

28 December 2012

Report on gas sampling on the Red Creek and Red River, Oklahoma: 12-December-2012
Prepared by USEPA/ORD/NERL-ESD/ECB/T.L. Jones-Lepp

On September 26, 2012, the State of Oklahoma Department of Environmental Quality (OK DEQ) contacted USEPA Region 6 to provide assistance to determine the source (biogenic vs. thermogenic) of stray gases bubbling in the Red Creek and Red River (near vicinity of Ketchum's Bluff, OK). On September 26, 2012 Region 6 contacted ORD (NRMRL) for support with this request. On October 31, 2012 ORD/NERL-ESD received a request for assistance from NRMRL to assist Region 6 and OK DEQ. The area around Ketchum's Bluff (Red River, OK) had previously been the site of three recent fish kills (July and September 2011, and June 2012). During the fish kill events Region 6, and ORD (NERL-ESD/ECB), had provided laboratory support for water analyses of unknown toxins.

On November 27, 2012 ORD (NERL-ESD/ECB, Jones-Lepp) arranged with a private company, Isotech Laboratories (Champaign, IL), to perform a chemical composition analysis of the stray gas, as well as, isotope analysis ($\delta^{13}\text{C}$ and δD) of the methane present in the samples.

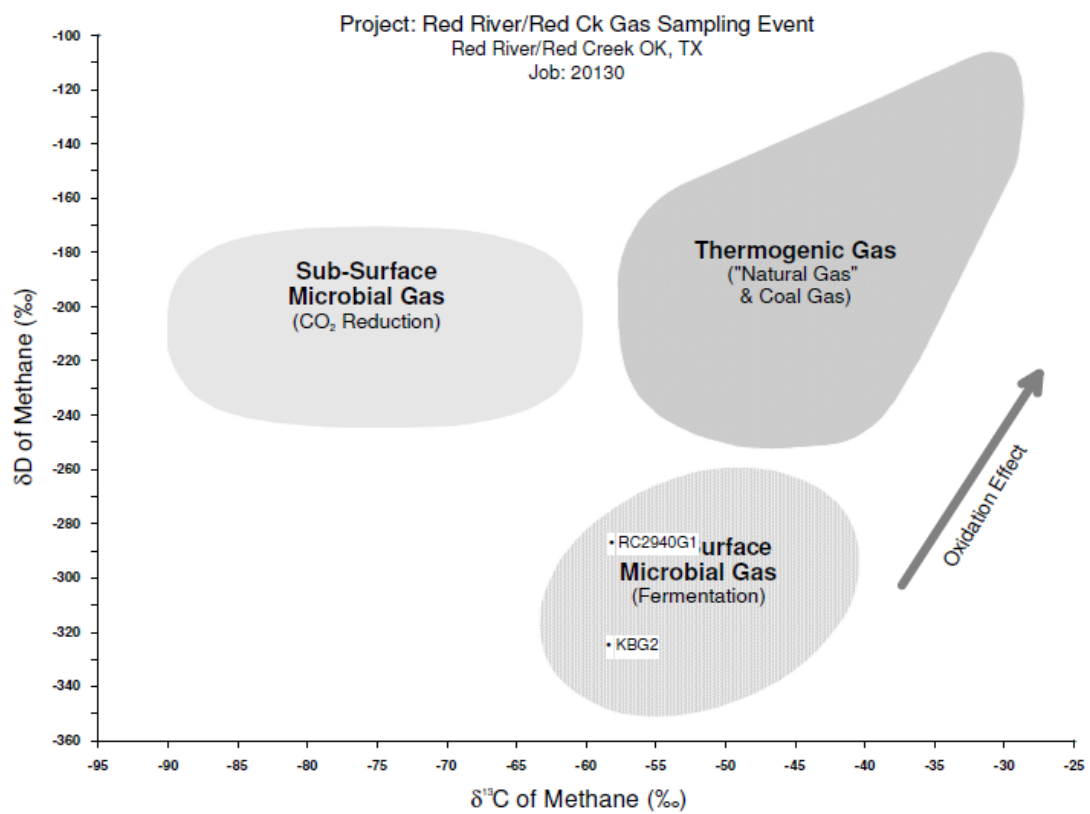
On November 28, 2012 Isotech shipped 4 sampling jars (IsoJars), along with an SOP (Appendix A) on sampling stray gas emissions to OK DEQ. On December 12, 2012, OK DEQ, along with personnel from EPA Region 6, went into the field and collected 4 stray gas samples; two from each site selected by OK DEQ and Region 6 (hereafter named G1 and G2). The samples were shipped overnight to Isotech and were received by Isotech on December 13, 2012.

