Investigation of Occurrences of *tert*-Butyl Alcohol in Raton Basin Groundwater, Huerfano and Las Animas Counties, Colorado

COGCC Special Project #2130

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Executive Summary

Beginning in July 2013, the Colorado Oil & Gas Conservation Commission (COGCC) implemented a special project to investigate the occurrence of *tert*-butyl alcohol (TBA) in groundwater produced from aquifers in the Raton Basin. The presence of TBA in Raton Basin groundwaters was documented in samples collected by COGCC in parallel with a national study of hydraulic fracturing being performed by the Environmental Protection Agency (EPA) in its Study of Hydraulic Fracturing for Oil and Gas and Its Potential Impact on Drinking Water Resources. The EPA study had identified the presence of TBA in groundwater present in two small areas within Raton Basin. The purpose of the COGCC special project was not only to determine the broader spatial occurrence, but also to identify potential sources of TBA related to oil and gas activity and to evaluate potential fate and transport mechanisms of TBA from any sources identified in the study.

The COGCC study area was broken into four distinct geographic areas within the Raton Basin as follows: the North Fork Ranch and Wet Canyon Area, the Rancho la Garita and Arrowhead Ranchettes Area, the Burro Canyon Area and the Gulnare Area. The EPA collected the majority of their samples from two areas in the Raton Basin: the North Fork Ranch area in Las Animas County and in and near the River Ridge Ranch area in Huerfano County. The EPA conducted limited sampling at two domestic wells in the Rancho la Garita area in Las Animas County.

TBA is a branched four carbon alcohol ($C_4H_{10}O$) used as a raw material in many industrial processes. It is found in many consumer products and has been used as a gasoline fuel oxygenate additive. It is also produced in groundwater, under certain conditions, as a metabolite of the gasoline fuel oxygenate additive methyl *tert*-butyl ether (MTBE). It has been detected in alcoholic beverages, which may indicate that the compound is naturally occurring, although its presence in shallow groundwater as a naturally occurring organic compound is not documented in current literature. The presence of TBA in drinking water in homes has been associated with the use of cross-linked polyethylene piping known as PEX. In terms of its occurrence related to oil and gas activity, when the compound *tert*-butyl hydroperoxide is used as a gel breaker in frac fluids, TBA can be produced through a linked oxidation/reduction process. TBA may also be produced through in situ microbial degradation of naturally occurring iso-butane.

COGCC coordinated the investigation with the Colorado Department of Public Health & Environment (CDPHE). Samples were collected from 49 sites in the Raton Basin within Las Animas and Huerfano Counties. COGCC collected samples from CBM and domestic wells. With results provided by other entities there are data for water samples collected from the following sources: domestic water wells, monitoring wells, surface water, coal bed methane (CBM) produced water, permitted CBM produced water discharges to waters of the state and flow back from hydraulic fracture stimulation frequently referred to as fracing. Analytical data from additional sites sampled by EPA and by Pioneer Natural Resources were made available to COGCC for this investigation resulting in a total of 108 sites or types of water samples evaluated for the presence of TBA.

Water samples were analyzed for major anions and cations, volatile organic compounds (VOC) (including TBA) and dissolved gas composition. Isotopic composition of methane (when possible), isotopic composition of water and isotopic composition of dissolved inorganic carbon were determined in most cases. Analytical results from natural gas produced in the basin as well as frac flow back fluids from two CBM wells were also used to investigate potential sources of TBA. In addition to the analytical results, COGCC reviewed the composition of frac fluids used in the basin as well as other materials used to drill and complete CBM wells such as drilling fluids and cement. The possibility of direct introduction of contaminants to groundwater by the introduction of frac fluids was also investigated. Permitted discharges of produced water to surface water were evaluated and the use of unlined pits to dispose of exploration & production (E&P) wastes was evaluated. Surface spills of E&P waste were also considered as a potential source. Lastly, the in situ microbial degradation of naturally occurring isobutane was investigated as a source of TBA as well as the degradation of MTBE and isobutane from gasoline spills.

TBA was present in groundwater samples collected from 24% of the domestic water wells sampled. It was also present in produced water samples from 22% of the CBM wells sampled. TBA was not present in any CBM produced water discharges and it was not present in the two samples of frac flowback fluids collected. The reported composition of frac fluids currently used in the study area does not include products known to contain TBA or known to contain TBA precursor compounds such as *tert*-butyl hydroperoxide. As a result, COGCC has found no evidence to indicate that the source of TBA is from the introduction of contaminants to groundwater from frac fluids.

The investigation determined that the occurrence of TBA in the domestic water wells is not likely to be related to recent spills or discharges of produced water at the surface. In the Burro Canyon study area, TBA was detected in groundwater from one domestic well that is located approximately 3 miles from the nearest CBM well. Based on the distance and estimated flow rates, there is no natural transport mechanism that would point to a CBM well as the source of TBA in the distant domestic water well considering the average hydraulic conductivity for the geologic formations that make up the aquifer.

COGCC in consultation with CDPHE also investigated the occurrence of TBA in common products used in both domestic water well and CBM well construction. An immersion sample of pipe sealant commonly used in well construction was found to contain TBA and TBA was detected in the groundwater pumped from the well in which the sealant product was used. It was also detected in an air equipment blank sample collected from the compressor used during air percussion drilling of two monitoring wells and TBA was also detected in the groundwater samples from one of monitoring wells air-drilled during the course of the project. These two occurrences may represent anthropogenic sources of TBA in groundwater in the Raton Basin. The fact that more than 60% of the samples that contained TBA also contained one or more aromatic organic compounds may also be an indicator of impacts related to spills of gasoline fuels. The TBA-BTEX association also may be from the presence of naturally occurring thermogenic gases and hydrocarbons including aromatics generated from coals with subsequent degradation of isobutane.

None of the samples collected contained MTBE; therefore, TBA derived as a degradation product of MTBE is not likely. The presence of methane at moderate to high concentrations in all but one of the samples that contained TBA may be an indicator of a natural occurrence whereby methanotrophic (methane degrading) bacteria may be able to oxidize methane, isobutane and other hydrocarbons, if present, into an equivalent chain length alcohol as TBA. The presence of the five-carbon equivalent of TBA known as *tert*-amyl alcohol (TAA) was reported in several samples that had the highest concentrations of TBA. The presence of TAA may be another indicator of microbial oxidation of short chain hydrocarbons. Although the absence of TBA in Huerfano County samples with relatively high methane concentrations does not seem to support a microbial oxidation process, the differences in gas composition with relatively lower amounts of available isobutane in the Huerfano County wells may limit the formation of TBA as a metabolic breakdown product.

Based on the results of this investigation, there is no data indicating that recent oil and gas activity related to the drilling and operation of CBM wells is the source of TBA in the domestic water wells in the Raton Basin. Anthropogenic sources of TBA in groundwater may result from immersion of products commonly used in well construction such as pipe sealant or from compressed air used during air percussion drilling of wells. Lastly, natural occurrences of TBA in groundwater may result from the oxidation of isobutane by methanotrophic bacteria.

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List of Acronyms and Abbreviations

Acronym or Abbreviation	
AOC	administrative order by consent
API	American Petroleum Institute
BTEX	benzene, toluene, ethylbenzene and isomers of xylene
C_1/C_2	methane to ethane ratio
CASRN	Chemical Abstracts Service Registry Number
CBM	coal bed methane
CDPHE	Colorado Department of Public Health & Environment
cells/ml	cells per milliliter
COGCC	Colorado Oil and Gas Conservation Commission
DIC	dissolved inorganic carbon
E&P	exploration and production
EPA	United States Environmental Protection Agency
Fm.	Formation
frac	hydraulic fracture well stimulation
frac fluids	fluids used during hydraulic fracture well stimulation
GWML	global meteoric water line
MCF	thousand cubic feet
MIMMP	Petroglyph Energy's Methane Investigation, Monitoring and Mitigation Program
meq/l	milliequivalent per liter
mg/l	milligrams per liter
MSDS	material safety data sheet
mol%	mole percent
MTBE	methyl *tert*-butyl ether (CASRN 1634-04-4)
MW	monitoring well
n-	As in n-butyl alcohol indicates a straight (unbranched) hydrocarbon chain
PCR	polymerase chain reaction
PEX	cross-linked polyethylene
TAA	*tert*-amyl alcohol (CASRN 75-85-4)
TBA	*tert*-butyl alcohol (CASRN 75-65-0)
TDS	total dissolved solids
tert	tertiary
VOA	volatile organic analysis
VOC	volatile organic compounds
µg/l	micrograms per liter
USGS	United States Geological Survey

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Many individuals and families graciously consented to sampling of domestic wells and their cooperation is greatly appreciated. Pioneer Natural Resources cooperated in sampling efforts at CBM wells and the assistance of Pioneer staff (in particular Dave Holland and Jerry Jacob) aided data collection considerably. Konrad Quast, Bill Ward and Aaron Caudill (all with Norwest) helped in sampling and in coordination of sampling at many of the CBM wells and sites sampled during the frac study and this assistance is greatly appreciated. In 2013, Pioneer and their consultants worked with COGCC staff in planning and coordinating the drilling of two additional monitoring wells as well as paying for the installation of the monitoring wells. Those efforts and cooperation are greatly appreciated.

