STABLE ISOTOPE FORENSICS AS A MEANS OF IDENTIFYING THE SOURCE OF METHANE IN A DOMESTIC WATER WELL, CADDO PARISH, LOUISIANA

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This report presents the results of Geosyntec's assessment of the occurrence of natural gas discharging with groundwater from a domestic well owned Mr. John Parker of the community of Dixie, Caddo Parish, Louisiana. Anadarko Petroleum Corporation (Anadarko), in coordination with the Louisiana Department of Natural Resources, engaged Geosyntec in December 2013 to conduct an investigation into the source or sources of the gas in response to the landowner's concern that nearby wells owned by Anadarko and completed in the Haynesville Formation were the possible sources of the gas in his water well (Shirley, 2013).

OBJECTIVES

Geosyntec proposed a program of work designed to address the matter through the application of geochemical methods that are well established and widely used in the resolution of problems involving sources of natural gas, differentiation of gases, and the occurrence of natural gas in groundwater. The findings and opinions expressed in this report are based on Geosyntec's evaluation of the following:

- mole percentages of dissolved gas in groundwater from two Wilcox Formation water wells;

- mole percentage of fixed gases, carbon dioxide (CO_2), and C1 – C6+ (methane – hexane-plus) in produced gas from three Haynesville Formation wells;

- abundances of the carbon and hydrogen isotopes, carbon-13 (^{13}C) and deuterium (D), from Wilcox dissolved gas and Haynesville produced gas; and

- major-ion chemistry, specifically sulfate concentrations, and measurements of reduction-oxidation potential (redox or ORP) from the two Wilcox water wells.

Note the hydrocarbon naming convention represents the number of carbon atoms in a particular hydrocarbon (e.g., C1 indicates a hydrocarbon with one carbon atom [methane] and C6+ indicates a hydrocarbon with six or more hydrocarbon atoms [hexane-plus]).

**BASIS FOR GEOSYNTEC'S PROPOSED ANALYTICAL PROGRAM**

Natural gases can be differentiated on the basis of normalized mole percentages of the C1 – C6+ hydrocarbons and the abundances (that is, stable isotope ratios) of carbon-13 ($^{13}C/^{12}C$) and deuterium ($^{2}H/^{1}H$ or $D/^{1}H$) with respect to the C1 fraction. Furthermore, natural gases can be divided into two types: (1) microbial [biogenic] and (2) thermogenic. Biogenic gases form at shallow depths through microbial activity by two methanogenic pathways (Chappelle, 1993; Kehew, 2001):

Reduction of CO_2

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

and

Acetate fermentation

$$CH_3COOH \rightarrow CO_2 + CH_4$$
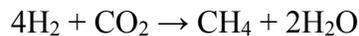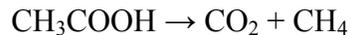
The first process, CO_2 reduction, is common in environments in which nitrate, ferric iron, and sulfate have been consumed as electron acceptors by microbial metabolism. The reduction of CO_2 occurs as the final step in this microbial pathway to the generation of methane (Kehew, 2001). This is a common factor underlying the formation of methane in groundwater systems. The second process, acetate fermentation, is more characteristic of the generation of natural gas in landfills and wetlands. It occurs through the degradation of acetate or acetic acid by fermentative bacteria (Kehew, 2001). Pure biogenic gases are dominated by methane (characteristically 99 mole percent). Such gases typically lack heavier components other than minor ethane, and are considered to be "dry."

Thermogenic gases form at greater depths (hence, under higher temperature-pressure regimes) than biogenic gases, by the thermal cracking of sedimentary organic matter into gases and liquid hydrocarbons. Although thermogenic gases can be dry, most contain significant fractions of ethane (C2), propane (C3), butanes (C4), pentanes (C5), and hexanes C6).

With regard to isotopic composition, the methane component of biogenic gas is relatively more depleted with respect to ^{13}C and D than that of thermogenic gases – that is, the stable isotope ratios ($\delta^{13}C$ and δD) of biogenic methane are more negative than those of thermogenic methane (Kehew, 2001). The differences in isotope abundance are related to the composition of the source(s) and the process(es) that fractionate the isotopes of the elements that make up the source.

