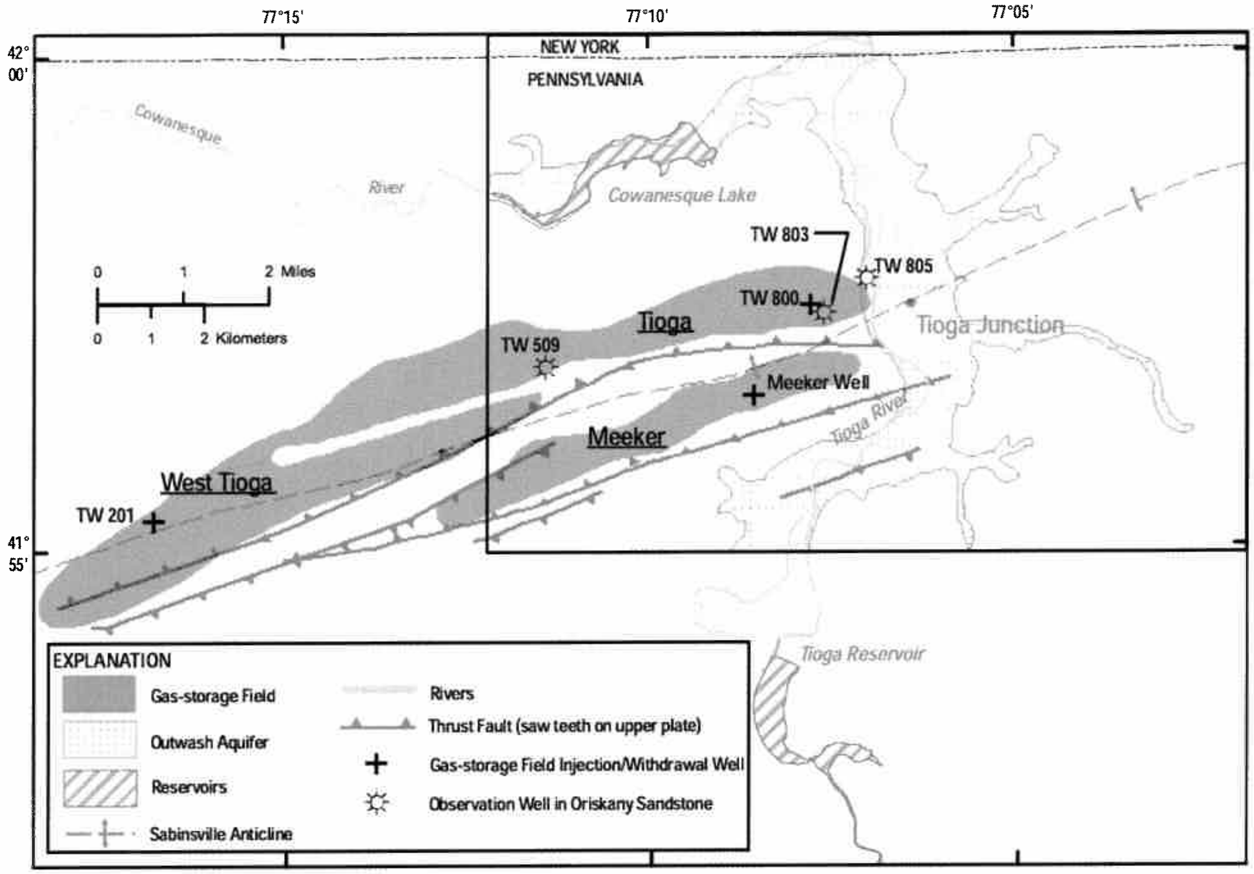

Fig. 2. Gas-storage-field area near Tioga Junction showing the major geologic structures at depth in the Oriskany Sandstone, boundaries of the Meeker, Tioga and West Tioga gas-storage fields, gas-wells sampled, and the extent of the outwash aquifer within the boundary of the ground-water study area in northeastern Tioga County, Pennsylvania. Gas-storage-field boundaries and geologic data from Cathcart and Myers (1934), Lytle (1963), NE Hub Partners, L.P., (1996) project application on file at PADEP Bureau of Oil and Gas Management, and Beardsley et al. (1999). The faults in the Oriskany Sandstone do not extend into bedrock aquifers within 76 m of the land surface (Beardsley et al., 1999, p. 289). The outlined area is expanded in Fig. 3.

(Fig. 2). In the vicinity of Tioga Junction, the top of the Oriskany Sandstone along the axis of the anticline is about 1190 m below land surface. Faults are shown in Fig. 2 as mapped at the top of the Oriskany Sandstone by Cathcart and Myers (1934), Lytle (1963), and Luce and Edmunds (1981). Recent exploration seismic studies and drilling data have been used to refine the Oriskany Sandstone structure (Beardsley et al., 1999, p. 289; NE Hub Partners, L.P., 1996, project application on file at Pennsylvania Bureau of Oil and Gas Management). The faults in the Oriskany Sandstone do not extend into near-surface rocks (Beardsley et al., 1999, p. 289). Unconsolidated sediments of glacial and postglacial origin cap the geologic section. Details of the unconsolidated sediments on the uplands and glacial outwash in the valleys are summarized in Breen et al. (2007).

Production of natural gas from the Oriskany Sandstone near Tioga Junction began in 1930. During the next several decades, the Oriskany gas was produced by many gas wells in the Sabinsville anticline area and from the fault blocks adjacent to the Sabinsville anticline. Drilling efforts also resulted in dozens of non-productive holes, and many productive drill holes were later abandoned as production declined. In the 1960s, the natural gas resource was depleted, and the pools or reservoirs were converted into gas-storage fields (Lytle, 1963). These reservoirs (Fig. 2) are now called the Tioga, Meeker, and West Tioga gas-storage fields, respectively, and are collectively referred to as the Tioga gas-storage field (Breen et al., 2007). The gas-storage field lies below a ridge at depths of 1190–1250 m below land surface on the western side of the Tioga River valley near Tioga Junction and extends about 13 km westward (Fig. 2).

The gas-storage field receives gas primarily from the gas-producing areas of the Gulf of Mexico region of the USA but also from other areas of the Appalachian Plateaus Physiographic Province in the USA and Canada. Gas from a given pipeline is injected into the field during spring, summer and fall for future withdrawal. Traditionally during winter, gas is withdrawn from the Tioga gas-storage field and transmitted for distribution and use.

2.2. Hydrogeologic setting

Groundwater for rural-domestic supply and other uses near Tioga Junction is from two aquifer systems in and adjacent to the Tioga River valley (Breen et al., 2007). An unconsolidated aquifer of outwash sand and gravel of Quaternary age underlies the main river valley and extends into the valleys of tributaries (Fig. 2). Fine-grained lacustrine sediments separate shallow and deep water-bearing zones within the outwash. Outwash-aquifer wells are seldom deeper than 30 m. The river-valley sediments and uplands adjacent to the valley are underlain by a fractured-bedrock aquifer in sandstones and shales of Devonian age, primarily the Lock Haven Formation. Most bedrock-aquifer wells produce water from the Lock Haven Formation at depths of 76 m or less in upland and valley settings.

Regional patterns of fractures or faults in the Lock Haven Formation have not been mapped. However, the SW to NE orientation of selected reaches of the Cowanesque and Tioga Rivers may be due to regional patterns of weakness or increased fracturing that allowed glacial and weathering processes to preferentially incise the bedrock leading to the present-day river channel orientation. Reports by PADEP oil and gas inspectors of natural gas bubbling into streams at the channel bottoms (Robert Gleeson, Pennsylvania Department of Environmental Protection, pers. comm., 2006) may indicate that stream channels are zones of increased fracture density (Wyrick and Borchers, 1981) and preferential pathways for migration of natural gas from depth.

2.3. Possible sources for combustible gases in groundwater

Identifying sources of combustible gas is complex because there are two basic origins of hydrocarbon gases and the gases could have undergone alteration by secondary processes such as mixing or microbial oxidation. As discussed above, the natural gas could be thermogenic (number 1 in this paper), formed by the thermal breakdown of organic material in sediments resulting from high temperatures created by deep burial (Laughrey and Baldassare, 1998); or microbial (number 2 in this paper), formed in the shallow subsurface by microbial reduction of CO_2 or methyl-type microbial (acetate) fermentation of organic matter (Whiticar, 1999).

Possible sources of thermogenic gas at Tioga Junction include deep native natural gas in the Oriskany Sandstone (1A), non-native gas imported by pipeline and injected into the Tioga, West Tioga, and Meeker natural gas-storage fields (1B), mixtures in the storage fields (1C), and shallow native gas from shale strata or "shale gas" (1D) (Osborn and McIntosh, 2010). Minor "shows" (gases encountered while drilling deep wells) at depths of about 305 m are occasionally reported in drilling records of deep gas wells in the area. The deep native natural gas is known to be associated with abandoned gas wells and other gas wells mapped in the area (Breen et al., 2007).

Possible sources of microbial gas include sub-surface gas generated by methanogenesis from buried organic material in the outwash deposits or from shale organic matter (2A), and near-surface gas such as swamp gas or landfill gas (2B). The landfill source was unlikely as there were no licensed municipal landfills in the vicinity of Tioga Junction.

3. Methods

3.1. Gas-well data collection

Eight gas wells were sampled for this study (two are shown in Fig. 1 and six are shown in Fig. 2). Gas from the wellhead was collected in a gas-sampling bag for analysis by a commercial laboratory (Isotech Laboratories, Inc.) and in a glass container for analysis by the USGS Reston Stable Isotope Laboratory (RSIL).