The samples were subsequently analyzed and the report was sent on December 26, 2012 to ORD (NERL-ESD/ECB/Jones-Lepp). A brief outline of the methods and QA procedures followed by Isotech are attached (Appendix B). Following is a synopsis of the Isotech report and the actual report results are attached (Appendices C and D).

Results and Conclusions

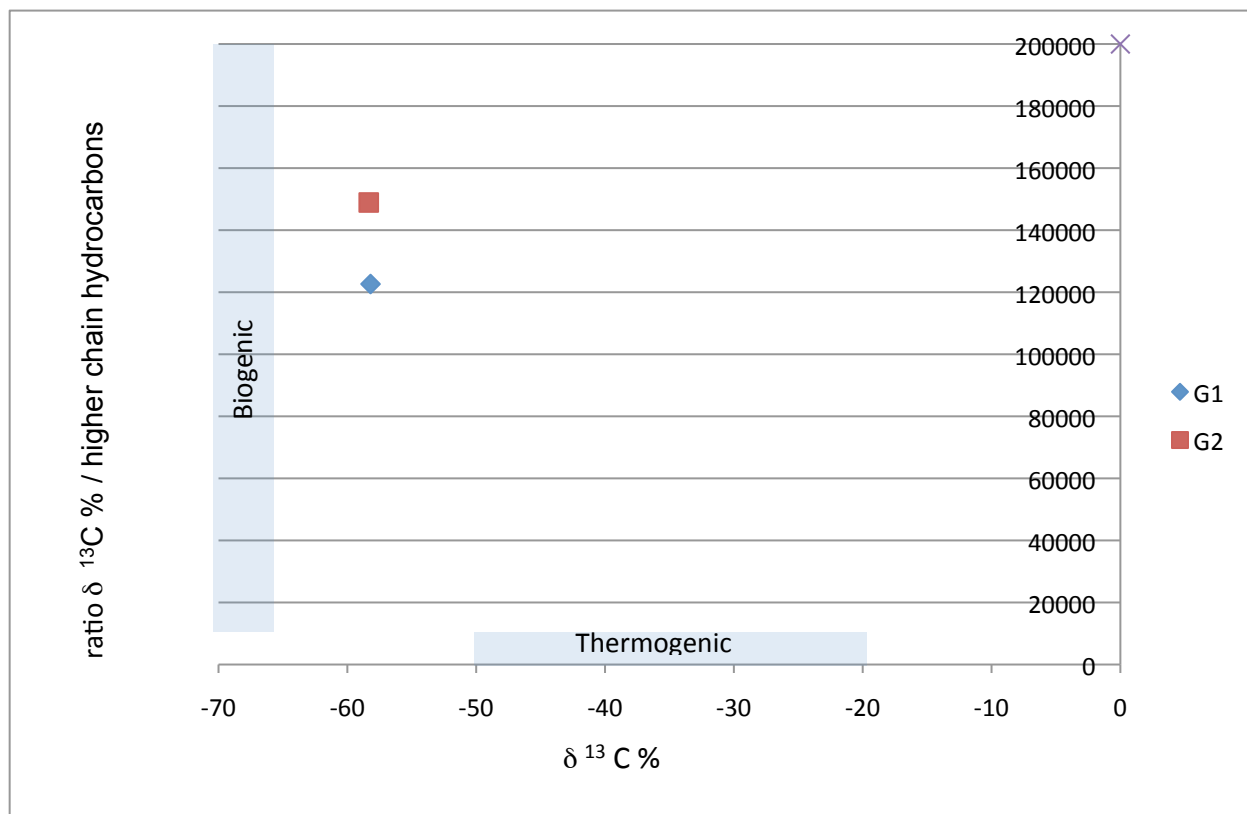
Reviewing the plot provided by Isotech, figure 1. The figure shows that the gasses emitted from sites G1 and G2 both fall into the microbial (fermentation) process.

Figure 1.