Greg Oberley and Rick Wilkin (both U.S. EPA) also helped coordinate EPA frac study sampling events in which COGCC participated. Their assistance in sampling as well as their participation in early discussions of the presence of TBA was of great help.

Both the EPA and Pioneer provided analytical data from many sites that were used in this report. Without their cooperation the scope of this report would be considerably smaller. Thanks to both organizations for sharing data with COGCC and thus also sharing with the public as well.

Many current and former co-workers at the COGCC have helped greatly and in many ways with this project. Thanks to all of them. Staff of the Colorado Department of Public Health & Environment participated in coordination of early stages of the field sampling effort as well as later overview of the project and both are appreciated. In particular the efforts of Andrew Ross (CDPHE) in obtaining landowner consent and in assistance with sampling were very helpful.

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Introduction

Samples of groundwater from domestic wells, monitoring wells and coal bed methane (CBM) wells collected by Colorado Oil & Gas Conservation Commission (COGCC) staff revealed the previously undocumented presence of *tert*-butyl alcohol (TBA) in some groundwater samples from Raton Basin aquifers. Many of these samples were collected in parallel with samples collected by the Environmental Protection Agency (EPA) as part of a national study of hydraulic fracturing (EPA's Study of Hydraulic Fracturing for Oil and Gas and Its Potential Impact on Drinking Water Resources) with sampling from fall 2011 to spring 2013. In one instance, TBA had been reported as present in baseline samples from one domestic well in 2006 that was collected as part of COGCC complaint response. In the summer of 2013, COGCC staff initiated discussions with staff from EPA and staff from the Colorado Department of Public Health and Environment (CDPHE) regarding the presence of TBA in groundwater. As a result of those discussions the COGCC began an investigation with the primary purpose of understanding the spatial occurrence of TBA in a broader areal context than in the EPA study which focused on two relatively small areas within the Raton Basin. A second purpose of the special project was to attempt to identify potential source(s) of the TBA detected in groundwater. A third purpose of the special project was to evaluate potential media and potential mechanisms of TBA migration from any sources thought to have been or to currently be present in the Basin.

COGCC special project 2130 was initiated in July of 2013 after planning discussions with CDPHE staff and sampling concluded in April 2014. During the project, samples from 49 sites were collected and analyzed. The analytical results from the 49 sampling sites have been uploaded to the COGCC database and are available for public review through the GIS layer of the COGCC website. In addition to the sites sampled by COGCC and CDPHE, this report also includes discussion of samples collected by the staff or contractors for EPA and Pioneer Natural Resources and analyzed on behalf of those groups as part of their independent studies of groundwater quality in the Basin. Additional TBA analytical data have also come from groundwater sampling and analysis conducted as an integral part of COGCC baseline groundwater or groundwater quality complaint response. COGCC has requested laboratories to add TBA to the standard analytical suites reported to COGCC for groundwater samples from the Basin. A discussion of general results and interpretation of the data is presented below.

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TBA Chemistry and Occurrences

Tertiary butyl alcohol (CASRN 75-65-0, synonyms; 2-methyl-2-propanol, *tert*-butyl alcohol, *tert*-butanol, TBA) is a branched four carbon alcohol ($C_4H_{10}O$) that is miscible in water (McGregor, 2010). TBA is used as a raw material in many industrial processes (McGregor, 2010). A major industrial use of TBA is the production of butylene elastomers subsequently used in synthetic rubber production (McGregor, 2010). One industrial process to produce TBA involves reduction of *tert*-butyl hydroperoxide to the same chain length branched alkane alcohol which is TBA. The Raton Basin is a largely rural area with no current, large industrial users of TBA known.

TBA is also present in some consumer products such as perfumes and cosmetics including hair sprays and aftershave lotions (Cosmetic Ingredient Review Expert Panel, 2005). TBA has been used as a denaturant in ethanol not intended for human consumption. TBA is present in deodorant, shampoos, household detergents, sunscreen products and flavoring agents as an alcohol denaturant and is present in solvents such as paint thinners (Cosmetic Ingredient Review Expert Panel, 2005).

TBA has been used as a gasoline fuel oxygenate additive and also has been shown to be produced as a metabolite of the gasoline fuel oxygenate additive methyl *tert*-butyl ether (MTBE) (Shipp *et al.*, 2005). Sales of gasoline with MTBE as a fuel oxygenate in Colorado ceased by May 2002 following passage of Senate Bill 00-190 in 2000 (Colorado Department of Labor and Employment Division of Public Safety, 2005). Anderson (2004) reported that use of oxygenated fuels was required in areas along the Colorado Front Range starting in 1988 with MTBE as the primary additive containing oxygen. By November of 1996 the use of ethanol as the oxygen additive to fuels had largely supplanted use of MTBE in Colorado (Anderson, 2004).

The presence of TBA in shallow groundwater as a naturally occurring organic compound is not documented in current literature. TBA has been reported to be present in alcoholic beverages (Cosmetic Ingredient Review Expert Panel, 1989) and this indicates that the compound may be naturally occurring. Additionally, TBA has been documented to be a bacterial degradation product of the branched hydrocarbon isobutane in laboratory studies (Patel *et al.,* 1982, Imai *et al.*, 1986 and Dubbels *et al.,* 2007). TBA has also been shown to be produced as a degradation product of isobutane by a common soil fungus in laboratory experiments (Onodera *et al.,* 1990).

The presence of TBA in shallow groundwater from direct and indirect anthropogenic impacts is documented in the scientific literature. Examples of direct anthropogenic sources include gasoline spills in which TBA was an ingredient in the fuel as an octane enhancer, or spills of TBA at industrial sites where TBA was utilized in process chemistry.

One example of an indirect source of TBA in groundwater in which TBA is present is the microbial degradation of MTBE, which was used as an oxygenate additive in gasoline (Schmidt *et al.*, 2004, Kamath *et al.*, 2012). A second example of an indirect anthropogenic source of TBA in groundwater is the microbial oxidation of isobutane present in spills to groundwater of gasolines that do not contain MTBE (Jones *et al.*, 2007). A third potential indirect anthropogenic source of TBA in groundwater (Hyman, 2014) is microbial oxidation of isobutane present in some stray natural gases from oil and gas production wells or from isobutane present in some naturally occurring gas seeps. Naturally occurring seeps of liquid and gaseous hydrocarbons are common in areas with oil and gas production and have been successfully used to find new prospects (Philp and Crisp, 1982).

The presence of TBA in shallow groundwater near Killdeer, North Dakota has been verbally communicated to COGCC by EPA staff to possibly be a result of oxidation of *tert*-butyl hydroperoxide contained in a release of hydraulic fracturing fluids through a leak in the casing of an oil and gas well. Use of *tert*-butyl hydroperoxide was reported as a gel breaker in the frac fluids that were released near Killdeer. The Killdeer site is also one of the retrospective case study sites in the EPA national study. *Tert*-butyl hydroperoxide is a strong oxidant and when present in fluids used during hydraulic fracture well completions is intended to react with guar or other gelling agents present in the fluids. The *tert*-butyl hydroperoxide in the fluids would be reduced to TBA in this paired oxidation-reduction reaction. The degradation of *tert*-butyl hydroperoxide to TBA is the fourth potential indirect anthropogenic input to be considered.

Review of scientific literature indicates that a fifth possible anthropogenic source of TBA in drinking water in homes can be cross-linked polyethylene piping (called PEX). PEX is utilized in home plumbing applications as a replacement for copper pipe. PEX is not typically utilized downhole in domestic wells in Colorado (personal communication, Doug Stephenson, Chief Well Inspector CO DWR, 2014). The available literature as summarized in a State of California report indicates TBA and MTBE are leached into water in contact with the PEX pipe, particularly when the PEX pipe is new and first exposed to water (California Building Standards Commission, 2010). Published studies indicate the concentration of TBA leached from new PEX pipe decreases rapidly from concentrations as high as 50,000 micrograms per liter (µg/l) as it is exposed to incremental volumes of water (NSF Toxicology Services, 2003). The NSF Toxicology Services report also reported that TBA was frequently detected from leaching of other products evaluated by NSF (2003). NSF staff attributed the presence of TBA in products other than PEX to the decomposition of organic peroxide polymerization initiators that they reported being used in some industrial processes to produce materials such as polyethylene, PEX, nitrile butadiene rubber, ethylene propylene diene monomer and styrene butadiene rubber (NSF Toxicology Services, 2003).