To characterize the native natural gas from the Oriskany Sandstone (1A), 3 gas wells were sampled (Krause well, Bolt1 well, and TW805 well). The Krause well (Fig. 1) is an Oriskany production well used as an observation and sampling point for this investigation. The Bolt1 well (Fig. 1) is an Oriskany production well serving as an observation well for the Oriskany gas because it had reportedly been plugged but yields gas (Doug Welsh, Pennsylvania Department of Environmental Protection, pers. comm., 2005). The TW805 well, labeled as gas-storage-field observation well in Fig. 2, is an Oriskany production well that was depleted and abandoned. It is an observation point approximately 150 m outside and NE of the eastern boundary of the Tioga gas-storage field. One sample from each of these wells was collected in June or September 2005. Data from additional samples from the Krause and Bolt1 wells, collected by the PADEP in October 2004 and analysed at Isotech Laboratories, Inc. (Christine Miner, Pennsylvania Department of Environmental Protection, pers. comm., 2005), are also used in this paper.

To represent the non-native gas (1B) injected into the gas-storage field, 3 wells, TW800, Meeker, and TW201 (Fig. 2), that function to inject or withdraw gas in the Tioga, Meeker, and West Tioga gas-storage fields, respectively, were sampled twice about two months apart in June 2005 and in August or September 2005. Data for an additional sample collected by PADEP from gas well TW201 and analysed at Isotech Laboratories, Inc., also are used in this paper (Christine Miner, Pennsylvania Department of Environmental Protection, pers. comm., 2005).

To represent the gases in the gas-storage field (1C), two gas wells (TW803 and TW509 in Fig. 2), used for observation of pressures in the gas-storage field, were also sampled twice. Well TW803 reportedly had been plugged but continues to yield gas, and during drilling of the well, shallow gas was encountered at about 30 m below land surface (Doug Welsh, Pennsylvania Department of Environmental Protection, pers. comm., 2005). No gas wells solely representative of native gas from shale strata or "shale gas" (source 1D) could be identified to obtain samples for characterization.

3.2. Water-well data collection

During reconnaissance observations on water wells (referred to as reconnaissance sampling or inventory), 91 privately owned wells used for household supply and by local businesses (rural domestic use) were inventoried (Fig. 3). The well inventory was initiated based on reports of problem areas at Tioga Junction. The inventory was expanded outward in an attempt to delineate the extent of gas occurrence. Population density was not directly a factor in the inventory; however, the rural nature and low density of homes in the uplands and parts of the valleys influenced where potential inventory data could be gathered. Data on well depth, well-construction characteristics, and water levels were reported in Breen et al. (2007).

Combustible-gas fractions were determined in the field on the headspace of water samples using a Mine Safety Appliances Gascope Model 60 combustible-gas indicator, calibrated to 2% methane gas, with a detection limit of 0.1%. Of the 91 water wells inventoried, 49 wells (36 wells completed in bedrock and 13 in outwash) had combustible-gas concentrations equal to or greater than 0.1% and were selected for detailed sampling at a later date; 10 of the 49 wells could not be resampled because of access problems or low yield (Breen et al., 2007) resulting in detailed samples from 27 bedrock wells and 12 outwash wells (Fig. 3). Wells selected for sampling included 19 along the eastern edge of the gas-storage field near Tioga Junction and 20 in other locations to obtain a broad representation of samples throughout the study area (Fig. 3). The detailed sampling included a repeat determination of the fraction of combustible gas in gases associated with raw well water and a repeat field measurement of water characteristics (Table 2 of Breen et al. (2007)).

Samples of groundwater were collected from 37 wells by USGS for analysis at USGS laboratories for dissolved gas concentration, stable C and H isotopes of CH_4 and stable O and H isotopes of water (water isotopes). At each of the 39 wells used for detailed sampling and at "background" wells (81 and 83) representing both aquifers where field measurements indicated no combustible gas was present, a dissolved inorganic C (DIC) sample was collected according to standard USGS methodology (Singleton et al., 2010) and stable C isotopes of DIC were determined. The samples for dissolved gases were collected in 125-mL serum bottles and sealed with rubber stoppers according to methods developed by USGS Reston Dissolved Gas Laboratory (Busenberg et al., 1998). Samples for analysis of stable C and H isotopes of CH_4 by Reston Stable Isotope

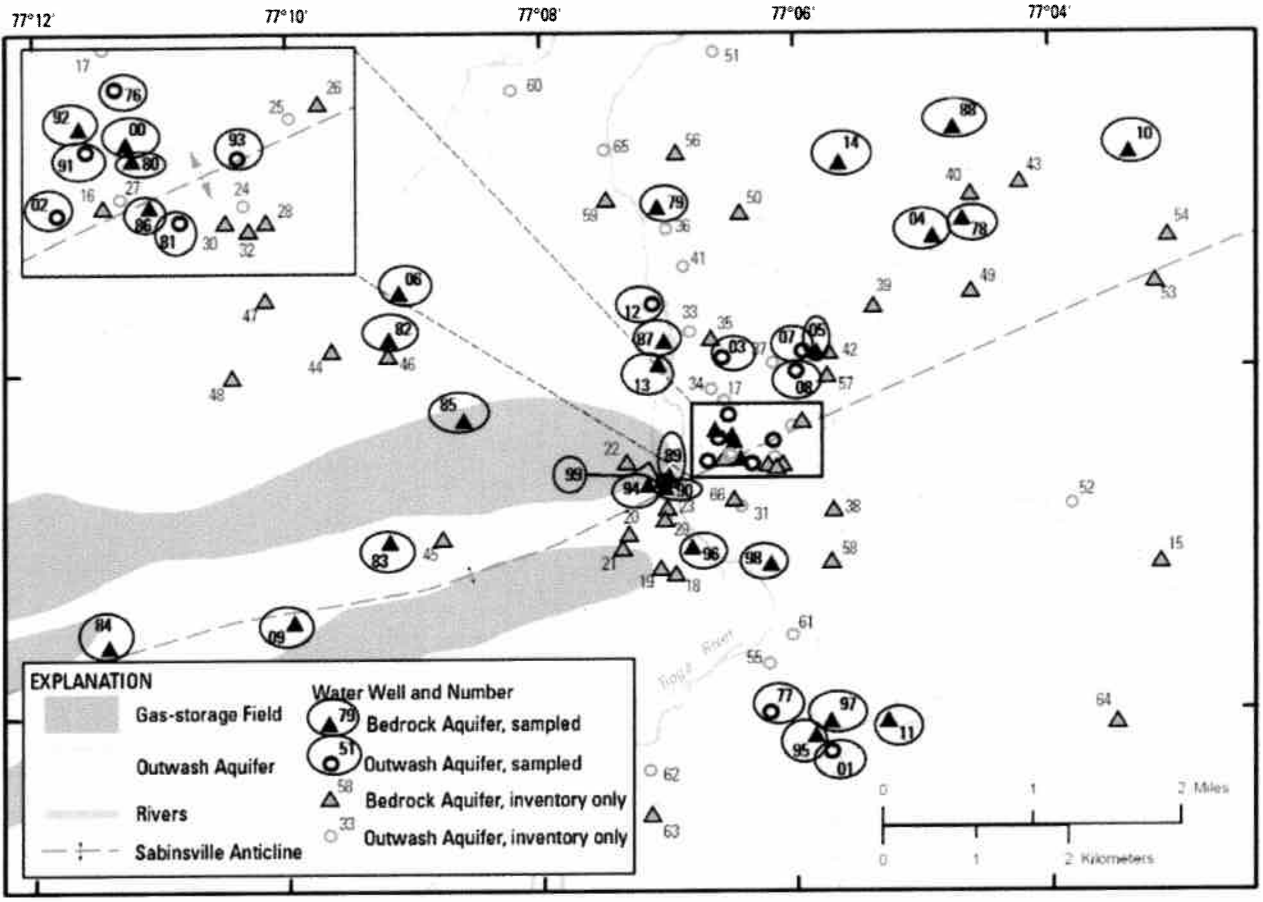

Fig. 3. Area of groundwater investigation near Tioga Junction, Tioga County, Pennsylvania, showing wells in the outwash-aquifer (oval symbol) and bedrock aquifer (triangle symbol) inventoried to determine extent of combustible gases in groundwater (91 wells). Inventory wells shown in circle had water with measureable concentrations of combustible gas and were selected for detailed sampling during June–August 2005 for analyses of the chemical and isotopic composition of dissolved gases in groundwater.

Laboratory (RSIL) were collected using methods developed by Révész et al. (1995).

Of the 39 water samples collected and submitted for compositional and isotopic analyses by the USGS, 37 sequential replicates were collected using protocols suggested by Isotech Laboratories, Inc. (Coleman et al., 1977; Keech and Gaber, 1982) and modeled after protocols of the Colorado Oil and Gas Conservation Commission (Pelphrey, 2005). These replicate groundwater samples were sent for gas analyses to Isotech Laboratories, Inc.

Of the 37 samples submitted to Isotech Laboratories, Inc., all 37 were analysed for gas composition, 35 had sufficient CH_4 to determine isotopic composition of C and H, and 21 of the 35 samples had sufficient amount C_2H_6 to determine isotopic composition of C and H. Of the 35 wells with isotopic data from Isotech Laboratories, Inc., 10 were drilled into the outwash aquifer and 25 were drilled into the bedrock aquifer. Activity of ^{14}C was used as an additional constraint on the origin of natural gas in groundwater. Methane in nine water-well samples was analysed for ^{14}C content by Isotech Laboratories, Inc. Seven of the nine samples were from outwash-aquifer wells; two of the nine samples were from the bedrock aquifer.

3.3. Isotopic nomenclature

The isotope data are reported in the updated standard δ – notation ($\delta^{13}C$, $\delta^{2}H$) expressed here in ‰.