To confirm the Isotech results a new plot was generated using the raw data provided by Isotech and the procedure as outlined by Osborn (Osborn et al., 2011), whereby the ratio of methane to higher chain hydrocarbons vs. the $\delta^{13}\text{C}$ ‰ is plotted. The results and conclusions are the same, figure 2, the two samples, G1 and G2, plot near the biogenic region.

Figure 2.



In conclusion the results from the analyses from the two sites indicate that the stray gas samples collected, from both sites, are the result of biogenic (microbial) gas emissions.

Appendices

- A SOP for sampling stray gas, Isotech.
- B Isotech EPA QAP for Job 20130, provided by Isotech 28-Dec-2012
- C Isotech report on stray gas sample analysis, chemical composition and isotope analysis
- D Raw data spreadsheet format, Isotech

References

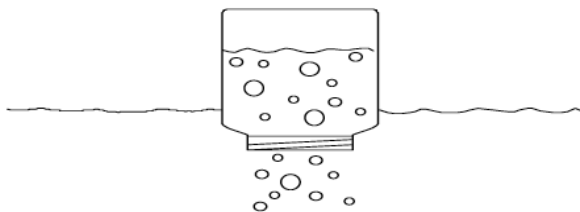
Osborn, S.G., Vengosh, A., Warner, N.R., Jackson, R.B., 2011. Methane contamination of drinking water accompanying gas-well drilling and hydraulic fracturing. *Proceedings of the National Academy of Sciences* 108, 8172-8176.

Appendix A. SOP for sampling stray gas, Isotech.

INSTRUCTIONS FOR SAMPLING GAS SEEPS WITH ISOJARSTM

Please read these instructions thoroughly before going to the field and if you do not completely understand them or if you have any questions, please call us (217) 398-3490.

1. Remove the special lid from one of the IsoJars™.
2. Submerge the jar under water so that it becomes completely filled with water and then, keeping it submerged, invert it.
3. In deep water, lift the jar so that about two thirds of it is out of the water and move it over the top of the seep as shown on the diagram below. The bubbles will accumulate in the jar and displace the water.



Note: if you can't reach the seep while holding onto the jar, you can tape the jar to a stick or pole (using electrical tape) so that it can be extended out over the seep.

4. If the gas flow is sufficient, it will be possible to completely fill the jar with gas, but leave a little bit of water in the jar, to provide a liquid seal. If the seep is very slow, an attempt should be made to fill the jar at least half full of gas, preferably three fourths full.
5. When sufficient gas has been collected, continue to hold the jar under water in an inverted position, then place the lid onto the jar.
6. Wipe the jar dry, identify the source of the sample on the jar label. If the samples can not be shipped the same day they are collected, store them upside-down in a refrigerator to prevent bacterial activity which can alter the gas composition.
7. Return the inverted jar to the shipping container and when all samples are collected, seal the plastic bag around the samples (this is protection in case one of the jars should leak or get broken; shippers get very nervous when they see liquid running out of a box) and ship them to Isotech via overnight.

Isotech Laboratories, Inc.
1308 Parkland Court
Champaign, IL 61821

1. Gas Chromatographic Analysis of Gases

A. Analysis of hydrocarbons

Equipment Shimadzu 2010 Gas Chromatograph. This (complete) GC system is equipped with two 2010 instruments; one containing a thermal conductivity detector (TCD) and a flame ionization detector (FID), and the other containing dual TCD's. Data processing is done on GC solutions software and a personal computer.

Method/Procedure The sample loop on the GC is evacuated between each sample. Samples are injected into the evacuated sample loop and adjusted to atmospheric pressure. Sample identification is entered into the GC solutions software and the run is initiated.

The Shimadzu 2010 and 2014 utilizes several different packed columns and valve switching to separate the various components. Instrument configuration was designed by Shimadzu specifically to meet the requirements of Isotech. Helium is used as the carrier gas. All valve switching during the analysis is computer-controlled. The resulting component peak areas are then quantified by the software (given raw percent values) by comparing them to previously run standards. The lab technician checks the raw total for each analysis to ensure that all components have been detected. The raw total can vary from day to day depending on atmospheric pressure, with acceptable raw totals of 96% to 104%. The lab technician also checks all baselines for accuracy from the chromatograms shown on the computer screen. This raw computer record is maintained for each sample corresponding to its individual lab number. The raw percentage values for each sample are downloaded into the main sample database, and are normalized to 100% when the Analysis Report is generated.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. Septa in the sampling valves are replaced as needed.