Polyethylene pipe is used downhole in some water wells as drop pipe to connect the pump to the surface (personal communication, Stephenson, 2014). And based on the NSF Toxicology Services (2003) report, polyethylene pipe used downhole in domestic wells could be a sixth potential source of TBA in groundwater in domestic wells where polyethylene drop pipe has been installed. Stephenson (personal communication, 2014) indicated that polyvinyl chloride (PVC) drop pipes were typically used by professional pump installers in Colorado domestic wells and that polyethylene drop pipe usage was more common in homeowner pump installations.

CDPHE staff relayed suggestions from water well drillers of other possible sources of TBA in groundwater that hypothesized that products used by water well drillers and, in some instances, the same or similar products used in drilling CBM wells could be sources of TBA. Several foaming products used in water wells are listed in a Wisconsin Department of Natural Resources Bureau of Drinking Water and Groundwater compilation of products they authorize for use in water wells (2009). A review of Material Safety Data Sheets (MSDS) and product information summaries indicates the presence of other alcohols such as ethanol, isopropanol and isobutyl alcohol in some foamers, but the MSDS do not indicate the presence of TBA in the foamers. Drilfoam® is a foamer product listed as approved for use in Wisconsin water wells (Wisconsin DNR, 2009). Drilfoam® is also a foamer product sometimes used in drilling CBM wells in the Basin, as the author of this report has observed containers of this product on CBM locations in the Basin. Alcohols listed as present in this anionic surfactant foamer product used as an aid to lifting cuttings during air drilling of water or CBM wells are ethanol and isopropanol (Halliburton, 2014) with no mention of use of TBA in Drilfoam®.

Cement is frequently used in completions of monitoring and water wells and always used in completions of CBM wells in the Basin. Water well construction reports for wells sampled as part of this study show that bentonite is not frequently used in water well construction in this area of the state but has been used in construction and completion of monitoring wells for which analytical data are available for this report. These products could also be sources of organic chemicals detected in groundwater samples from wells in which the products were used. However in a recent study, TBA was not detected in samples of five Portland cements (Siegel *et al.*, 2013). TBA was not detected in 10 samples of bentonite materials used in drilling or grouting when tested in analyses conducted as part of the same study (Siegel *et al.*, 2013). At present the data available do not indicate drilling foamers, Portland cements and bentonite as potential sources of TBA in groundwater. For this report these three types of products will not be evaluated further as sources of TBA in groundwater.

From data collected and available as part of this project, seventh and eight possible sources of TBA in groundwater are compressed air used in air percussion drilling of wells and drilling pipe thread sealants (pipe dope) used with threaded PVC pipe typically used in water well pump installation.

Microbial oxidation of isobutane present in gasoline spills is thought to be one source of TBA in groundwater (Jones *et al.*, 2007). Discussions with Professor Michael Hyman of North Carolina State University (personal communication, 2014) have led to consideration of a possible natural source of TBA in groundwaters containing light hydrocarbons, in particular groundwater that contains methane and heavier gaseous hydrocarbons such as isobutane. Lab studies have indicated that methanotrophic bacteria are able to oxidize isobutane to the alcohol of equivalent chain length and branched nature, which is TBA (Patel *et al.,* 1982, Imai *et al.*, 1986). Methanotrophs are bacteria that primarily oxidize methane but may also oxidize isobutane and other hydrocarbons in a cometabolic process. A cometabolic process is one in which a microorganism degrades one compound (for example isobutane) when the primary compound (methane) is present and the methane is the primary source of energy to the microorganism (Hyman, 2014).

Sites Sampled

Samples from 107 facilities in the Raton Basin in Las Animas and Huerfano counties have been collected and analyzed for the presence of TBA with data made available for this review. Samples of flowback following hydraulic fracturing of one well with sampling of the same well's produced water more than two years following the well completion bring the number of combined facilities and matrices sampled to 108. A list of the locations of and matrices of samples is included as Appendix 1. Locations of sampling are identified by the facility number in the COGCC environmental database. Geographic coordinates in latitude and longitude of each COGCC facility sampled are also provided in Appendix 1. Sites and matrices sampled included groundwater from domestic water wells, surface water and permitted discharges to surface water, flowback from hydraulic fracture stimulation and monitoring wells installed by oil and gas operators as well as groundwater produced from CBM wells. In addition to the 49 sites with samples collected as part of the COGCC special project, 25 sites were sampled one to four times by EPA and those data have been provided to COGCC. Norwest (on behalf of Pioneer Natural Resources) sampled 48 sites with data made available to the COGCC. Some locations and matrices were sampled by more than one of the groups providing data.

The typical laboratory detection limit for TBA in the samples was 5µg/l. The reported detections limits varied between laboratories from 2-50µg/l and report limits also varied by matrix. Attached as Map 1 is a map displaying selected portions of the Basin showing the locations where samples were collected, the types of samples collected and if TBA was detected in the samples. Information on the map reflects data provided by all of the entities listed above. Map 1 includes the outcrop pattern of the Vermejo Formation (Fm.), which for the purposes of this report will be considered the general boundary of the Basin with respect to lithologies containing coal.

A generalized description of formations in which the majority of Raton Basin water wells and oil and gas wells are completed along with descriptions of other formations discussed in the report is presented in Table 1. More detailed summaries of geology of the Basin are found in Geldon (1989), Watts (2006) and Topper *et al.*, (2011).

Formation	Thickness (feet)	Lithology
Poison Canyon Fm.	0-2500	arkosic conglomerates and alluvial sandstones, siltstones and shale
Raton Fm.	0-2000	sandstone, siltstone, shale and coal with conglomerate near base
Vermejo Fm.	0-380	silty and coaly shale, carbonaceous siltstone, sandstone beds and coal
Trinidad Sandstone	0-260	sandstone
Pierre Shale	1300-2300	dark gray fissile shale and siltstone
Niobrara Fm.	560-850	chalk, marine gray shale and thin limestones, limestone at base

Youngest at top. Descriptions after Topper et al., 2011 following Tremain, 1980.

Table 1. Formations Discussed in this Report

Summary of Study Results and Groundwater Geochemistry

TBA was detected in 24 of the 108 facilities/matrices sampled or just over 22% of the samples available at the time of this report. In general the samples discussed below (with and without TBA detections) have been sampled and analyzed multiple times with confirming results by different labs, different preservatives and even by different analytical methods and techniques. Review of analytical reports indicates TBA has not been detected in aqueous trip blanks, aqueous equipment blanks or laboratory method blanks associated with the samples. TBA was detected in an air equipment blank sample collected from the compressor used during air percussion drilling of two monitoring wells and will be discussed below in conjunction with discussion of results from the monitoring wells. A summary of numbers and types of samples collected and detections of TBA is shown in Table 2 below.

Type of Facility/Matrix Sampled	# sampled	# TBA not detected	# TBA detected	% of Samples with TBA detected
CBM well produced H_2O	27	21	6	22%
CBM well frac flowback	2	2	0	0%
Surface water	6	6	0	0%
Surface water or CBM produced water at permitted outfalls	13	13	0	0%
Monitoring well	9	3	6	67%
Domestic well	51	39	12	24%
Totals	**108**	**84**	**24**	**22%**

Table 2. Summary of Sites Sampled

CBM Produced Water Sampling

Analytical data for produced water from 27 CBM wells are included in Table 2. The groundwater produced from CBM wells will be referred to as produced water throughout the report. TBA has been detected in six of the CBM wells or approximately 22% of produced water samples for which the COGCC has data. TBA was not detected in the other 21 CBM produced water samples. The CBM wells sampled are in the Las Animas County portion of the Basin as there were no producing CBM wells in the Huerfano

County portion of the Basin when the majority of the sampling and analysis discussed in this report was conducted (October 2011–April 2014).

Flowback Sampling

Samples of flowback following hydraulic fracture stimulation of two CBM wells were collected and analyzed for TBA and other analytes within a matter of hours after completion of the frac in one case (Panther 33-5, API # 05-071-09671) and shortly after initiation of pumped flowback in the second case (J & P 33-12R, API # 05-071-08956). TBA was not detected in samples of flowback from either of the two recently stimulated CBM wells with detection limits of 2 to 50µg/l.