The modern international standard for reporting the abundance of ^{13}C is Vienna-Pee Dee Belemnite, or V-PDB; and the standard for abundance of D is Vienna-Standard Mean Ocean Water, or V-SMOW (Mazor, 1997). Isotope abundance is expressed as deviation from a standard

in units of parts per mil. Because, hydrocarbons are depleted in ^{13}C and D with respect to V-PDB and V-SMOW (that is, hydrocarbons are enriched in carbon-12 [^{12}C] and protium [^{1}H] compared with ^{13}C and D), $\delta^{13}C$ and δD values of hydrocarbons are negative with reference to their respective standards.

The analysis of the compositions (in molar percentages) of gases and the isotopic compositions of gases are highly effective means of differentiating between biogenic and thermogenic gases. Grossman and others (1986 and 1989), for example, have demonstrated that biogenic gases of Eocene formations of the Texas Gulf Coast are characteristically dry compared with thermogenic gases from Tertiary and Cretaceous reservoirs of the same region.

The distinction between biogenic (microbial) gases and thermogenic gases is also illustrated by a simple plot of the $\delta^{13}C$ vs δD values of methane (Figure 1). On such a figure, the $\delta^{13}C$ vs δD values of purely microbial gases should plot within the fields designated "CO_2-reduction" and "acetate fermentation," and purely thermogenic gases should plot within the "thermogenic" field in the upper right corner of the diagram.

The above geochemical factors underlie Geosyntec's approach to the evaluation of the origin of natural gas in the landowner's well. Specifically, it is Geosyntec's hypothesis that the samples of gas from the water well should differ from Haynesville gas samples both with respect to overall composition and $\delta^{13}C$ and δD values if there is no communication between Wilcox and Haynesville gas reservoirs. Overlapping signatures outside of the fields demarcated in Figure 1 might reasonably be interpreted as a result of the mixing of gases from both sources.

Factors related to major-ion chemistry and ORP should also come into play if biogenic processes are accountable for the generation of methane. As noted above, CO_2 reduction becomes the operative process in the generation of methane after sulfate is exhausted by anaerobic respiration (Kehew, 2001). In such cases, the concentration of sulfate in groundwater should be low (Zhang and others, 1998), and measurements of ORP should be negative owing to reduction of CO_2.

COLLECTION OF SAMPLES

Overview

Representatives of Geosyntec met with representatives of Anadarko on 6 December 2013 to collect groundwater water samples from the landowner's well and to survey Haynesville gas wells to be sampled after the wells were in production. A representative of Geosyntec returned to Caddo Parish to collect samples of groundwater from another Wilcox well on 18 December 2013. Representatives of Southern Petroleum Lab (SPL) of Carthage, Texas and Anadarko collected samples of produced gas from three Haynesville wells on 16 December 2013. The Haynesville wells are the following: Comegys 32-29H, Comegys 6-7H, and Volentine 5-33H. Two samples were drawn from each of the Comegys wells. The locations of the two Wilcox water wells and the three Haynesville gas wells are shown in Figure 2.

Sampling of Wilcox Water Wells

The groundwater sampling method involved monitoring and recording of temperature, conductivity, pH, dissolved oxygen, and oxidation-reduction potential (ORP) before samples were collected. At each well, water was diverted through a flow line to a closed flow cell with probes attached to a calibrated YSI meter. The above variables were recorded on field data sheets at five-minute intervals until the measurements became stable – that is, until the variables changed by approximately five percent (plus or minus) over two consecutive five-minute intervals.

After the variables were determined to be stable, the flow line was removed from the flow cell and the flow of water to the line was shut off at the outflow valve to which the flow line was attached. A 0.45-micron filter pack was attached to the end of the flow line and the outflow valve was re-opened, allowing water to flow through the line again and to charge the 0.45-micron filter. Filtered water was then discharged to a 0.5-L Nalgene bottle to which nitric acid had been added by the laboratory. That sample was designated for analysis of metals. A second 0.5-L Nalgene bottle without nitric acid was filled. That sample was marked for analysis of non-metals. Each filled and marked sample container was placed inside a chilled ice chest. The flow-cell data for each well are found in Attachment A.