Eq. (1) is from Révész and Coplen (2008) and is based on the general expression of $\delta = (R_{sample} - R_{std})/R_{std}$:

$$\delta^iE = \delta(^iE) = \delta(^iE/^jE) = \frac{N(^iE)_B/N(^jE)_B - N(^iE)_{std}/N(^jE)_{std}}{N(^iE)_{std}/N(^jE)_{std}} \qquad (1)$$

where $\delta(^iE)$ refers to the delta value of isotope number i and j (heavy and light isotopes, respectively) of element E of sample B relative to the same element E in an international measurement standard (std); $R_{sample} = N(^iE)_B/N(^jE)_B$ and $R_{std} = N(^iE)_{std}/N(^jE)_{std}$ are the ratios of the number of isotopes in unknown sample (B) and the international measurement standard. A positive $\delta(^iE)$ value indicates that the sample is more enriched in the heavy isotope than the international measurement standard. A negative $\delta(^iE)$ value indicates that the sample is depleted in the heavy isotope relative to the international measurement standard. The symbol $\delta(^iE)$ commonly is shortened to δ^iE and has been reported in %, ‰, and part per ten thousand (pptt).

Stable C isotope ratios are relative to Vienna Pee Dee Belemnite (VPDB), which is defined by assigning a value of +1.95‰ to National Bureau of Standards (NBS) 19 $CaCO_3$. Hydrogen isotope ratios are relative to Vienna Standard Mean Ocean Water (VSMOW) (Gat and Gonfiantini, 1981) on scales such that the H isotopic value of Standard Light Antarctic Precipitation (SLAP) is −428‰ (Gonfiantini, 1978).

The ^{14}C concentrations are expressed as percent modern C (pMC) and 100 pMC is the "natural" pre-atomic-bomb-testing

^{14}C concentration of atmospheric CO_2. The percent modern C can be greater than 100% for gases from materials formed during and after atomic-bomb-testing years.

4. Results and discussion

4.1. Characterization of native and non-native thermogenic gases

To evaluate the source of CH_4 in groundwater, the known thermogenic natural gases (native Oriskany source 1A and non-native source 1B) in the vicinity of Tioga Junction were first characterized. Compositional and isotopic analyses of samples from gas wells were used to define characteristics of natural gas (Table 7 of Breen et al. (2007), Révész et al. (2006, 2007)).

Molecular compositions indicated the non-native gases (1B) from wells in the gas-storage field and native gases from wells producing from the Oriskany Sandstone (1A) were similar overall in chemical composition (95–97% CH_4 and 2–2.5% C_2H_6). Propane concentrations were higher in the storage field injection well gas (1B) samples (0.33–0.39 vol.%) compared to native Oriskany gas (1A) samples (0.09–0.19 vol.%). The storage-field observation wells (1C) propane concentration was in between the two (0.12–0.15 vol.%). Butane, pentane and hexane isomers were about an order of magnitude greater in concentration in the non-native storage-field I/W (injection/withdrawal) well (1B) gas samples compared to native Oriskany gas (1A) samples and gas-storage-field observation wells (1C) were in between the two (Breen et al., 2007). However, the isotopic compositions of C and H in CH_4 and of C in C_2H_6 were different (Fig. 4a). The CH_4 in Oriskany gas (1A) has a median $\delta^{13}C_{CH_4}$ of about −34.54‰; non-native gas (1B) injected into the gas-storage field is of a different source and has a median $\delta^{13}C_{CH_4}$ of about −44.47‰. The non-native gas (1B) also has CH_4 depleted in ^2H (−168.78‰) compared to Oriskany gas (1A) (−158.36‰). The C_2H_6 in the non-native gas (1B) injected into the gas-storage field has a median $\delta^{13}C_{C_2H_6}$ of about −30.24‰ whereas C_2H_6 in the native Oriskany gas (1A) has a median $\delta^{13}C_{C_2H_6}$ of about −40.42‰ (Fig. 4b). The isotopic composition of the gas from the storage-field observation wells (1C) is intermediate to the native gases from wells producing from the Oriskany Sandstone and the imported non-native gases (1B) injected into the storage field, $\delta^{13}C_{CH_4} = -38.86‰$, $\delta^{13}C_{CH_4} = -167.70‰$ and $\delta^{13}C_{C_2H_6} = -33.94‰$ (Fig. 4a and b).

The native Oriskany gas (1A) is more thermally mature than the non-native storage-field gas and is more enriched in the ^{13}C and ^2H isotopes. These data correlate with limited published data for the Oriskany gas and a more comprehensive dataset for Appalachian Basin production (Jenden et al., 1993; Claypool et al., 1978; Baldassare and Laughrey, unpublished data, 1999–2005). The $\delta^{13}C_{C_2H_6}$ data from Jenden et al. (1993) are all less (more negative) than −32‰; most are less than −35‰ and are consistent with the present observations.

The samples of non-native storage-field gas from injection wells (I/W) (1B) and observation wells (O/W) (1C) reveal a larger range of $\delta^{13}C_{CH_4}$, $\delta^{2}C_{CH_4}$, and $\delta^{13}C_{C_2H_6}$ values (standard deviation (std) for O/W 1.49‰, 2.54‰, and 1.49‰, and for I/W gas 0.69‰, 2.06‰ and 0.41‰, respectively) than do the samples of Oriskany gas (1A) (std 0.22‰, 1.1‰, and 0.09‰). Isotopic variability of the non-native storage-field I/W (1B) gases is attributable to mixing of gases of different sources; however, the reason for the wide variation in composition in samples for TW800, in particular, collected only 2 months apart (Table 7 of Breen et al. (2007)) is not known.

Isotopic mass-balance calculations were used to determine the fractions of native Oriskany (1A) and non-native gases from I/W (injection/withdrawal) wells (1B) in the storage-field observation wells (O/W) (1C) based on Eq. (2):

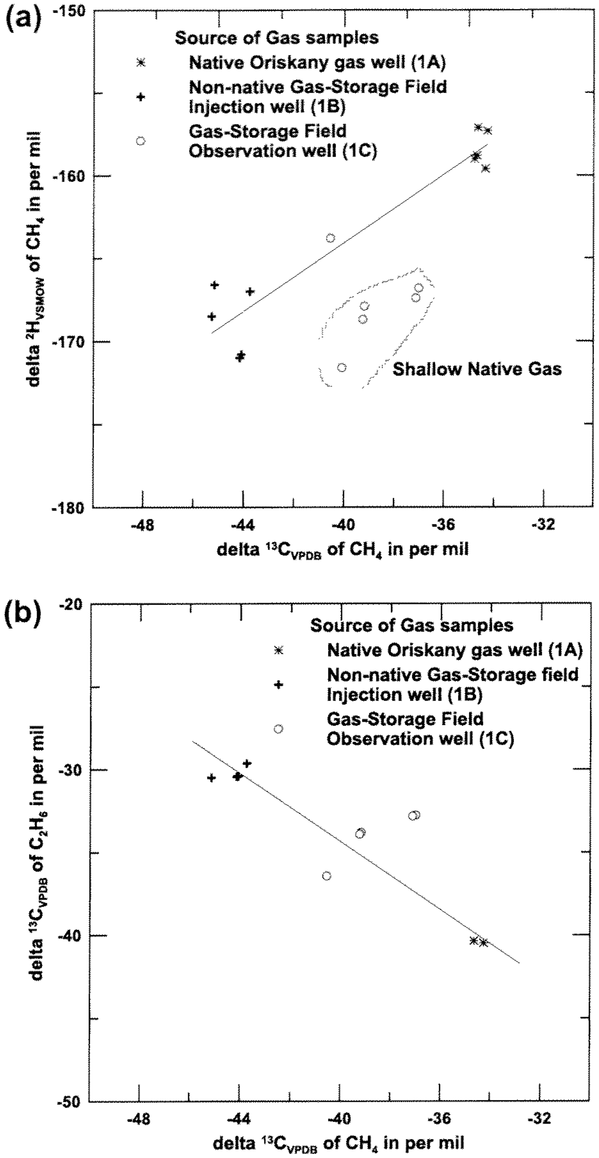

Fig. 4. Stable C and H isotopes of CH_4 (a) and stable C isotopes of CH_4 and C_2H_6(b) for samples from 8 gas wells representing native natural gases in the Oriskany Sandstone (source 1A) and non-native natural gases (source 1B) associated with the gas-storage fields (source 1C) near Tioga Junction, Tioga County, Pennsylvania, October 2004-September 2005.

$$\mathrm{AVG}\delta^{13}C_{CH_4 O/W} = (X * \mathrm{AVG}\delta^{13}C_{CH_4 I/W} + (1 - X) * \mathrm{AVG}\delta^{13}C_{CH_4 \text{Oriskany gas}})/1 \qquad (2)$$

where AVG $\delta^{13}C_{CH_4 O/W} = -38.8652‰$; AVG $\delta^{13}C_{CH_4 I/W} = -44.31‰$; AVG $\delta^{13}C_{CH_4 \text{Oriskanygas}} = -34.54‰$; X is the fraction of I/W (1B) and, $1 - X$ is the fraction of Oriskany gas (1A) in the observation wells (1C).

The same calculation could be performed by using the measured values of $\delta^{2}H_{CH_4}$ and $\delta^{13}C_{C_2H_6}$. The calculations for storage-field gas observation-well sample (O/W) (1C) indicate a combination or mixing ratio of Oriskany gas (1A):non-native storage-field gas (I/W) (1B) of about 57:43 using $\delta^{13}C_{CH_4}$; 10:90 based on the $\delta^{2}H_{CH_4}$ values, and 36:64 based on $\delta^{13}C_{C_2H_6}$ values assuming native Oriskany (1A) and non-native I/W well (1B) gases are the only two gases mixing.

Overall, the gas-well results are consistent with earlier work on storage gases. Coleman (1994) described isotopic compositions of storage gases in western Pennsylvania and New York (with gas from the Gulf of Mexico as the principal storage gas) and compositions of natural gases from the northern Appalachian Basin. The $\delta^{13}C$ results from Coleman's study indicate the non-native storage-field gases have $\delta^{13}C_{CH_4}$ values of about $-50‰$ to $-42‰$. Moreover, the samples of Oriskany gas are typical of Lower Devonian production from the northern Appalachian Basin with $\delta^{13}C_{CH_4}$ values of about $-38‰$ to $-34‰$ (Jenden et al., 1993).