TBA was not listed as being present in any of the chemicals and products used in these CBM well stimulations. There was no listing of use of strong oxidant gel breaker products or chemicals containing *tert*-butyl hydroperoxide, as has been suggested to be a source of TBA in groundwater at Kildeer, North Dakota, in these two hydraulic fracture treatments in data submitted to FracFocus by the operator. Enzymatic gel breakers were reported in use in both of the Las Animas County well completions sampled and, based on review of MSDS, the enzymatic gel breakers products utilized in these wells are not thought to be a sources of TBA.

TBA was not detected at the laboratories' established limits of quantification in the flowback samples. The TBA analytical data for flowback samples from wells in which the enzymatic breakers were utilized indicates that there is no detectable source of TBA in the fluids used for completion of these wells. Other alcohols including methanol (listed on FracFocus) and ethanol, isobutyl alcohol and n-butyl alcohol (not listed on FracFocus) were detected in flowback samples from the Panther 33-5 CBM well. Ethanol and n-butyl alcohol were also detected in flowback samples from the J & P 33-12R well and not listed on FracFocus.

Surface Water and Permitted Discharge Sampling

Historically 50-70% or more of the produced water in Raton Basin CBM operations has been disposed of by discharge to waters of the state under Colorado Discharge Permit System (CDPS) permits issued by CDPHE. Samples of CBM produced water discharged to dry drainages or to surface water under CDPS permits were collected at 13 sites. TBA was not detected in any of these samples with detection limits between 2-10µg/l. In addition to the samples from discharge outfalls, six samples of surface water from sites in Las Animas County have been analyzed for the presence of TBA with typical limits of detection of 5µg/l with TBA not detected. The data for discharge outfall sampling and surface water sampling are from sampling and analysis efforts by EPA and Pioneer Natural Resources.

Monitoring Well Sampling

Groundwater from nine monitoring wells has been sampled and analyzed for the presence of TBA. No groundwater was present in a tenth monitoring well (PXD-3 MW) drilled in the NFR area in 2013 during the course of this investigation. TBA was reported above laboratory established detection limits in samples from six of the nine monitoring wells for which TBA analyses are available for this report. All six of the monitoring wells in which TBA was detected are in the North Fork Ranch (NFR) subdivision in western Las Animas County. One of the monitoring wells in which TBA has not been detected in groundwater samples is in the NFR and two of the monitoring wells in which TBA has not been detected in groundwater samples are in Huerfano County.

Three of the NFR monitoring wells were installed by Pioneer Natural Resources as sites to monitor possible pressure transients in shallow aquifers subsequent to an air rotary drilling accident at the Molokai 13-36 Tr (API # 05-071-08837) in the NFR area in 2006. The drill bit became stuck in the hole most likely due to the reported failure of one of two air compressors used during the drilling of the surface casing hole. After repairs to the compressor, the drilling crew attempted to continue drilling the hole and to get the drilling tool free by applying air pressure to the bottom of the hole through the drill pipe from the compressors on site. The application of increased air pressure did not free the drilling string but did result in elevated water levels in two domestic wells (COGCC facilities 704681 and 704682) to the west of the Molokai 13-36 Tr drill hole. Groundwater periodically geysered from the casing of water well 704681 for several days following the drilling accident. The Commission approved two administrative orders by consent (AOC) with respect to groundwater impacts from this incident (COGCC Orders 1V-345 and 1V-360).

The installation of the three NFR monitoring wells in 2006 was part of a monitoring plan agreed to by the COGCC and the operator with a particular emphasis on monitoring changes in groundwater levels during nearby CBM drilling and completion operations. The three monitoring wells drilled in 2006 are the Keystone MW, the Niagara MW and the Sanchinator MW. Subsequently three water wells in the NFR area were converted to monitoring wells and added to the pressure transient monitoring program. The three water wells converted to use as monitoring wells are the Dolores MW, the PXD-1 MW and the Anna MW. Two monitoring wells (PXD-2 MW and PXD-3 MW) were drilled in the NFR area in late 2013 by contractors to Pioneer Natural Resources in conjunction with the COGCC investigation as part of an attempt to understand subsurface extent of the groundwater present in the Sanchinator MW that contains the highest concentrations of TBA in groundwater of any facility sampled in the Basin to date. Only a shallow source of groundwater was present during drilling of the PXD-2 MW, which is only 110 feet from the Sanchinator MW. TBA was not detected in water samples from the PXD-2 MW by three laboratories with detection limits of 5µg/l (two labs) and 50µg/l (third lab). A fourth lab with a 2µg/l reporting threshold reported TBA as present (3.7µg/l) in aliquots of the same water. No source of water was present in the PXD-3 MW during drilling (December 2013) to 442 feet below surface and the well bore was cemented and abandoned shortly after drilling ended. Since no water was present in this tenth monitoring hole, no groundwater samples could be collected and analyzed for the presence of TBA. The PXD-3 MW was drilled 70 feet west of the location of the Molokai 13-36 Tr (API # 05-071-08837) CBM well at which the drilling accident occurred in 2006. The PXD-3 was drilled to a depth greater than that the total depth achieved in drilling the CBM well before it was plugged and abandoned subsequent to the drilling accident. The two Huerfano county monitoring wells were part of Petroglyph's methane investigation, monitoring and mitigation plan (MIMMP) developed subsequent to migration of methane into the Poison Canyon formation by upward migration of gases from Vermejo Fm. coals. The MIMMP and associated data can be found on the COGCC website under the Library tab by clicking on Raton Basin (http://cogcc.state.co.us/).

Domestic Water Well Sampling

Samples from 51 domestic wells have been collected and analyzed for TBA, with detections of TBA at 12, or approximately 24% of the domestic wells. The percentage of detections of TBA in domestic water wells is similar to the percentage of TBA detections in CBM wells. The domestic wells in which TBA has been detected are all in the Las Animas County portion of the Basin. Seven domestic wells in the Huerfano County portion of the Basin were sampled with no TBA detections reported. Eight of the domestic wells sampled were greater than 0.5 mile from CBM operations and TBA was detected in one of those distant samples. TBA was detected in a Colorado Canyon domestic well completed in conglomerate of the lower Raton Fm. approximately 3 miles east of and updip of the nearest CBM well. It is improbable that CBM operations could be the source of TBA in this domestic well due to distance, groundwater transport rates and location updip of CBM activities. Possible sources of TBA in the Colorado Canyon water well will be discussed in a later section of this report.

Overview of Raton Basin Groundwater Geochemistry

MTBE was not detected in samples from any of the 108 facilities/matrices discussed in this report. Review of scientific literature indicates that MTBE in groundwater has been documented to break down to TBA at many sites where MTBE was or is present. The absence of even very low concentrations (<0.5-1µg/l) of MTBE in any of the groundwater samples is an indicator that MTBE is not likely a source of the TBA detections (by degradation of MTBE) even if other compounds present in gasoline such as benzene and related aromatic compounds were detected.

Concentrations of one or more of the BTEX (benzene, toluene, ethylbenzene, xylene isomers) and related aromatic compounds (propylbenzene and propyltoluene isomers, butylbenzene isomers, trimethylbenzene isomers, naphthalene and methyl naphthalene isomers) have been detected in 15 of the 24 samples (63%) in which TBA was also detected. Reported detection limits for the BTEX compounds in most of these samples are in low microgram per liter range (0.5-3µg/l). COGCC database searches indicate that benzene has been detected in 11 Las Animas County monitoring or domestic wells. Reported benzene concentrations in monitoring and domestic wells range from just over the detection limit to 440µg/l. TBA was a target analyte and was detected in groundwater from 8 of the 11 domestic and monitoring wells in which benzene was detected. At present TBA has not been analyzed in the other three groundwater samples in which benzene has been detected.

COGCC database searches indicate the benzene has been detected in produced water from 51 CBM wells in Las Animas County. The reported benzene concentrations in samples of produced water range from just over the detection limit to 220µg/l (Dahm *et al.*, 2011). BTEX or related aromatic compounds have been detected in each of the six CBM wells in which TBA was detected. The presence of naturally occurring BTEX and other aromatic compounds in waters produced in contact with natural gases of thermogenic origin is known from the general literature (Veil *et al.*, 2004) and these aromatic compounds are also known to specifically be present in CBM produced waters from the Powder River Basin (Orem *et al.*, 2007) and from the San Juan Basin and the Raton Basin (Dahm *et al.*, 2011). Operators of CBM wells in both the San Juan and Raton Basins have reported the occasional presence of long chain, waxy hydrocarbons (paraffins) in produced water which is another indicator of thermogenic generation of hydrocarbons from coal source rocks with subsequent transfer to groundwater. A lined, fenced and netted skim pit has been in operations at the Hill Ranch 15-11 CBM well (API# 05-071-08472) in the Raton Basin for several years to remove the longer chain hydrocarbons from the water produced from this CBM well. Aromatic organic compounds as well as isobutane were also detected in produced water from the Hill Ranch 15-11.