After the above samples were collected, the flow of water was shut off at the tap, the flow line removed and then replaced with a specially designed attachment with a flow line and valve designed to transfer water to an Isoflask$^©$ bladder used for the collection of groundwater samples for analysis of dissolved gas and stable isotopes of dissolved gas. After water flowed through the new line for one minute, the valve was inserted into the flask. The flow line was removed from the flask when the container expanded to a thickness of approximately 2 inches. A check valve prevented water and gas from leaking from the filled flask.

Sampling of Haynesville Gas Wells

At each sampling location, a stainless steel cylinder was attached to an outflow valve at the wellhead. After the outflow valve was opened, gas flowed through the cylinder for 30 seconds or longer. Closure of a ball valve at the top end of the cylinder allowed the cylinder to fill until the gas was under sufficient pressure to allow for extraction at the laboratory.

Each cylinder was marked with Anadarko's official designation for the sampled well, and the filled cylinders were placed in a box designed for the shipment of hazardous gas.

Sample Shipping

Geosyntec delivered all samples of groundwater designated for analysis of major cations and anions, along with chain-of-custody forms, within 24 hours to Accutest Labs, Lafayette, LA. Geosyntec also shipped, by way of Fedex, the filled Isoflasks to Isotech Laboratories, Inc.

(Isotech), Champaign, IL. Personnel with SPL arranged for shipping of the gas-filled cylinders to Isotech.

ANALYSIS OF GAS FRACTIONS

The mole percentage of gases from the two water wells and the three natural gas wells are illustrated by Figure 3. Dissolved gas samples from both water wells have significant mole percentages of argon (Ar), oxygen (O_2), nitrogen (N_2), and carbon dioxide (CO_2). With respect to the C1 - C6+ hydrocarbons, C1 is the dominant gas in samples from the Parker (77.14 mole percent) and Thomas (52.46 mole percent) wells. The dissolved gases, however, are deficient with respect to C2 and heavier hydrocarbons.

The samples of thermogenic gas from Haynesville wells range from 78 to 88 percent C1, with N_2 and CO_2 as significant non-hydrocarbons. These samples yield measureable C2 - C6+ fractions.

The differences between the dissolved gases and the thermogenic gases are further highlighted when only the C1 - C6+ fractions are considered and those fractions normalized to 100 percent (Figure 4). Figure 4 illustrates that the normalized hydrocarbon component of the dissolved gases is more than 99 percent C1. Although C2 and C3 hydrocarbons are present in samples from both the Parker and Thomas wells, those fractions are less than 0.10 mole percent of the hydrocarbon mass. Both samples are representative of "dry" gas.

Compared with the samples of dissolved gas from the Parker and Thomas wells, the produced Haynesville samples are "wet" – that this, there are significant hydrocarbon components other than C1 (Figure 4). With respect to the C1 – C6+ fractions of the Haynesville gas samples, methane accounts for 82 to 91 percent of the normalized fractions. Hydrocarbons in the C2 – C6+ range are measureable in all samples, with C2 accounting for 5.4 to 10.5 percent and C3 from 1.7 to 3.7 percent.

Stable Isotope Ratios

The $\delta^{13}C$ and δD signatures of dissolved gas from the Parker and Thomas wells and thermogenic gas from the Haynesville wells are plotted in Figure 5. The Haynesville samples form a cluster of points defined by $\delta^{13}C$ values of -40.97 to -44.21$^0/_{00}$ (PDB), with associated δD of -169.1 to -187.2$^0/_{00}$ (V-SMOW). These points lie well within the thermogenic gas field. The samples of dissolved gas from the Parker and Thomas wells yielded $\delta^{13}C$ of -64.55 to -68.65$^0/_{00}$ (PDB) and δD of -202.6 to -202.8$^0/_{00}$ (V-SMOW). All of the points plot within the CO_2-reduction field. The isotopic data further underscore that the gas samples were derived from different geochemical reservoirs, one biogenic, and the other thermogenic.

GROUNDWATER CHEMISTRY

The hydrochemical composition of each sample is sodium:chloride-bicarbonate, as illustrated by a Durov diagram (Figure 6). The basis of the Durov diagram (Zaporezec, 1972) is percentage plotting, in separate trilinear diagrams of cations and anions in units of millequivalents per liter (meq/L). Lines from each pair of points in the cation and anions triangles are projected into the central rectangle to form a common point, which represents the overall composition of the samples. The additional fields representing pH and total dissolved solids also allow for additional comparison/differentiation of samples.