4.2. Distribution of water-supply wells with combustible gases

Well depth was a factor influencing the observed occurrence of combustible gas for the 62 water wells inventoried for the bedrock aquifer (Breen et al., 2007). As the well depth range increased, the percentage of wells with combustible gas increased. The relationship of topographic setting where the bedrock wells were drilled (hilltop, hillside or valley) and the occurrence of combustible gas in well water was more difficult to discern. However, combining well depth and topographic setting as factors, bedrock wells with depths of 46 m or more in valley settings had the greatest likelihood of combustible gas in groundwater.

For the 29 outwash wells, on the basis of known geology and the extent of aquifers in the Tioga River valley, there was a pattern of combustible-gas occurrence as a function of well depth. Artesian or confined conditions, as indicated by flowing wells, were observed for the outwash aquifer in the center of the Tioga River valley. A confining unit in the main Tioga River valley, formed by lacustrine deposits, may play a role in keeping gas confined to the lower outwash aquifer in the valley and the underlying bedrock aquifer.

The observation of increased combustible gas in deeper water wells may also be explained as a function of CH_4 solubility in water. The solubility of CH_4 in water, for example, increases with increasing hydrostatic pressure. The deeper water wells inventoried during this investigation contained greater hydrostatic pressure than the shallow water wells, and, therefore, the greater potential for higher concentrations of CH_4 to be dissolved in the groundwater.

Whether structural geologic factors have influenced the distribution of combustible gases at high concentrations in groundwater is not certain. Spatially, there is an apparent SW to NE alignment and pattern of high concentrations of combustible gas in groundwater from wells on or near the axis of the Sabinsville anticline and parallel to the axis along the flanks of the anticline (see Fig. 3 noting wells circled generally had water with measureable combustible gas). The distribution pattern on or near the axis involves bedrock and outwash wells. The distribution pattern along the northern flank of the anticline involves only bedrock wells but not all bedrock wells. Gas occurrence was patchy; outwash-aquifer wells and other bedrock-aquifer wells in close proximity to the northern flank wells with combustible gas had no measureable combustible gases in groundwater. A prominent cluster of high readings of combustible gas is manifest in groundwater wells at the eastern edge of the Tioga gas-storage field (Fig. 3); another cluster includes three bedrock and two outwash wells over the southern flank of the anticline (Fig. 3) at the eastern end of a fault with SW to NE orientation mapped at depth in the Oriskany (Fig. 2) near a reach of the Tioga River having a similar SW to NE orientation.

Temporal variations in combustible gas percentages in groundwater headspace samples were evident when comparing the inventory and detailed sampling results over a period of months in 2005; variations ranged up to 20% points (Table 2 of Breen et al. (2007)). The sudden onset of CH_4 in water wells reported by PADEP in 2001 showed no evidence of dissipating through 2005. There was a follow-up sampling by Dominion Gas Company in 2007. The general range in concentration of gas from 2005 was replicated by the 2007 sampling and there was a tendency for CH_4 concentrations to be higher in 2007 that in 2005. This provided further evidence that the gases in groundwater were persistent and remained at concentrations of concern.

4.3. Origin of methane and ethane in water-supply wells

For the 37 water samples analysed for composition of headspace gases, two had nondetectable concentrations and, therefore, were used as background water wells. In the other 35 samples, the dominant gases measured were CH_4 (volume fraction ranging from

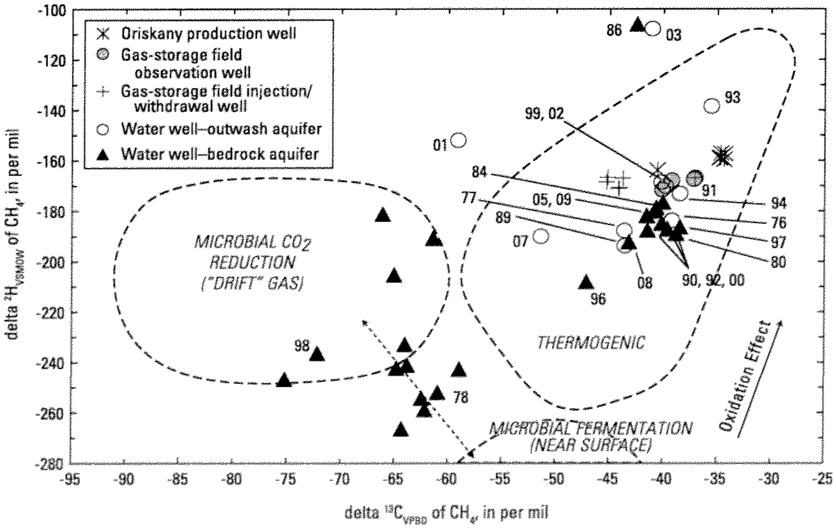

Fig. 5. Stable C and H isotope data for CH_4 in water and gas wells near Tioga Junction, Tioga County, Pennsylvania, June–August 2005. Data are superimposed on dashed areas (modified from Coleman et al. (1993), based on the dataset of Schoell (1980)) representing compositions resulting from two microbial process origins and a thermogenic origin.

0.0066% to 94.4%), N_2 (volume fraction ranging from 2.02% to 93.7%), O_2, (volume fraction ranging from 0.11% to 22.6%), CO_2 (volume fraction ranging from 0.067% to 3.30%), and Ar (volume fraction ranging from 0.09% to 1.9%) (Breen et al., 2007). Ethane was detected in 32 of 37 wells (volume fraction ranging from 0.003% to 1.61%); however, only 16 samples had volume fractions of C_2H_6 greater than about 0.02%. No propane or higher hydrocarbons were detected in groundwater samples. Therefore, CH_4 and C_2H_6 are the gases collectively termed "combustible gases" in groundwater.

Isotopic composition of headspace gases in the 35 samples show $\delta^{13}C_{CH_4}$ and $\delta^{2}C_{CH_4}$ ranging from −35.54‰ to −75.18‰ and −105.9‰ to −266.4‰, respectively. There are bimodal distributions of $\delta^{13}C_{CH_4}$ and $\delta^{2}C_{CH_4}$ results with $\delta^{13}C_{CH_4}$ modes at about −40‰ and −62‰ and $\delta^{2}C_{CH_4}$ modes at about −180‰ and −250‰.

Microbially generated gases associated with fermentation or CO_2 reduction (Fig. 5) are indicated by the −62‰ mode for $\delta^{13}C_{CH_4}$ (14 samples); the −250‰ mode for $\delta^{2}C_{CH_4}$ also points to a microbial origin (Coleman et al., 1993; Whiticar, 1994, 1999).

Thermogenic gas origin is indicated for the 21 samples in −40‰ mode for $\delta^{13}C_{CH_4}$ (Rowe and Muehlenbachs, 1999). The −180‰ mode for $\delta^{2}C_{CH_4}$ also points to a thermogenic origin.

The 21 samples with sufficient C_2H_6 for $\delta^{13}C_{C_2H_6}$ determination yielded $\delta^{13}C_{C_2H_6}$ results ranging from −28.73‰ to −39.03‰; the median was −32.17‰. The frequency distribution for $\delta^{13}C_{C_2H_6}$ does not have the bimodal character of the $\delta^{13}C_{CH_4}$ and $\delta^{2}C_{CH_4}$ results.

Comparing the $\delta^{13}C_{CH_4}$ and $\delta^{2}C_{CH_4}$ results from samples collected in 2005 with samples from 2007 from 11 wells (two for the outwash aquifer and nine for the bedrock aquifer) revealed nearly identical gas compositions (Fig. 6a and b). The samples are chiefly representative of thermogenic gases, although one sample appears to be microbial. These data suggest a gas source that is not changing with time. The similar compositions also suggest neither oxidation nor fractionation by microbial or physical processes was changing the gases observed in the aquifers in 2005 to different compositions in 2007. Given the observed similarities in isotopic composition, it appears likely that gases from a source or sources of thermogenic origin and a source or sources of microbial origin are entering groundwater in these aquifers in a continual manner.

Methane in water from nine water wells analysed for ^{14}C was found to have measurable ^{14}C. The two samples from bedrock-aquifer wells represent microbial mode CH_4 and contain the highest concentrations of ^{14}C (4.8% pMC). The seven samples from the outwash-aquifer wells have CH_4 chiefly representative of the thermogenic mode and contain lower concentrations of ^{14}C (ranging from 0.8% to 4.4% pMC) than the two microbial mode samples.

By comparing the ^{14}C results to the data in Coleman et al. (1993), microbial gas (probably glacial drift gas) is present in the study area (Fig. 7a). Methane in the aquifers resulting solely from marshes or swamps or landfill gas was ruled out based on the ^{14}C results and typical ranges for those gas sources (Fig. 7a).

The amount of ^{14}C is low in the seven samples with a thermogenic gas signature—an indication that the microbial gas represents either a minor component relative to the thermogenic gas or that the microbial CH_4 was formed a long time ago but within 25 ka, and has decayed substantially, or both. Nevertheless, there is a correlation between the ^{14}C and $\delta^{2}C_{CH_4}$ values (Fig. 7b) for the same gas, indicating simple mixing between the microbial and thermogenic gases.

4.3.1. *Microbial gases in water-supply wells*

Microbial CH_4 is in groundwater from 14 water-supply wells; 13 are wells completed in the bedrock aquifer and 10 of the 13 wells are overlying the northern flank of the Sabinsville anticline at depth (Fig. 8). Well 85 is nearest the Tioga gas-storage field; the other wells are north and east of the storage field. Microbial CH_4 is also in groundwater in three bedrock-aquifer wells overlying the southern flank of the Sabinsville anticline at depth east and south of the storage fields; well 01, clustered among other water wells with combustible gases, is the only outwash-aquifer well that yields groundwater with a CH_4 isotopic composition that indicates a microbial origin. Methane generated from shale organic matter by methanogenesis is most probable given the gas and isotopic composition similarities between the data and recent data for shallow groundwaters in Devonian organic-rich shale along Lake Erie (Osborn and McIntosh, 2010).