Methane (CH_4) is present in a majority of the groundwater samples collected in Las Animas and Huerfano Counties in the Basin. As of September 24, 2014, there were 498 water well locations in the two counties with analytical results for dissolved methane. Methane was reported as present above laboratory established reporting threshold in groundwater samples from 283 of those wells (57%). Methane was detected at concentrations that enabled isotopic analyses of the methane in all but one of the 24 samples in which TBA was detected. Isobutane was detected in 13 of the 24 samples with TBA detected but not in the other 11 samples in which TBA was detected with typical detection limit for isobutane of 0.0001mol% of the dissolved gases. Some labs can achieve lower detection limits for isobutane but we do not have enough data in our database from that lab to evaluate the 24 samples in which TBA was present for lower concentrations of isobutane.

Most of the samples discussed in this report are from wells developed in alluvium, the Poison Canyon Fm., the Raton Fm. and the Vermejo Fm. Water wells developed in alluvium typically have the lowest concentrations of methane if even detected. The presence of relatively high concentrations of methane in groundwater pumped from most Vermejo Fm. and Raton Fm. water and CBM wells is not unexpected as these wells typically draw water from coal seams or sandstones in contact with coals. Methane is frequently present in Poison Canyon Fm. water wells, typically at lower concentrations than in wells completed in formations with thicker coals present. However the presence of frequently occurring methane accumulations in the three formations was noted prior to the onset of CBM development in the Raton Basin by Dolly and Meissner (1977). The following note is quoted directly from that paper "..gas flows encountered during the drilling and testing of exploratory and shallow water wells are of a nearly universal nature in sandstones, coals and fracture zones present in Poison Canyon, Raton, Vermejo and Trinidad formations." (Dolly and Meissner, p. 259, 1977).

Groundwater samples from the Las Animas County portion of the Basin with detections of TBA also have methane detected at moderate to high concentrations (≈0.5 milligrams per liter [mg/l] to >30mg/l) with the exception of groundwater samples from the PXD-2 MW (methane <0.005µg/l). However, TBA was not detected at nine groundwater sampling sites in the Huerfano County portion of the Basin and six of those sampling locations also contain as great or greater concentrations of methane than samples collected in Las Animas County. The six sites in Huerfano County with high methane concentrations are samples of groundwater impacted by upward migration of methane into the Poison Canyon Fm. from Vermejo Fm. coals.

The Vermejo coals were the target of an attempt by Petroglyph Energy Inc. (Petroglyph) to produce CBM in Huerfano County. All of Petroglyph's CBM wells in Huerfano County were plugged and abandoned in 2011. There is considerable analytical data for produced water from Petroglyph's operations but there are no analyses of the produced water from Huerfano County specifically for TBA. BTEX or related aromatic compounds have been detected in two of the nine sites in Huerfano County with detections solely of toluene and not other aromatic compounds. Isobutane was detected at low concentrations in the two Huerfano county samples in which toluene was detected. TBA was not detected in groundwater from the two wells in which toluene and isobutane were detected.

Methane isotopic composition data from CBM wells in the Basin indicate the produced gas is typically of thermogenic origin (Figure 1) with some methane from immature sources (to the lower left of the thermogenic gas zone). Isotopic composition of methane is characteristic of the source of the methane and processes that produced the methane. Isotopic composition of methane can also be useful in understanding possible migration of methane from source rocks, as well as aiding understanding of alteration or degradation of methane in groundwater.

Methane isotopic composition for produced water samples in which TBA has not been detected spans the entire range of methane isotopic composition shown for methane from coal bed production in the Basin. Isotopic composition of methane from produced water samples in which TBA has been detected lie within the thermogenic range of the plot below. Data from samples of two non-CBM production gases are included in Figure 1 for reference and later discussion. Those samples are from wells developed in the Pierre and Niobrara formations underlying the deepest coals produced in the Basin (Vermejo Fm.) as shown in Table 1.

Composition of gases from CBM production wells in the Basin (water and or gas samples) is typically very dry. Dryness of gas is a conceptual evaluation of the ratio of methane to heavier gaseous hydrocarbons. Increasing ratios of methane to either ethane or to ethane plus longer hydrocarbons are considered dryer gas (Tissot and Welte, 1984). Ethane (chemical formula C_2H_6 or frequently shortened to C_2) is typically present in the CBM production from the Basin but straight or branched longer chain hydrocarbon gases such as propane, butane, isobutane, pentane, isopentane and hexane when present are typically at low concentrations (<0.02mol%).

Higley (2007) summarized the work of several earlier publications (in particular Close, 1988, A.R.I. Inc., 1991 and Flores and Bader, 1999) and concluded that the thermal maturity of the coal-bearing Vermejo and Raton formations was sufficiently great for gas generation to have taken place. The evaluation of the thermal maturity is based on vitrinite reflectance measurements on the coal maceral vitrinite. The presence of thermogenic methane produced from these coal bearing formations is shown in Figure 1 using the evaluation criteria utilized by Coleman et al. (1995) based on their work and also on work of Schoell (1980) and others.