Calibration/Standardization Multiple reference gases are used for standardization of the Shimadzu gas chromatographs. All standards are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The minimum and maximum concentration used for calibration cover the range of the majority of natural gases submitted for analysis. At least four points are used for each component. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the GC Solutions software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis.

Reference Samples The reference sample used as the 1st run of each day and every tenth sample thereafter is representative of the majority of natural gas samples received for analysis. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a replicate. This replicate analysis is done approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the GC Solutions software.

B. Analysis of fixed gases

Equipment Shimadzu 2010 Gas Chromatograph. This GC system is equipped with two 2010 instruments; one containing a thermal conductivity detector (TCD) and a flame ionization detector (FID), and the other containing dual TCD's but quantification of fixed gases is done using only the TCD's. Data processing is done on GC solutions software and a personal computer.

Method/Procedure The procedure for analysis of fixed gases is identical to that for analysis of hydrocarbons, with one exception (for 2010 only). For separation of oxygen and argon, an external column on the Shimadzu 2010 is used. This column operates at -78°C ; therefore a dewar of dry ice/isopropyl alcohol is placed on the column before each run. The lab technician checks all baselines to verify peak integration. The Shimadzu 2014 system is not equipped with the external column, thus argon and oxygen values are reported as one value. Also the 2014 system cannot detect helium and can only quantify hydrogen at limited concentrations.

Maintenance GC columns are periodically baked out according to manufacturer's instructions. The septum on the injection valve is periodically replaced.

Calibration/Standardization Multiple reference gases are used for standardization of the Shimadzu gas chromatographs. All standards are analyzed on the same day during a new standardization to minimize the effects of barometric pressure variations. The minimum and maximum concentration used for calibration cover the range of the majority of natural gases submitted for analysis. At least four points are used for each component. For each new standardization, the peak area of each concentration for each compound is inserted into a table within the GC Solutions software. This table is then accessed by the software, which uses point-to-point interpolation, to determine component concentrations for gas samples during analysis.

Check Sample Multiple reference sample are used to verify instrument performance and calibration. Data obtained for reference samples and expected results based on previous analyses can be provided as part of a QA/QC report.

Replication Every tenth analysis is a duplicate. This duplicate analysis is performed approximately five samples following the check sample, thus a system check is performed at least every five analyses.

Calculation Each individual component for each sample is manually compared to the computer generated output to insure that the peak was labeled correctly and integrated correctly by the GC Solutions software.

2. Procedures for Stable Isotope Analysis of Gas Samples

$\delta^{13}\text{C}$ and δD (Carbon and Hydrogen Isotope Analysis) for Hydrocarbon Gases, Offline Prep Systems

Equipment and Supplies: 3 SRI 8610C Gas chromatographs; Evacuated transfer system; Copper oxide combustion furnace; Dry ice; Isopropyl alcohol; Liquid nitrogen; Electronic manometer; Electronic vacuum gauge; Helium; Oxygen; Gas-oxygen torch.

Method/Procedure The determination of carbon and hydrogen isotopic ratios for hydrocarbons in gas mixtures (e.g. natural gas) requires a sample preparation system capable of first separating the individual hydrocarbons and then quantitatively converting them into carbon dioxide (CO₂) and water for mass-spectrometric analysis. There are 2 systems utilized for processing natural gases. The systems employed are helium purged flow systems consisting of two major units.

The first unit consists of sample injection syringes, SRI 8610C gas chromatographs, a personal computer, and several flow-control valves. This configuration separates the hydrocarbon of interest from the sample and channels it into the combustion-collection unit. The second unit is the combined combustion-collection unit which includes quartz combustion tubes filled with cupric oxide (CuO), and vacuum lines. This system converts the hydrocarbon of interest into CO₂ and water, which are then collected and purified for isotopic analysis.

The water of combustion is transferred into a length of Pyrex tubing that has been sealed at one end and contains a weighed quantity of zinc turnings. The sample tube is sealed off for later mass spectrometric analysis. Similarly, the CO₂ is then transferred into Pyrex tubing and sealed off for later mass spectrometric analysis.