The −250‰ mode for $\delta^{2}C_{CH_4}$, suggests a very light (very negative) $\delta^{2}C_{CH_4}$ for a microbial gas composition. Very negative $\delta^{2}C_{CH_4}$ values could be the result of gas formation in Pleistocene-age waters with very light isotopic composition for $\delta^{2}H$. However, the isotopic composition of groundwater as sampled in 2005 does

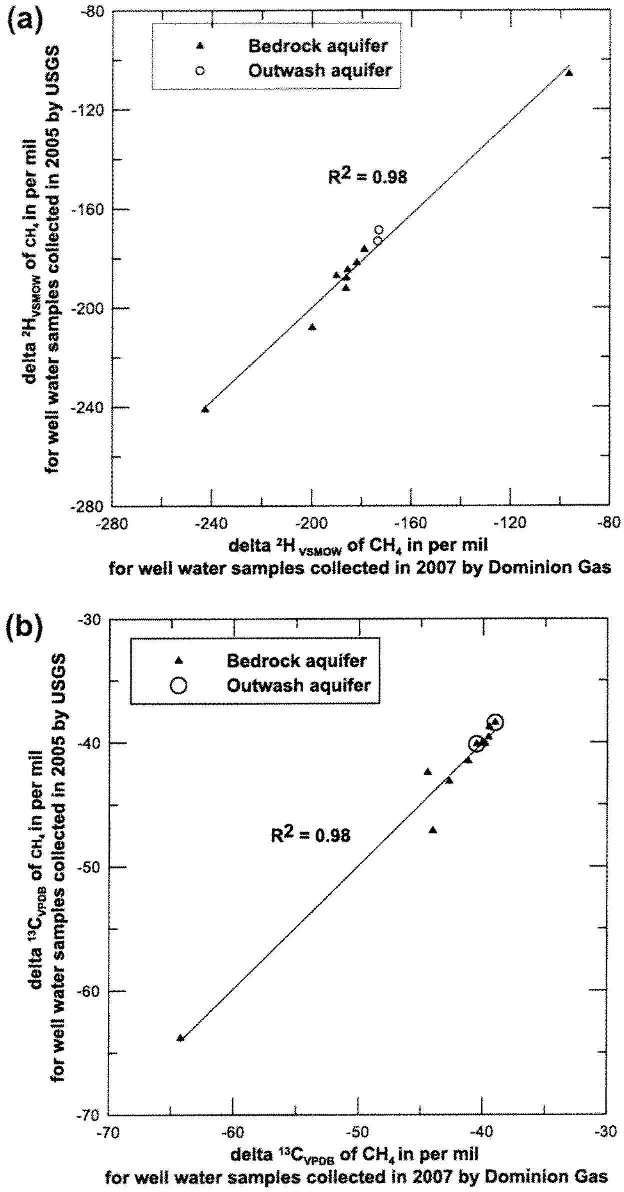

Fig. 6. Stable C (a) and H (b) isotopes of CH_4 for groundwater samples near Tioga Junction, Tioga County, Pennsylvania, collected by USGS in June–August 2005 and by Dominion Gas Co. in December 2007. Least squares regression lines show R^2 values of 0.98 for $\delta^{13}C$ and $\delta^{2}H$ in CH_4, between the two sets of samples.

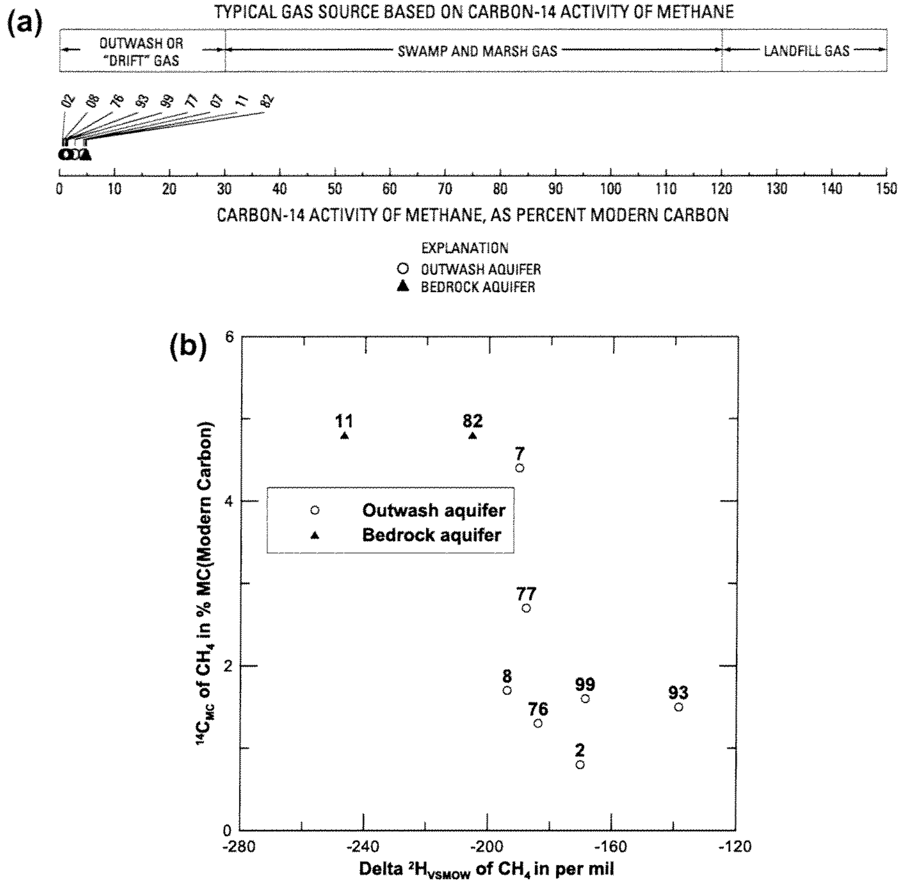

Fig. 7. Carbon-14 content of CH_4 in groundwater from seven wells (a) in the outwash aquifer (circle) and two wells in the bedrock aquifer (triangle) near Tioga Junction, Tioga County, Pennsylvania, collected by USGS in June–August 2005 (data from Breen et al. (2007)), compared to typical ranges of ^{14}C content of CH_4 for gases of different sources from Coleman et al. (1993). (b) The apparent correlation between ^{14}C concentration and δ^2H in CH_4.

not have this characteristic. Hydrogen and O stable-isotope characteristics of groundwater provide no additional information on the origin or source of the CH_4 gas (Breen et al., 2007).

Analyses of dissolved inorganic C (DIC) or alkalinity in groundwater can be used to help understand the source of and processes affecting microbial CH_4. DIC was present in sufficient quantities for analysis of $\delta^{13}C_{DIC}$ in groundwater; these analyses provide evidence that microbial CH_4 is being produced in the bedrock aquifer. The $\delta^{13}C_{DIC}$ values for groundwaters were analysed for 12 outwash-aquifer wells and 28 bedrock-aquifer wells and ranged from −2.17‰ to −21.82‰; the corresponding alkalinities ranged from about 50 to 300 mg/L as $CaCO_3$ (Breen et al., 2007). The $\delta^{13}C_{DIC}$ values for groundwaters with microbial CH_4 are compared to alkalinity and CH_4 concentrations in Fig. 9.

The background concentration and isotopic composition of DIC in outwash and bedrock aquifer in the absence of CH_4 is 117; 157 mg/L as $CaCO_3$, and −13.47‰; −15.66‰, respectively. They are shown in Fig. 9 with symbol "+". The positive correlation of $\delta^{13}C_{DIC}$ with parallel association of CH_4 and alkalinity concentrations in groundwater is a sign of CH_4 production.

Aravena et al. (1995), describing a similar positive linear correlation for data from a methanogenic aquifer in Canada, concluded that the $\delta^{13}C_{DIC}$ results could not be from inorganic C reactions; rather, they were influenced by microbial production of CH_4. These relationships of the parameters point to an *in situ* microbial production process (Whiticar and Faber, 1986; Whiticar, 1999; Révész et al., 1995); however, data for ^{14}C of DIC and the chemical constituents in groundwater would be needed to prove this theory. A source reservoir for CH_4 of microbial origin was not found; hence, the source of C in CH_4 with isotopic composition in the microbial mode is not clear.

The data in Fig. 9 also provide insights as to gas origin in some individual wells. For example, measurements in well 78 indicate a production pathway for CH_4 by acetate fermentation rather than by CO_2 reduction. At low alkalinity and CH_4 concentrations, however, results from well 98 suggest CH_4 production by CO_2 reduction, yet this pathway is uncertain due to the proximity of the measurements to the background $\delta^{13}C_{DIC}$ values. Furthermore, there is evidence that some oxidation of microbial CH_4 is occurring in groundwater from individual wells. Oxidation of CH_4 or other hydrocarbons would cause the $\delta^{13}C$ of DIC in groundwater to become more negative and the alkalinity would increase. Groundwaters from wells 01 and 95 have alkalinities greater than background yet the $^{13}C_{DIC}$ is depleted. Oxidation of CH_4 could explain this shift in composition (Whiticar, 1999). Groundwaters with $\delta^2C_{CH_4}$ more positive than −120‰ (Fig. 5) are from one outwash aquifer sample (well 03) and one bedrock aquifer sample (well 86); these results also indicate possible bacterial oxidation, which results in enrichment of the residual CH_4 in ^{13}C and ^2H (Coleman et al., 1993).