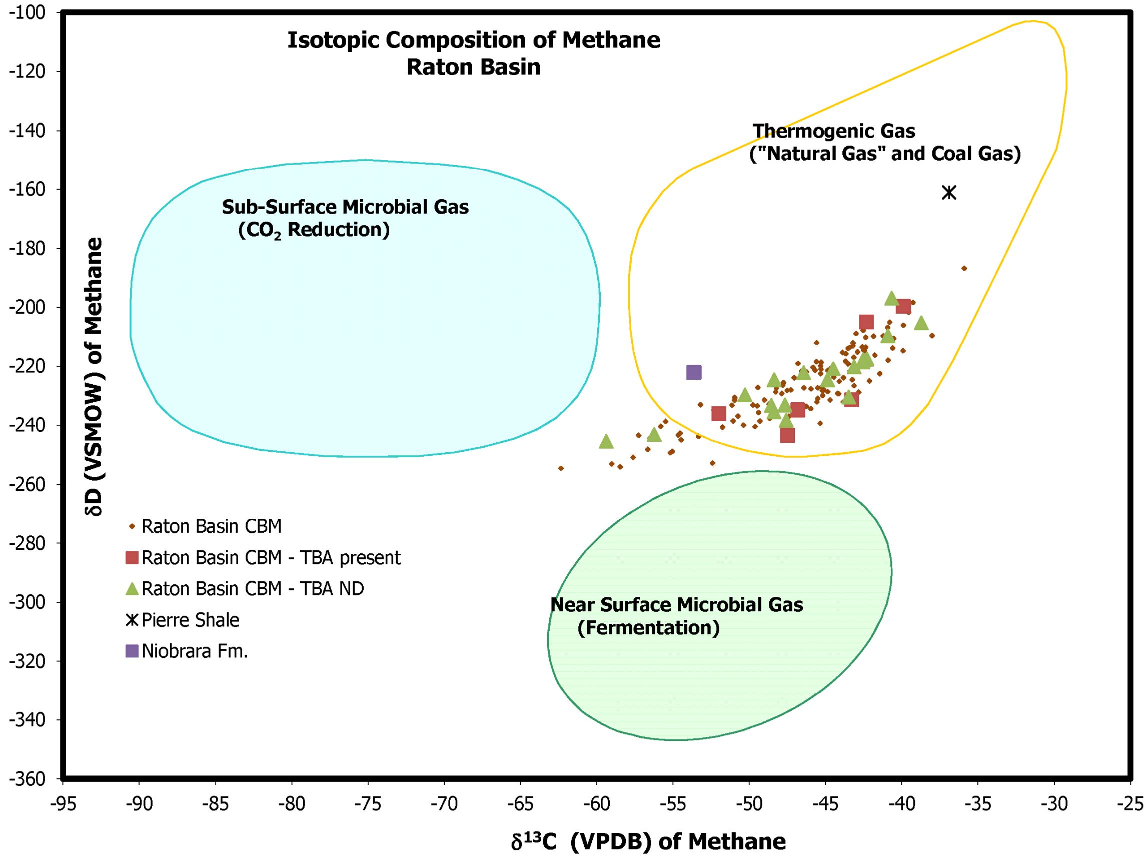

Figure 1. Raton Basin Production Methane Isotopic Composition

Figure 2 below illustrates the methane to ethane ratio (C_1/C_2) of produced Raton Basin CBM gases plotted versus the carbon isotopic ratio of the methane in the same sample. The ratio of methane to ethane is plotted on a logarithmic scale because of the large range of ratios present in the data set. Typically the gases produced from coals in the Basin have methane to ethane ratios of 1,000 or greater with some gases having methane to ethane ratios as high as 25,000. Gas composition of only one of the CBM wells in which TBA has been detected has a lower methane/ethane ratio by a factor of three than any of the CBM production gases for which data are available. Data from samples of two non-CBM production gases are included for reference and later discussion. Those samples are from wells developed in the Pierre and Niobrara formations underlying the deepest coals from which natural gas is produced in the Basin (Vermejo Fm.). The C_1/C_2 ratios of gases produced from the Pierre and Niobrara formations are the only Raton Basin production gases for which we have data with values less than 100. Waples (1983) provides a comprehensive review of factors influencing hydrocarbon generation from coals and other source rocks. Rice (1993) reviews the formation of gaseous and liquid hydrocarbons from coals. The lower C_1/C_2 ratio of gases from the formations underlying the coals reflects differences in organic matter composition (kerogen) and thermal history of these marine source rocks in comparison to the terrestrial coals of the Vermejo and Raton formations (Waples, 1983 and Rice, 1993).

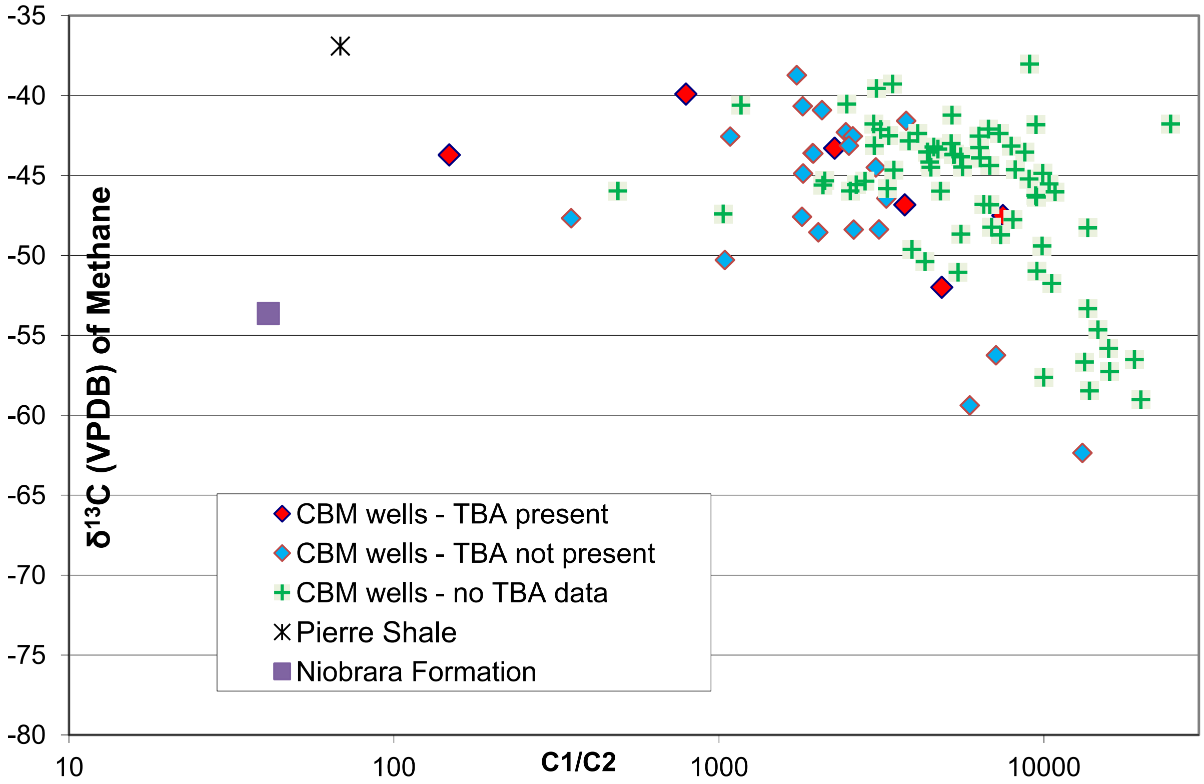

Figure 2. Methane to Ethane Ratio versus Carbon Isotopic Ratio of Methane from Raton Basin Production Gases

A more detailed discussion of results by geographic area of sampling follows in four sections. Results from Huerfano County will not be discussed in further detail in this report as TBA was not detected in groundwater from any of the nine Huerfano County sampling sites. Map 1 can be found at the back of this report and this map illustrates the distribution of sample sites and also illustrates the spatial relationships of the areas shown in the maps discussed below. Maps 2 through 5 detail the following geographic areas of Las Animas County within the Basin:

- Map 2 illustrates locations of samples in the North Fork Ranch and Wet Canyon areas;

- Map 3 illustrates locations of samples in the Rancho la Garita and Arrowhead Ranchettes area;
- Map 4 illustrates locations of samples in the Burro Canyon area; and
- Map 5 illustrates locations of samples in the Gulnare area.

Portions of Maps 2–5 overlap another of the area maps to better show continuity of the geography, geology and spatial relationships of sites and areas where data are available. Some sites appear on more than one area map, but primary discussion of a site will be done in one section and referenced where it appears elsewhere in the report. Appendix 1 lists the primary map designation for each facility sampled. Maps 2–5 can also be found at the back of this report.

Analysis of the sample results from 108 facilities/matrices evaluated in this investigation was not solely for TBA. In general, samples discussed were analyzed for major anions and cations, VOC (including TBA) and dissolved gas composition. Isotopic composition of methane (if possible), isotopic composition of water and isotopic composition of dissolved inorganic carbon were determined in most cases. Determination of microbial population characteristics and estimates of number of certain types of microbes present was performed in a limited number of samples. Determination of activities of several radionuclides was conducted on a limited set of samples. To present a more clear and informed interpretation of the data, the discussions in sections that follow will integrate many types of data gathered and reported from different sources. To better inform that discussion, the major ion chemistry of groundwater from the Basin is summarized below followed by a brief summary of isotopic composition of groundwater samples from the Basin.

Table 3 summarizes the major ion chemistry of Raton Basin samples of produced water and from groundwater samples from domestic and monitoring wells contained in the COGCC database. The number (n=) of analyses with concentrations greater than the reporting limit is shown. The number of samples is not the same as the number or wells sampled as some wells have been sampled multiple times. The minimum, maximum and median concentration for each of the six analytes is listed. The median concentrations (highlighted in blue) for each parameter are more characteristic of the general composition of these groundwaters than are the minimum or maximum for each parameter.

Generally the CBM wells are deeper than the domestic and monitoring wells and CBM produced water from the Basin is typically of sodium-bicarbonate character with lesser chloride. The sodium-bicarbonate character of the produced water is the result of microbial and geochemical processes, in particular sulfate reduction with resulting production of bicarbonate as has been well documented in coal bed aquifers in the Powder River Basin of Wyoming (Brinck *et al.*, 2008). The data in Table 3 represents typical concentrations (median) and ranges of concentration of these major ions in Raton Basin CBM produced water and shallower water sources.

		TDS (mg/l)	Na (mg/l)	Ca (mg/l)	Chloride (mg/l)	Sulfate (mg/l)	Bicarbonate Alkalinity (mg/l as $CaCO_3$)
Produced Water	Minimum	114	0.3	0.7	1	0.03	37.4
	Maximum	26900	5260	324	18000	168	9900
	Median	**1852**	**700**	**6.3**	**294**	**3**	**1160**
	n=	2896	1857	1868	2980	796	2841
Domestic and Monitoring Wells	Minimum	15	0.1	0.9	0.03	0.03	5
	Maximum	5620	2300	390	3870	1700	2200
	Median	415	109	49	12	66.9	284
	n=	612	683	665	716	642	618

Table 3. Summary of Major Ion Composition of Groundwater from the Basin

Stiff diagrams provide a means of categorizing similarities and differences in major ion composition and sources of waters (Hem, 1989). A Stiff diagram below (Figure 3) illustrates differences in major ion chemistry between groundwater samples from five sources on or near the location (pad) of the Sanchinator CBM wells. The width of each component of the Stiff plots is a measure of the concentration of and charges of in milliequivalents per liter (meq/l) of the major cations (plotted to the left) and the major anions (plotted to the right) in each water.