The Durov diagram is an effective format for comparing the hydrochemical compositions of samples from two or more wells. With regard to Figure 6, both points plot near the Na + K corner of the cation trilinear diagram and midway between the Cl and the HCO_3 + CO_3 corners of the anion diagram. The location of the cross-plotted points on that baseline of the anion diagram also indicates that sulfate (SO_4) is not a significant anionic component in either sample of groundwater. The cross-plotted locations in the square between the trilinear diagrams represent composition with respect to cations and anions. Total dissolved solids are calculated at approximately 1,100 to 1,300 mg/L, with pH of 7.6 to 7.8.

Among the laboratory analytes, sulfate is the most significant with respect to identifying CO_2 reduction as the geochemical process accounting for the occurrence of methane in Wilcox groundwater. Zhang and others (1998), for example, studied the distribution of methane based on water samples from 40 wells in aquifers of the east-central and central regions of Texas. The authors observed an inverse relationship between concentrations of sulfate and methane in east-central Texas aquifers. They also observed low methane concentrations in central Texas aquifers for which concentrations of dissolved oxygen and sulfate were high. The authors concluded that methane production does not begin until sulfate is depleted. This is consistent with the well-known "redox ladder" (Figure 7), which illustrates the sequence within which redox products are generated in aqueous environments ranging from "oxic" to "reducing."

With respect to this investigation, sulfate concentrations range from not-detected (Parker) to 10.7 mg/L (Thomas). The concentration reported for the Thomas well is within the range of sulfate concentrations associated with elevated methane, as reported by Zhang and others (1998).

That reduction is a factor driving the generation of methane in the Wilcox is also found in the redox measurements. The final ORP measurements before samples were drawn for analysis by Accutest were -210.4 millivolts (mV) and -248.1 mV (Parker and Thomas, respectively). The negative ORP values recorded for each sample indicate reducing conditions within the groundwater system at each location.

The redox ladder (Figure 7) illustrates the association between ORP (as measured in millivolts (mV) and different redox species. Under more oxidizing to moderately reducing conditions (that

is, between +600 to 0 mV), the reduction sequence is oxygen → nitrogen → manganese → iron. For negative values of ORP, sulfate and then carbon dioxide undergo reduction, leading to the formation of sulfide and then methane as ORP becomes increasingly negative.

LIGNITE AS A SOURCE OF METHANE IN GROUNDWATER

Lignite, a source of methane in sedimentary formations, is common in Tertiary formations of the Gulf Coast, especially the Wilcox Formation (Grossman and others, 1986 and 1989; Carlson (2007) and Carlson and Horn (2011). Grossman and others (1989) also found that CO_2 reduction is the principal pathway by which methane forms in aquifers of east-central Texas. In a summary document on lignite in north Louisiana aquifers, Carlson (2007) comments as follows:

> A number of northwestern Louisiana parishes have over 30% of their water wells including an identification of lignite within the borehole. So, as a result in northwestern Louisiana there are approximately 500 domestic wells that contain lignite within the well's screened interval, plus another 2,000 domestic wells that contain lignite within the boring log of the well.

Carlson also calculates that at least 34 percent of domestic wells in Caddo Parish include at least one lignite interval. With reference to the occurrence of methane in the Wilcox aquifer, Carlson and Horn (2011) found that average head-space methane (AHSM) in 447 samples of groundwater from wells in southern Caddo, southern Bossier, and northern DeSoto parishes were unrelated to proximity to oil and gas activity. They considered five factors in the investigation:

1. location;
2. depth to sand;
3. sand seam a well in screened in;
4. proximity to lignite in the aquifer;
5. and number of oil and gas wells in the same section as the water wells.

Carlson and Horn (2011) also subdivided number 5 above into a) wells drilled before 1950 and b) recent Haynesville shale gas wells. They reported the results of the investigation as follows:

> Results also show that oil and gas exploration and production in the study exert little or no influence on AHSM in the study area. The AHSM in nine sections with 3-4 Haynesville wells is ~-.5 the AHSM in 74 sections that have no Haynesville wells. Furthermore, the AHSM in 31 sections with 0-1 older oil and gas wells is ~2 times that of AHSM in 22 sections with more than 20 older oil and gas wells. However, where the screen position is known AHSM is ~4 times greater in the lower sand than in the upper sand. AHSM for wells with lignite in the screen interval is ~2.5 times that for wells that lack lignite. These imply a stronger relationship between AHSM and aquifer geology than proximity to oil and gas activity.