Ethane was typically present only at trace concentrations in groundwater with microbial CH_4. To determine if a microbial origin for C_2H_6 was likely, the concentration ratio of CH_4 to higher chain hydrocarbons and the isotopic composition ranges of C_2H_6 in near-surface aquifers as described and categorized by Taylor et al. (2000) were evaluated. For microbial C_2H_6 production, the

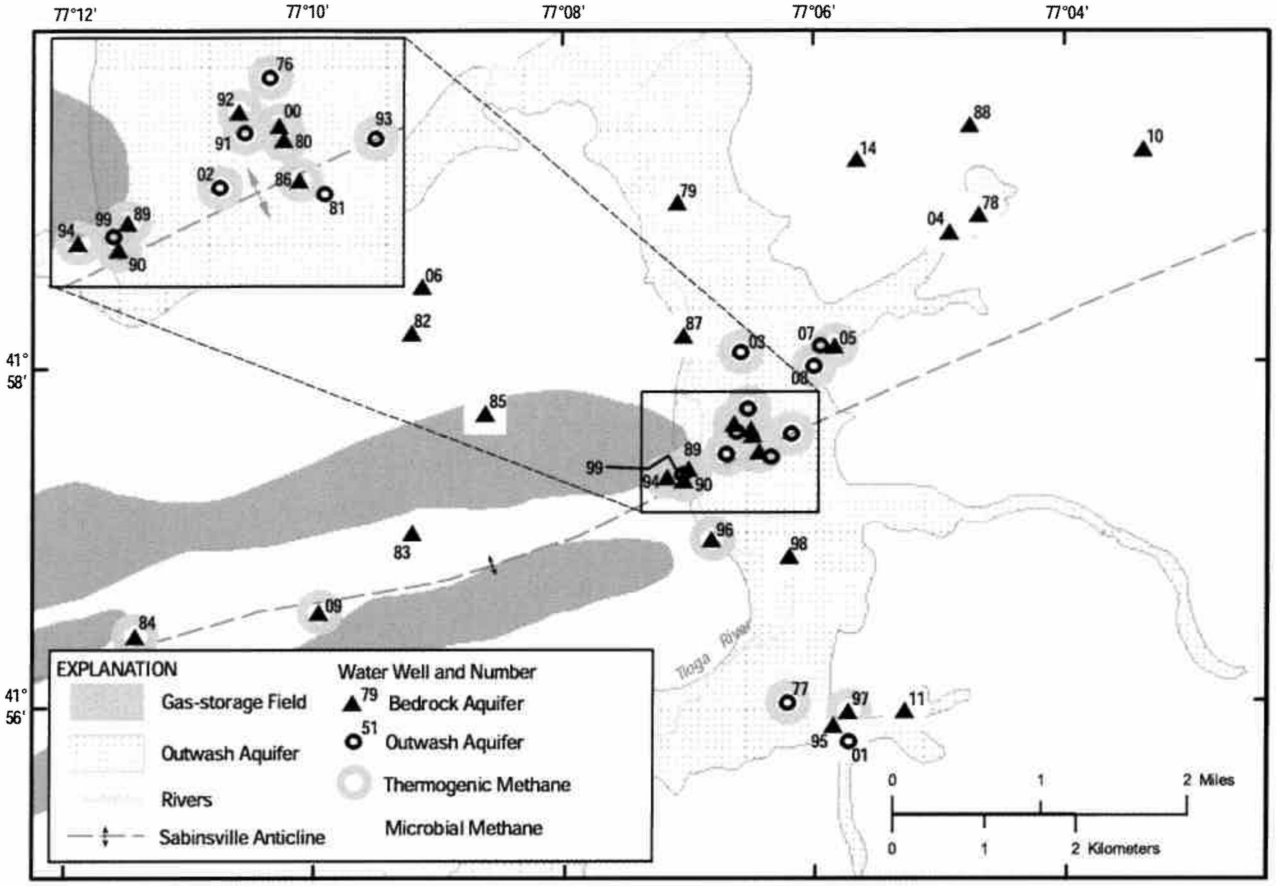

Fig. 8. Distribution of groundwater wells with CH_4 of microbial or thermogenic origins from bedrock- and outwash-aquifer wells near Tioga Junction, Tioga County, Pennsylvania, June–August 2005 (data from Breen et al. (2007)) based on the isotopic compositions of CH_4 and C_2H_6.

concentration ratio of CH_4 to higher chain hydrocarbons is typically >1000 and $\delta^{13}C_{C_2H_6}$ values range from −45‰ to −74‰. In gases containing thermogenic C_2H_6, the concentration ratio of CH_4 to higher chain hydrocarbons is typically <1000 and $\delta^{13}C_{C_2H_6}$ values range from −25‰ to −45‰. The isotopic data are in the range of thermogenic C_2H_6 (Fig. 10) but some samples contain so little C_2H_6 that they could be candidates for microbial C_2H_6. However, one of the samples shown on Fig. 11, well 77, contains ^{14}C (Fig. 7b) suggesting that the range of CH_4/C_2H_6 ratios shown in Fig. 10 is due to mixing between microbial CH_4 with no C_2H_6 and a thermogenic gas containing C_2H_6. Alternatively, microbial C_2H_6 that forms in a deep marine sub-surface environment (Hinrichs et al., 2006) can be enriched in ^{13}C with the $\delta^{13}C_{C_2H_6}$ ranging from −15‰ to −45‰. This range matches the present data; however, the deep marine conditions do not match the conditions at Tioga Junction. The conditions and observations described by Taylor et al. (2000) generally match the setting at Tioga Junction and, when combined with the lack of C_2H_6 occurring with microbial CH_4, suggests the C_2H_6 at Tioga Junction is thermogenic rather than microbial in origin.

4.3.2. Thermogenic gases in water-supply wells

Groundwaters with CH_4 isotopic compositions in the thermogenic range have isotopic compositions most similar to CH_4 from the gas-storage-field observation wells (1C) (Fig. 5). These are the groundwaters with C_2H_6 in the thermogenic range described by Taylor et al. (2000) and shown in Fig. 10. As previously noted, the wells yielding these waters are chiefly clustered at the eastern edge of the gas-storage field (Fig 8). Wells 09 and 84 are to the west of the main cluster along the axis of the Sabinsville anticline; the other wells with groundwater in the thermogenic mode are on a SE trending line that connects the main cluster first with well 96 and then with wells 77 and 97 in a southerly cluster (Fig. 8). The clustering suggests enhanced gas migration from depth along the axis of the Sabinsville anticline possibly associated with subsurface fractures and possibly complicated by improperly plugged, leaking, or abandoned gas wells at the eastern edge of the storage field. As is common in an area with a long history of natural gas exploration and production, this area has numerous abandoned wells and dry holes as noted in databases compiled by the Pennsylvania Topographic and Geologic Survey and shown in Fig. 12 for the eastern edge of the gas-storage field.

4.4. Isotopic evidence for mixing of gases in groundwater

Some of the isotopic compositions of CH_4 fall outside the fields which categorize different origins of natural gas (Fig. 5). For example, well 78 might indicate mixing of two types of microbial gases, produced by different pathways in the bedrock aquifer overlying the northern flank of the Sabinsville anticline. The samples from wells 07 and 96 plot inside the thermogenic field (Fig. 5) yet are intermediate to the two primary modes defined by $\delta^{13}C_{CH_4}$. These samples might indicate mixing of thermogenic and microbial gases. There is a correlation between the ^{14}C and $\delta^{2}C_{CH_4}$ values (Fig. 7b) indicating simple mixing between microbial and thermogenic gases.

The relationship between $\delta^{13}C_{CH_4}$ and $\delta^{13}C_{C_2H_6}$ results shown previously for gas-well samples in Fig. 4b is expanded in Fig. 11 to include water-well samples. All water-well results represent

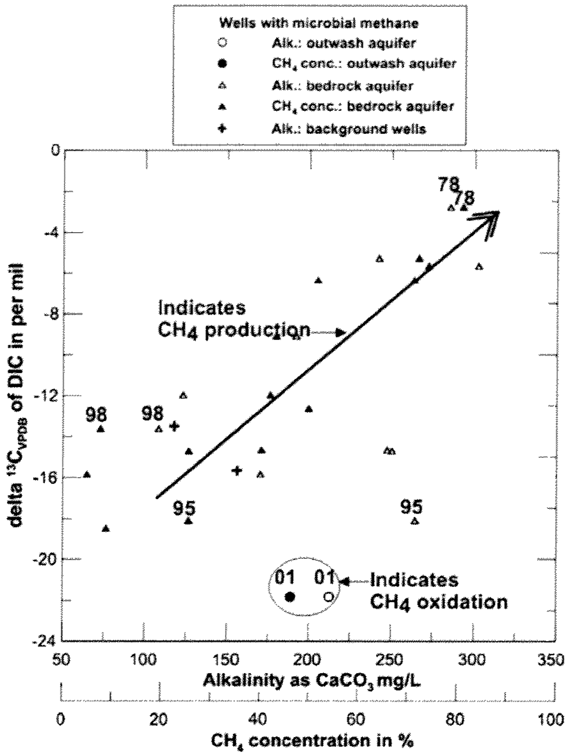

Fig. 9. $\delta^{13}C_{DIC}$ as a function of CH_4 concentration and alkalinity (acid neutralization capacity) in groundwaters with CH_4 of microbial origin from bedrock- and outwash-aquifer wells near Tioga Junction, Tioga County, Pennsylvania, June–August 2005 (data from Breen et al. (2007)). DIC is the abbreviation for dissolved inorganic C.