The upper Stiff plot (Anna MW) is from the shallowest the five water sources and is of calcium-bicarbonate character typical of shallow or alluvial groundwater in the Basin. The Stiff plots below that of the Anna MW are successively from deeper sources of water. The Sanchinator 11-36 CBM well is the deepest water source illustrated in Figure 3 and is completed in coals of the Vermejo Fm. The Sanchinator 11-36 Tr CBM well is completed in Raton Fm. coals overlying the Vermejo Fm. Both CBM wells are of sodium bicarbonate character with varying lesser chloride character with very low concentrations of calcium, magnesium and sulfate. The relative depths of the sources of water in each of the five wells in the Stiff diagram are shown on the fence diagram below (Figure 4).

Typical concentrations and ranges of concentration of these major ions in Raton Basin CBM produced water are included in Table 3 above. The PXD-2 MW sample is from a poorly producing Poison Canyon Fm. water source found at about 80 feet during drilling of this otherwise dry well. The PXD-2 MW water is of dominant sodium-sulfate character with lesser bicarbonate. The Sanchinator MW samples are from a screened zone between 565 and 585 feet deep. The source of water in the Sanchinator MW is possibly in the lower portions of the Poison Canyon Fm. or the uppermost portion of the Raton Fm. The predominantly sodium-chloride character of water from the Sanchinator MW is uncommon in Raton Basin groundwaters for which we have analytical data.

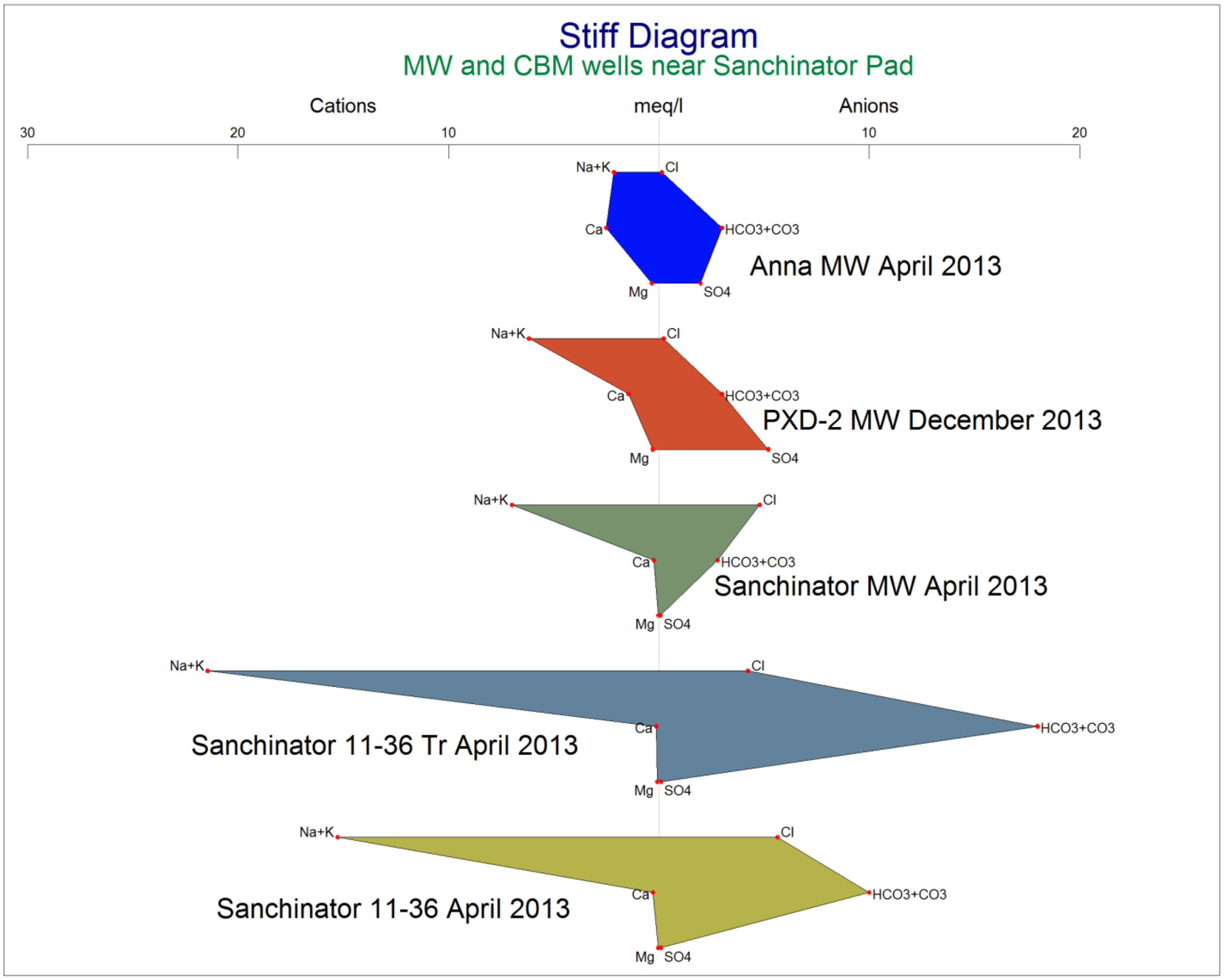

Figure 3. Stiff Diagram of Recent Water Samples On or Near Location of Sanchinator CBM wells

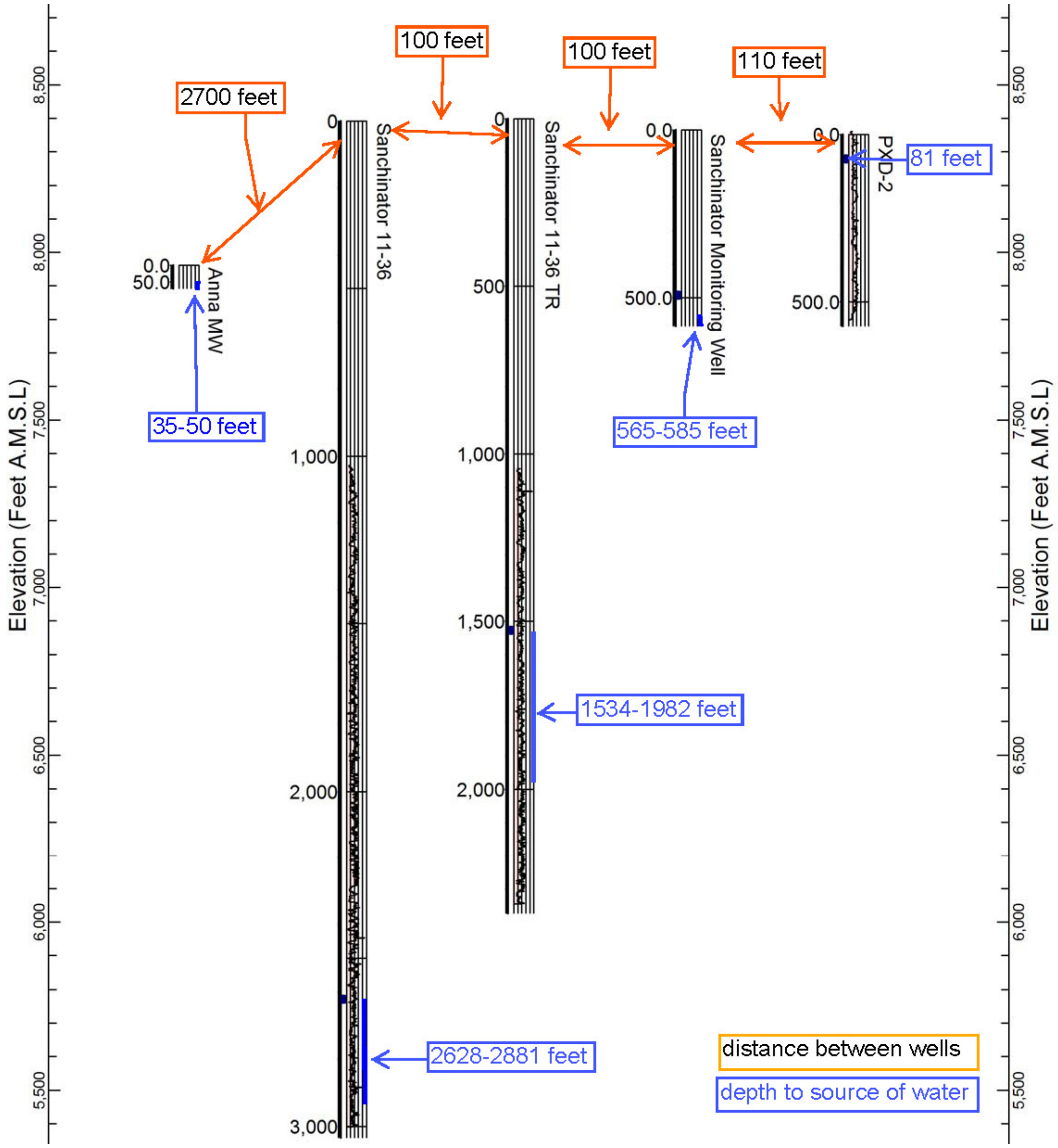

Figure 4. Fence Diagram of Well Depth and Depth to Water Source for Wells Included in Figure 3 and Figure 5

The horizontal separation in Figure 4 is not to scale. The vertical axis in Figure 4 is to scale. Blue lines in Figure 4 indicate zones of water sources at time of drilling.