Maintenance The packed columns are baked at manufacturer's recommended temperature when peak separation decreases. At the end of every work day, O₂ is flowed through the copper oxide combustion furnaces to regenerate the CuO. Valve o-ring seals within the evacuated transfer system are replaced as necessary.

Reference Samples The system is tested by analyzing a reference sample every tenth analysis performed.

Replication A duplicate analysis of one of the samples is performed approximately every tenth analysis. This duplicate analysis is performed approximately five analyses after the reference sample analysis is performed. Therefore, a test of the system operation is performed every five analyses.

Calculation The expected yield is calculated from the injection volume and the hydrocarbon concentration

Documentation All procedural tests, sample preparations and verifications performed are recorded in bound maintenance log books. All final data including the date prepared with analyst identification are recorded on laboratory log sheets and/or in bound log books. Digital copies of all chromatograms are stored and backed up regularly.

3. Dual Inlet Mass Spectrometric Analysis

A. Measurement of ¹³C/¹²C and ¹⁸O/¹⁶O in CO₂

Equipment Finnigan MAT Delta S Isotope Ratio Mass Spectrometer

Method/Procedure Because ¹³C/¹²C and ¹⁸O/¹⁶O analyses are performed simultaneously, the procedure described here generates both measurements. A mass spectrometric analysis involves comparisons of a sample to a reference standard; in this case the comparisons are measurements of mass 44, 45, and 46, giving the both the oxygen and carbon isotopic compositions. This is accomplished by a dual inlet system where the

sample and the reference standard are measured alternately. At the beginning of each day, a reference standard is introduced into the standard side of the inlet system, and this gas is generally used for the entire session. There are two different reference standards in aluminum cylinders which are permanently mounted on the MS inlet system. The sample to be analyzed against the standard is introduced into the system via an evacuated inlet system and tube-cracker. With the inlet system fully evacuated, the sample (which is sealed into ¼" Pyrex tubing) is introduced by breaking the glass sample tube and allowing the sample to fill a variable volume bellows. Once the sample has been introduced into the MS, the actual analysis is computer controlled using equipment obtained from the manufacturer. Each analysis is given a specific reference name and/or number, utilizing the lab number as the primary reference. Final results are calculated by the manufacturer's software, and are stored on the hard drive of the computer, recorded in a bound lab notebook, and stored as the computer generated printout.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first analysis of each session is a zero enrichment, where the working standard is analyzed against itself to check machine stability. Isotope ratio determination involves multiple direct comparisons of the sample to a reference standard (generally at least 6 comparisons). Stable carbon and oxygen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta X_{(\text{sample})} = [(R_{\text{sample}} - R_{\text{standard}}) / R_{\text{standard}}] \times 1000$$

Where X represents the isotope of interest, ^{13}C or ^{18}O , and R represents the ratio of $^{13}\text{C}/^{12}\text{C}$, or $^{18}\text{O}/^{16}\text{O}$. The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech, both of which have been calibrated multiple times relative to several standards (graphite, oil, carbonates, waters, etc.) available from the International Atomic Energy Agency and the National Institute of Standards and Technology.

Replication Because of replicate sample preparations, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the software obtained from the manufacturer.

B. Measurement of $^2\text{H}/^1\text{H}$ (Deuterium/Hydrogen) in H_2

Equipment: Finnigan Delta Plus XL isotope ratio mass spectrometer; Aluminum heating block; Personal computer.

Method/Procedure The H_3 factor, which is the portion of the mass 3 signal attributable to $^1H\text{-}^1H\text{-}^1H$ (instead of $^2H\text{-}^2H$), is determined before each run early in the day and periodically throughout the day based on machine performance (if the values start drifting, a new H_3 factor is determined). The reference standard must be replenished at least once during an 8 hour period.

Water samples for deuterium/hydrogen analysis are sealed into ¼" Pyrex tubing as H_2O , along with a measured quantity of zinc. Each sample tube is labeled and reacted in a heating block at $500^\circ C$ for 35 minutes to generate hydrogen gas. Once the sample has been reacted, it is introduced into the sample side of the MS inlet system and analyzed against the working standard. Each analysis is given a unique label, using the lab number as the primary reference. Once the sample has been introduced into the MS, the analysis is computer controlled. The raw result is calculated by the manufacturer's software and recorded into a bound lab notebook, as well as being stored on computer hard disk and computer generated printout of results.