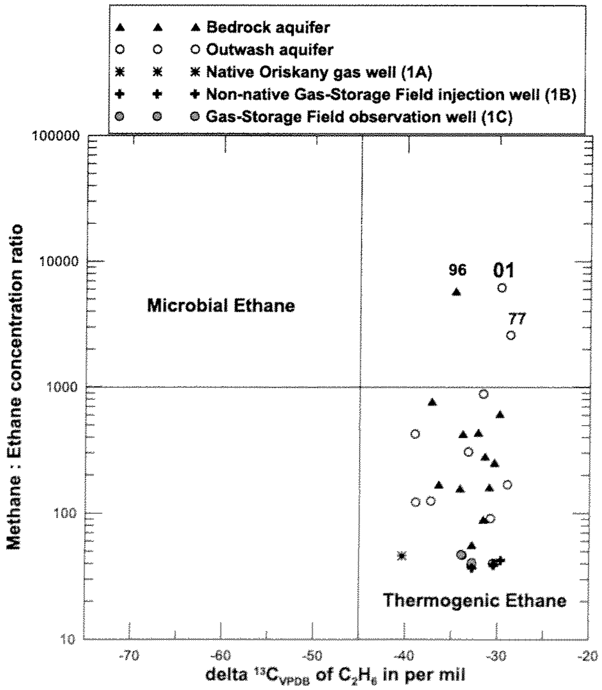

Fig. 10. Modified Bernard plot (Taylor et al., 2000) of the $\delta^{13}C$ of C_2H_6 vs. the ratios of CH_4 concentration to C_2H_6 concentration for gas-well and water-well samples collected in June–August 2005, Tioga Junction and vicinity, Tioga County, Pennsylvania (data from Breen et al. (2007)).

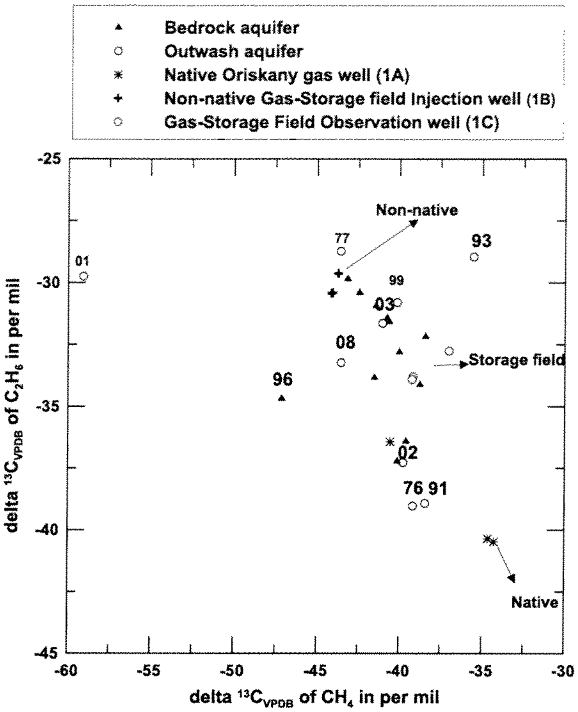

Fig. 11. The $\delta^{13}C$ of CH_4 and C_2H_6 for gas-well and water-well samples collected in June–August 2005, Tioga Junction and vicinity, Tioga County, Pennsylvania (data from Breen et al. (2007)).

thermogenic mode gases, except well 01, and are plotted by aquifer. The anomalous $\delta^{13}C_{CH_4}$ value in water from well 01 suggests a gas mixture that includes gas of microbial origin and gas with an C_2H_6 component matching the non-native gas in the injection well samples (1B) (+ symbol in Fig. 12). Isotopic compositions for 15 of the 21 samples from groundwater wells are mostly intermediate between or identical to the samples of non-native storage-field gas from I/W (1B) wells and the samples of storage-field gas from observation wells (1C). Results for well 96, plotting to the left of most other data, appear to be on a possible mixing line between a groundwater composition such as in well 01 and the composition of native Oriskany gas (1A) but this could not be proved by isotope mass-balance calculation. Well 93, with $\delta^{13}C_{C_2H_6}$ equivalent to wells 01 and 77 and the non-native gas (1B) from storage-field I/W wells, has a $\delta^{13}C_{CH_4}$ value that nearly matches the native Oriskany gas (1A) and plots to the right of most other data. The $\delta^{13}C_{C_2H_6}$ results for well 01 match the $\delta^{13}C_{C_2H_6}$ results for the thermogenic non-native gas (1B); however, because the possibility of oxidation of hydrocarbons in groundwater from well 01 was noted, it is possible that Oriskany gas (1A) mixed with C_2H_6 of depleted isotopic composition and later oxidized. This argument could be valid for well 93 also. Five samples plot between the samples of storage-field gas from observation wells (1C) (which may have a mix of native Oriskany (1A) and storage-field gas (1C)) and the samples of native Oriskany gas (1A). These 5 wells (00, 02, 76, 91, and 92) could have a greater fraction of Oriskany gas (1A) mixed with storage-field gas (1C) or they could contain a thermogenic gas from a source that was not characterized in this investigation.

The work of Bernard et al. (1976) provides an additional approach for plotting gas composition and $\delta^{13}C_{CH_4}$ to distinguish between microbial and thermogenic gases (Fig. 13). This approach can also illustrate intermediate compositions that may be related to mixing of gases. The Bernard plot, using the data, clearly distinguishes between thermogenic and microbial origins of gases in the

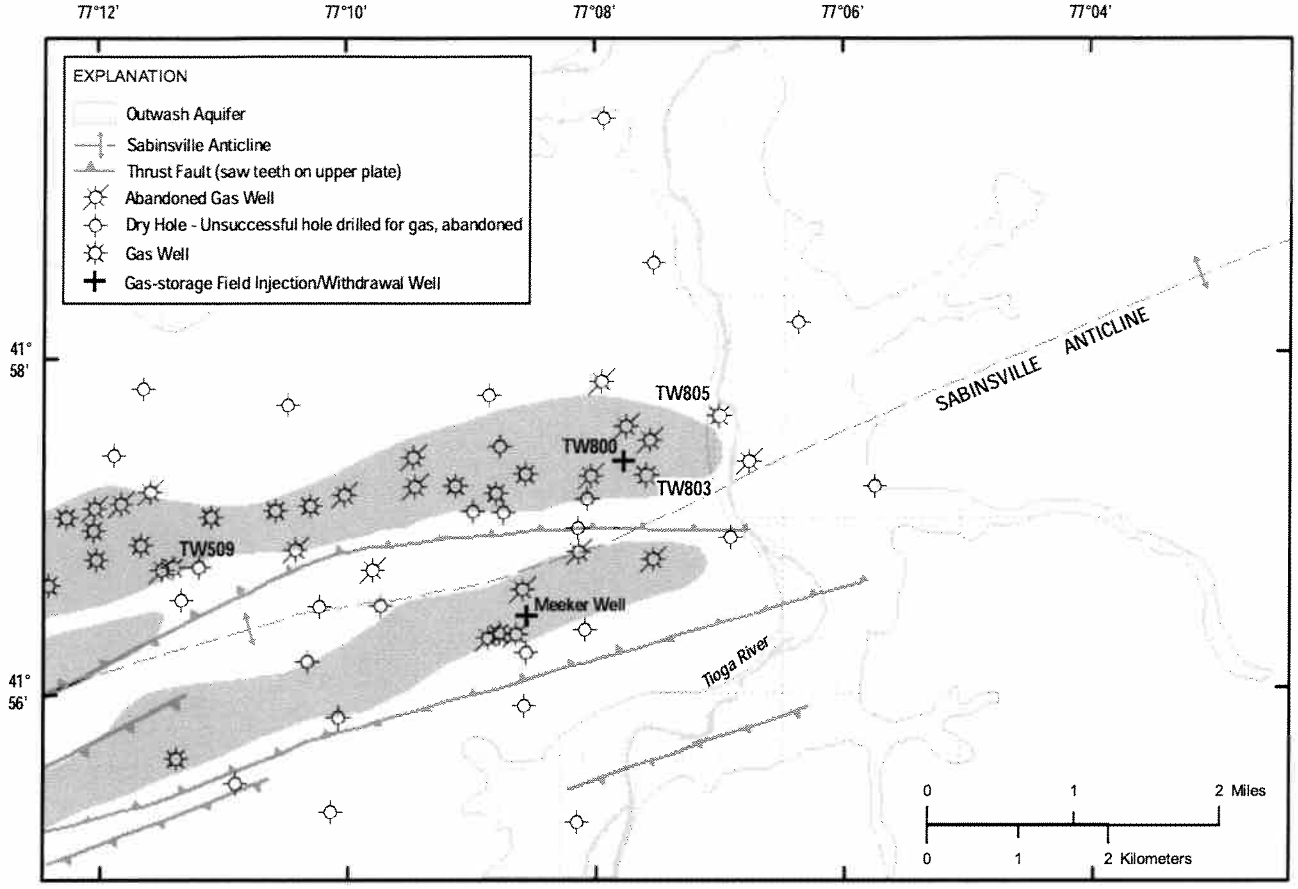

Fig. 12. Locations of various types of gas wells on file with the Pennsylvania Topographic and Geologic Survey near the eastern edge of the Tioga gas-storage field (shaded area) Tioga Junction and vicinity, Tioga County, Pennsylvania.

water wells; however, it does not indicate a simple mixing of two end-member gases in the samples. For demonstration, a typical mixing curve was calculated using the two extreme end members from the data set (see Fig. 13, mixing curve 1). The ^{14}C values (number labels on 9 data points for water wells) however indicate mixing of thermogenic and microbial gases in wells. Mixing curves (2 and 3) were calculated using different end members representing two possible mixing scenarios.

5. Limitations of data and suggestions for future investigation

Compositional and isotopic data are missing for two possible gas sources—a native gas in the bedrock below the depths of water wells and above the depths of gas wells and a "drift gas" in the shallow subsurface. With storage-field and Oriskany gases characterized, lacking these data places some constraints on conclusions about the origin and source of the CH_4 in groundwater. However, the authors are not convinced of the widespread presence of a native gas in the bedrock at depths deeper than water wells and shallower than gas wells. Historical well records and published literature revealed evidence of only occasional "shows" of native shallow Devonian gas at depths of about 305 m. There was no evidence that native shallow Devonian gas was a viable source of natural gas production in the area. It would be expected that if a native shallow thermogenic gas in bedrock (Osborn and McIntosh, 2010) or a "drift gas" was a source of the migrating gases then the occurrence of combustible-gas concentrations of concern would be more widespread and not be (a) characterized by a sudden onset of reports and complaints of gases in groundwater by well owners in 2001 and (b) in the clustered groupings of wells observed in the area of Tioga Junction.