Information provided to Anadarko by Mr. Roger Presley (Presley & Son Water Wells, Blanchard, Louisiana) for Mr. Parker's well includes completion and lithologic data. The well was drilled in February 2002 to a total depth of 127 feet and screened over the interval 77 – 127 ft. Within the screened interval is a 23-ft thick section (77 - 100 ft) described as a "mixture of sand, sandy shale and soft lignite" and a 10-ft thick section (100 - 110 ft) described as "primarily lignite with streaks of sand." In the section immediately above the screened section (70 - 77 ft), Mr. Presley describes a 7-ft thick section of "shale and lignite." Included in the material is the driller's comment that "the well had a very strong sulfur smell." The "strong sulfur smell" noted by the driller is a function of the reduction of sulfate to sulfide, the step on the redox ladder preceding the generation of methane by CO_2 reduction (Figure 7).

SUMMARY OF FINDINGS AND CONCLUSIONS

Dissolved gas from Mr. Parker's water well does not have the composition of produced gas samples from nearby Haynesville Formation wells completed by Anadarko. The samples of gas from the well are dominantly methane (C1), with very minor components of ethane and higher hydrocarbons (C2+). Samples of Haynesville gas are composed of hydrocarbons from the methane through hexane-plus range (C1 – C6+). Ms. Thomas' well also yields dissolved gas fractions similar to that of gas from Mr. Parker's water well. The dissolved gas samples are both "dry", whereas the Haynesville samples are "wet."

The dissolved gas and produced gas samples are further differentiated from each other on the basis of the signatures of the stable isotopes ^{13}C and D for the methane (C1) fraction. The signatures ($\delta^{13}C$ and δD) of the dissolved gas samples are significantly more negative with respect to both isotopes than are those of the Haynesville gas samples. The more negative (lighter) isotope values of the Parker and Thomas C1 fractions are consistent with the formation of methane by means of CO_2 reduction.

In stark contrast with the samples of dissolved gas from the Wilcox, all samples of Haynesville gas yielded C1 fractions with $\delta^{13}C$ and δD values that are well within the range of isotope ratios traceable to the formation of natural gas in high-temperature, high-pressure environments. Gas formed under such conditions is considered to be of "thermogenic" origin. The Haynesville samples also yielded C2 – C5 fractions for which measurements of $\delta^{13}C$ were made. This was not possible with respect to any of the dissolved gas samples. On a plot of $\delta^{13}C$ vs δD, the separation between the dissolved gas samples and the Haynesville samples is definitive.

Measurements of ORP made at the time of the collection of groundwater samples from the water wells and laboratory analyses of the concentrations of sulfate highlight the role of bacterial activity as the factor underlying the formation of methane. The test of whether these conditions are met is the combination of negative ORP measurements and low concentrations or non-detects reported for sulfate. Both conditions are met with respect to the Parker and Thomas wells.

As a last matter in this investigation, the driller's log of Mr. Parker's well includes references to three lignite intervals, two of which are within the screened section of the well. It is Geosyntec's opinion, that the lignite is the principal source of organic matter to support the formation of methane in the Wilcox Formation.

The data that form the basis of the above analysis militate very strongly against a thermogenic origin for the occurrence of natural gas in Mr. Parker's well. The mole fractions are consistent with dry gas generated by CO_2 reduction. This is supported by $\delta^{13}C$ and δD values that indicate hydrocarbon formation under subsurface conditions very different those in which thermogenic gas forms. The heavier (that is, less negative) isotope signatures of the Haynesville samples are well within the range of isotope ratios observed for thermogenic gases of the northern Gulf Coast (Grossman and others, 1986; Darling, 2009). The lighter (more negative) signatures of the dissolved-gas samples, are by contrast, fully consistent with gases that form as a result of biogenic activity. The occurrence of methane in both water wells underscores the likelihood that methane generation is a common process in the Wilcox aquifer of Caddo Parish.

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