Maintenance The source region of the MS is periodically disassembled and cleaned. The filament is replaced as needed. Oil levels in mechanical vacuum pumps are checked frequently and maintained at the proper level. Turbomolecular pumps are lubricated according to the manufacturer's recommendations.

Calibration/Standardization The first run each day is a zero-enrichment where the standard is run against itself to check machine stability. Stable hydrogen isotope compositions are always reported as the difference between the ratios of the two isotopes of interest in the sample and the ratio in a primary reference standard. That is,

$$\delta D_{(\text{sample})} = [(^2H/^1H_{\text{sample}} - ^2H/^1H_{\text{standard}}) / ^2H/^1H_{\text{standard}}] \times 1000$$

The δ value is expressed in terms of per mil (‰), or parts per thousand.

In practice, the difference between the sample and an internal reference standard is measured and then the value relative to the primary standard is calculated by the instrument manufacturer's software. Two internal reference standards are used at Isotech which have been calibrated relative to several water standards available from the International Atomic Energy Agency and the National Institute of Standards and Technology.

Replication Because of replicate preparation of samples, at least 10% of all analyses are replicates.

Reference Samples Because 10% of all samples prepared for stable isotope analysis are check samples or reference samples which have been previously analyzed, these samples also serve as check samples for the mass spectrometer.

Calculation All calculations are performed by the manufacturer's computer software. The raw data is then converted to final data using a spreadsheet on a personal computer. The spreadsheets are stored on computer hard disk and a copy is attached to the raw printouts for each batch of analyses.

Appendix C pg 1: Isotech report on stray gas sample analysis, chemical composition and isotope analysis



Lab #: 323164 Job #: 20130
Sample Name: RC2940G1 Co. Lab#:
Company: USEPA-ORD
Date Sampled: 12/12/2012
Container: IsoJar
Field/Site Name: Red River/Red Ck Gas Sampling Event
Location: Red River/Red Creek OK, TX
Formation/Depth:
Sampling Point:
Date Received: 12/14/2012 Date Reported: 12/26/2012

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	δD ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Hydrogen Sulfide -----	na			
Helium -----	0.0027			
Hydrogen -----	nd			
Argon -----	0.0676			
Oxygen -----	1.04			
Nitrogen -----	2.95			
Carbon Dioxide -----	10.09			
Methane -----	85.85	-58.20	-285.7	
Ethane -----	0.0003			
Ethylene -----	nd			
Propane -----	0.0004			
Propylene -----	nd			
Iso-butane -----	nd			
N-butane -----	nd			
Iso-pentane -----	nd			
N-pentane -----	nd			
Hexanes + -----	nd			
Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 871				
Specific gravity, calculated: 0.670				

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.



ANALYSIS REPORT

Lab #: 323165 Job #: 20130
 Sample Name: KBG2 Co. Lab#:
 Company: USEPA-ORD
 Date Sampled: 12/12/2012
 Container: IsoJar
 Field/Site Name: Red River/Red Ck Gas Sampling Event
 Location: Red River/Red Creek OK, TX
 Formation/Depth:
 Sampling Point:
 Date Received: 12/14/2012 Date Reported: 12/26/2012

Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	δD ‰	$\delta^{15}\text{N}$ ‰
Carbon Monoxide -----	nd			
Hydrogen Sulfide -----	na			
Helium -----	nd			
Hydrogen -----	nd			
Argon -----	0.152			
Oxygen -----	2.52			
Nitrogen -----	6.63			
Carbon Dioxide -----	1.35			
Methane -----	89.35	-58.34	-323.5	
Ethane -----	0.0004			
Ethylene -----	nd			
Propane -----	0.0001			
Propylene -----	nd			
Iso-butane -----	nd			
N-butane -----	nd			
Iso-pentane -----	nd			
N-pentane -----	nd			
Hexanes + -----	0.0001			

Total BTU/cu.ft. dry @ 60deg F & 14.73psia, calculated: 906

Specific gravity, calculated: 0.610

nd = not detected. na = not analyzed. Isotopic composition of hydrogen is relative to VSMOW. Isotopic composition of carbon is relative to VPDB. Calculations for BTU and specific gravity per ASTM D3588. Chemical compositions are normalized to 100%. Mol. % is approximately equal to vol. %.