Samples from the injection/withdrawal wells in the gas-storage field (non-native gas well, 1B) and storage-field observation wells (1C) provide only a limited representation of the storage-field gas composition. Storage-field wells used for observation also may also have "old" injection gas (1B) or mixtures of multiple vintages, sometimes mixed with native gas. The possibility of three or more source compositions and many possible mixing scenarios for gases also complicate the data interpretation.

Additionally, reviews of well records and inspection reports for Tioga Gas Storage Field wells reveals potential mechanical integrity issues for some of the storage field wells. Inspection reports document gas venting from the annuli of some the storage field wells. Gas venting from the annulus of storage field wells is not a normal condition and requires further evaluation (Craig Lobins, Northwest Regional Office Oil & Gas Manager pers. communication). Finally, as in any investigation in Pennsylvania where domestic water wells are used for collection of samples, detailed drilling records are not always available for the wells. This was the case for many of the water wells in this study. Hence, without expensive and invasive borehole tests, a detailed understanding of the gas occurrence in the aquifers could not be developed using the available well data. Moreover, the distinction between bedrock and outwash is equivocal. Many of the bedrock wells are completed just below the depth of glacial overburden; gases could migrate through the glacial overburden to the bedrock and vice versa.

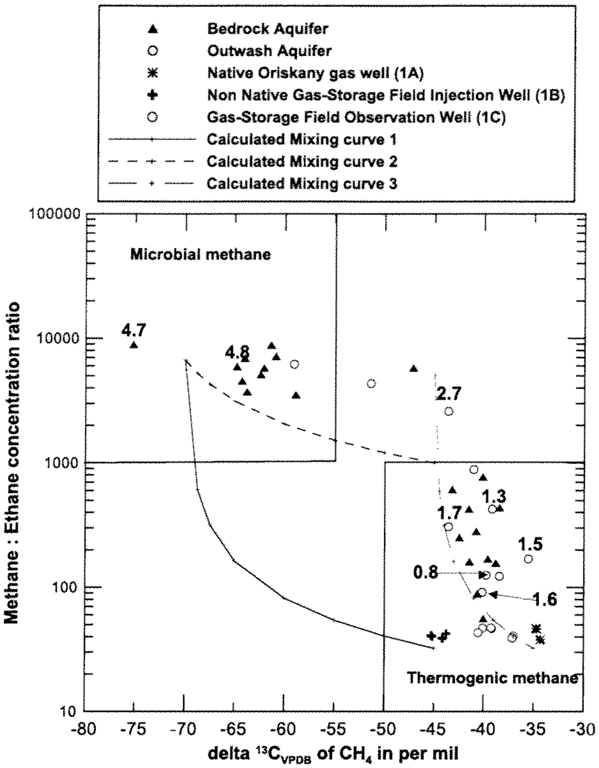

Fig. 13. Bernard plot (Bernard et al., 1976) of the $\delta^{13}C$ of CH_4 in relation to the ratios of CH_4 concentration to C_2H_6 concentration with theoretical mixing curves and for gas-well and water-well samples collected in June–August 2005, Tioga Junction and vicinity, Tioga County, Pennsylvania (data from Breen et al. (2007)). Mixing curve 1 is calculated using compositions of the measured two extreme end members: $\delta^{13}C$ of CH_4 −70‰ and −45‰, and C_2H_6 concentrations 0.015% and 3%, respectively. Mixing curve 2 was created by using the same $\delta^{13}C$ of CH_4 end members as mixing curve 1, but the C_2H_6 concentrations end members were 0.015% and 0.1%. Mixing curve 3 was created by using $\delta^{13}C$ of CH_4 −50‰ and −45‰ end members, and C_2H_6 concentrations 0.1% and 3% respectively. Labels are ^{14}C data of CH_4 in pMC.

The addition of wells with construction designed to target specific depths in the two aquifers would likely provide better data on gas origin and source in groundwater. Future sampling for study of combustible gases needs to include a more complete set of major and minor element analyses of groundwater to complement the isotopic geochemistry. Temporal sampling designed to correspond with seasonal operations and pressure variations in the gas-storage fields is also recommended for future investigation.

6. Summary

1. Similar volume percentages for gas chemical compositions overall (95–97% CH_4 and 2–2.5% C_2H_6) prevented differentiation of the native natural gas occurring at depths of about 1220 m in the Oriskany Sandstone (1A) and the non-native gas (1B) imported by pipeline and injected into a gas-storage field in a depleted Oriskany Sandstone gas reservoir. Isotopic compositions of C and H in CH_4 and of C in C_2H_6, however, were different. The CH_4 in Oriskany gas (1A) has a median $\delta^{13}C_{CH_4}$ of about −34.54‰ and δ^2H of about −158.35‰; the $\delta^{13}C$ of its C_2H_6 is about −40.42‰. The non-native gas (1B) injected into the gas-storage field is of a different source and has a median $\delta^{13}C_{CH_4}$ of about −44.47‰, δ^2H of about −168.78‰, and the $\delta^{13}C$ of its C_2H_6 is about −30.24‰. The isotopic composition of the gas from the storage-field observation well (1C) is $\delta^{13}C_{CH_4}$ = −38.86‰, $\delta^2C_{CH_4}$ = −167.70‰, and $\delta^{13}C_{C_2H_6}$ = −33.94‰ and is intermediate in composition to the native gases from wells producing from the Oriskany Sandstone (1A) and the imported non-native gases (1B) injected into the storage field.
2. Methane and C_2H_6 were the only hydrocarbon gases detected in headspaces of groundwater samples from two aquifers used for water supply at Tioga Junction, Tioga County, Pennsylvania. Combustible gas was detected in 49 of 91 water wells inventoried—36 of 62 wells in the bedrock aquifer and 13 of 29 wells in the outwash aquifer. Groundwater CH_4 concentrations greater than 10 mg/L (about 25 vol.% in headspace), a lower threshold for dangerous concentrations of CH_4 in groundwater, were measured in 26 of the 49 wells.
3. Based on isotopic evidence, CH_4 of microbial origin with trace or no associated C_2H_6 is chiefly in groundwater from bedrock-aquifer wells overlying the flanks of the Sabinsville anticline —10 overlying the northern flank, north and east of the gas-storage field and 3 overlying the southern flank, south and east of the gas-storage field. In these groundwaters, $\delta^{13}C_{CH_4}$ ranges from −75.18‰ to −58.92‰ and $\delta^2C_{CH_4}$ ranges from −266.4‰ to −180.7‰. Marsh or swamp gas and landfill microbial gases were ruled out as sources based on ^{14}C activity of CH_4 at < 5 pMC. Microbial CH_4 in groundwater from bedrock-aquifer wells shows evidence of mixing of CH_4 from acetate fermentation and CO_2 reduction processes. One well in the outwash aquifer had microbial gas that is likely from *in situ* degradation of organic material in the outwash. Fractionation of thermogenic gases through oxidation or diffusion would not lead to the observed isotopic composition in these 14 wells. Data for $\delta^{13}C_{DIC}$ also indicate that *in situ* processes likely form the microbial CH_4.
4. Isotopic evidence shows CH_4 of thermogenic origin co-occurring with C_2H_6 of thermogenic origin in groundwater from bedrock and outwash-aquifer wells—12 clustered at Tioga Junction near the eastern edge of the gas-storage field along the axis of the Sabinsville anticline and 3 overlying the southern flank of the Sabinsville anticline south of Tioga Junction. In these groundwaters, $\delta^{13}C_{CH_4}$ ranges from −51.37‰ to −35.54‰, $\delta^2C_{CH_4}$ ranges from −208.0‰ to −105.9‰, and $\delta^{13}C_{C_2H_6}$ ranges from −39.03‰ to −28.73‰. Methane of thermogenic origin also occurs in two bedrock-aquifer wells that overlie the axis of the Sabinsville anticline west of Tioga Junction.
5. Comparing the $\delta^{13}C_{CH_4}$ and $\delta^2C_{CH_4}$ results for samples collected in 2005 with samples collected in 2007 from 11 water wells (2 wells in the outwash aquifer and 9 wells in the bedrock aquifer) revealed nearly identical gas compositions.
6. The isotopic characteristics of thermogenic CH_4 and C_2H_6 in groundwater most closely match the characteristics of CH_4 and C_2H_6 in the observation wells (1C) at the eastern edge of the Tioga gas-storage field. The cluster of 12 water-supply wells at the eastern edge of the gas-storage field suggests enhanced gas migration from depth along the axis of the Sabinsville anticline possibly associated with subsurface fractures and possibly complicated by improperly plugged, leaking, or abandoned gas wells in an area with numerous abandoned gas wells and exploratory boreholes.

7. Conclusions

The sudden onset in 2001 of dangerous levels of combustible gas in water-supply wells, and the persistence of dangerous levels after efforts to plug abandoned gas wells, prompted this investigation of gas origin and source. The investigation was complicated by several possible sources of hydrocarbon gases with native and non-native origins. Through fieldwork and evaluation of laboratory data for gas molecular composition, stable and radioactive isotopes, it was established that groundwaters had evidence of both thermogenic and microbial CH_4 gas origins. The source of natural gases in those well waters with thermogenic CH_4 appears to be gases with the same source as gases in the storage field observation wells from storage fields (1C). It was also established that microbial CH_4 in groundwater from one well sampled twice had an isotopic signature that had not changed between 2005 and 2007. Thermogenic CH_4 in groundwaters from 10 wells sampled twice indicated that the CH_4 is migrating into the aquifers from a source reservoir that is changing little with time. The lack of variation over time also suggests that neither chemical reaction nor fractionation by microbial or physical processes had changed the gases observed in the aquifers in 2005 to different compositions in 2007.

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