Piper diagrams are a means of categorizing similarities and differences in sources of water using major ion compositions of the waters. Piper diagrams can also be used to evaluate the possibility of mixing of two water sources (Hem, 1989). Figure 5 below is a Piper diagram of the same sample set discussed above and included in Figure 3 above. Piper diagrams are in three parts. The two triangles at the bottom of the Piper plot illustrate cation composition (left triangle) and anion composition (right triangle). The scales of both the triangles are in percent of milliequivalents of the sum of cations and sum of anions in each sample.

The three deeper samples have nearly 100% sodium cations. In contrast the two shallower wells have between 20-60% calcium cations. The two shallower wells have between 40-60% sulfate as a percentage of anions while the deeper sources of water contain very low concentrations of sulfate as shown for deeper wells (mostly CBM) in Table 3.

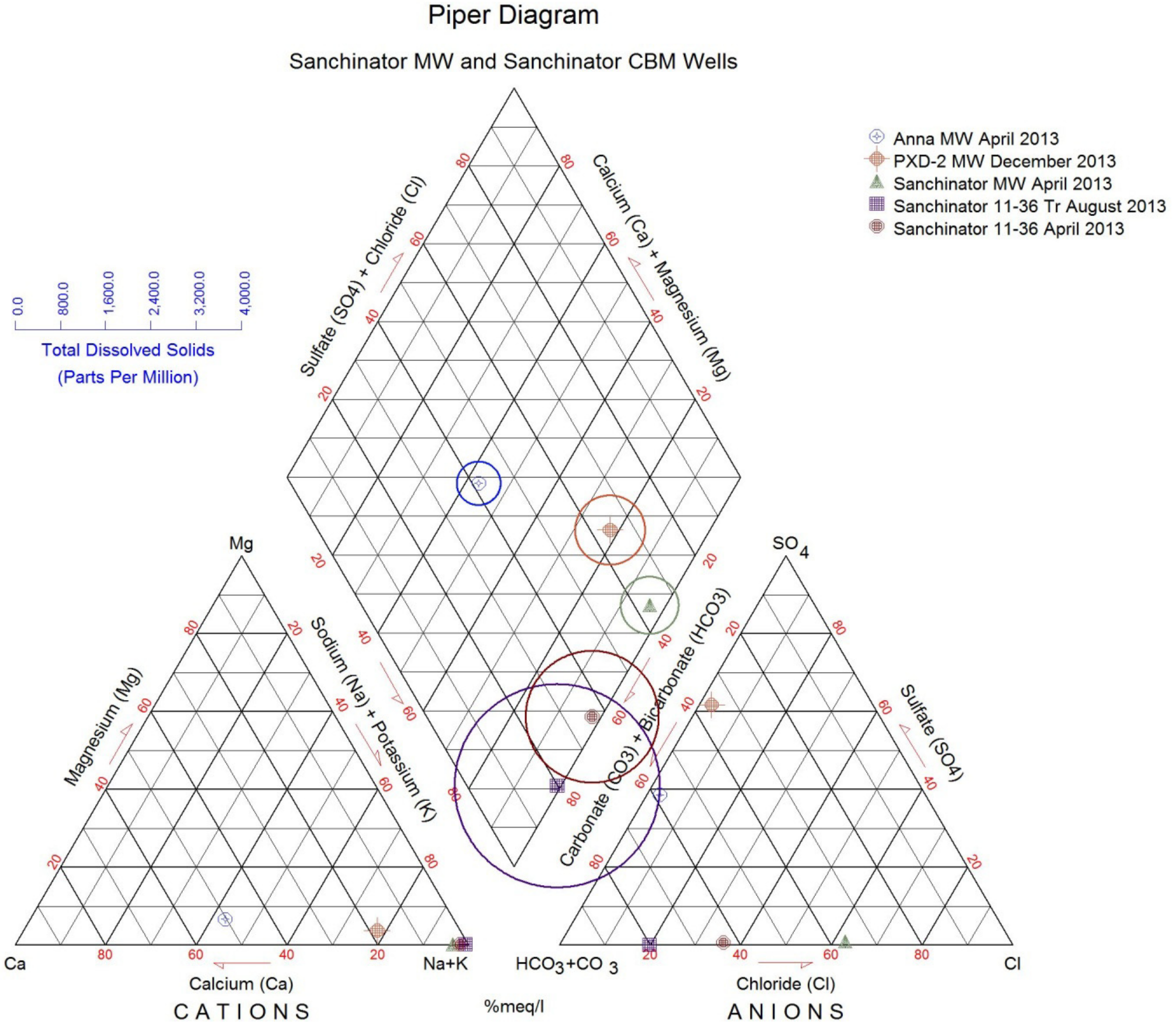

Figure 5. Piper Diagram of Recent Water Samples On or Near Location of Sanchinator CBM Wells

The diamond portion of the Piper plot above is the projection of the anion and cation triangles into the diamond and combines the major anion and major cation compositions into one plot. The sizes of circles drawn around each point in the triangle are representative of the concentration of dissolved solids in that sample. The diamond plot illustrates typical levels of dissolved solids in produced waters and typical lesser concentrations of dissolved solids in domestic well groundwaters in the Raton Basin as documented in Table 3. Interpretation of possible changes in water composition due to mixing of water sources can be evaluated using Piper plots. The ability to infer changes in composition is enhanced if data collected over time is available.

Isotopic composition of the oxygen and hydrogen that make up water (H_2O) can be utilized as a tool in understanding differences in sources of groundwater in the Basin. Water isotopic data available for this report are plotted below with water oxygen isotope ratios plotted as the x-axis and water hydrogen isotope ratios plotted as the y-axis. The hydrogen isotope (^2H) ratio plotted is also referred to as deuterium and the label on the plot of δD refers to the ratio of deuterium to the ^1H isotope. The line diagonally across the plot is known as the global meteoric water line (GWML) and represents a regression line to unevaporated precipitation data from across the world (Craig, 1961, Rozanski *et al.,* 1993). The isotopic composition of precipitation (meteoric water) is a function of source of the atmospheric moisture giving rise to the precipitation with isotopically depleted waters associated with cold regions and enriched waters in warm regions as noted by Craig (1961). Variability of δD and $\delta^{18}O$ in precipitation reflects the source region of the moisture and seasonal changes in moisture transport patterns, amount of the moisture that has already precipitated and fallen with orographic effects on composition as well (Bowen and Revenaugh, 1993).

Figure 6 illustrates that there is a large degree of water isotopic composition variability between sources of groundwater in the Basin. There is some overlap between the water isotopic composition of groundwater from aquifers reached by domestic wells and sources of produced water pumped from CBM wells in the Basin. Many of the water wells sampled are completed in the Raton Fm. and many of the CBM wells produce gas and water from the Raton Fm. The similarities of water isotopic composition may simply indicate similar sources and history of waters pumped from the same geologic formations no matter what the purpose of the well is. Figure 6 does show some differentiation between water isotopic compositions of samples from CBM wells with most of these waters being less depleted than many of the samples from water wells in the Basin. The CBM produced waters might be interpreted as being from warmer climate than water from many of the water wells based on the isotopic composition of water from the wells (Clark and Fritz, 1997). Water isotopic compositions from two CBM wells are outliers to the general trend of data and are labeled on Figure 6. The water isotopic composition of produced water from the WD Federal 14-7 R (API # 05-

071-09482) and the Burro Fed 11-18 (API # 05-071-06236) plot as distinctly different from the hundreds of other waters sampled in the Basin. One possible cause of the differences in water isotopic composition between these two CBM wells and the other water samples plotted may be due to evaporation of the water before infiltration to groundwater (Clark and Fritz, 1997).

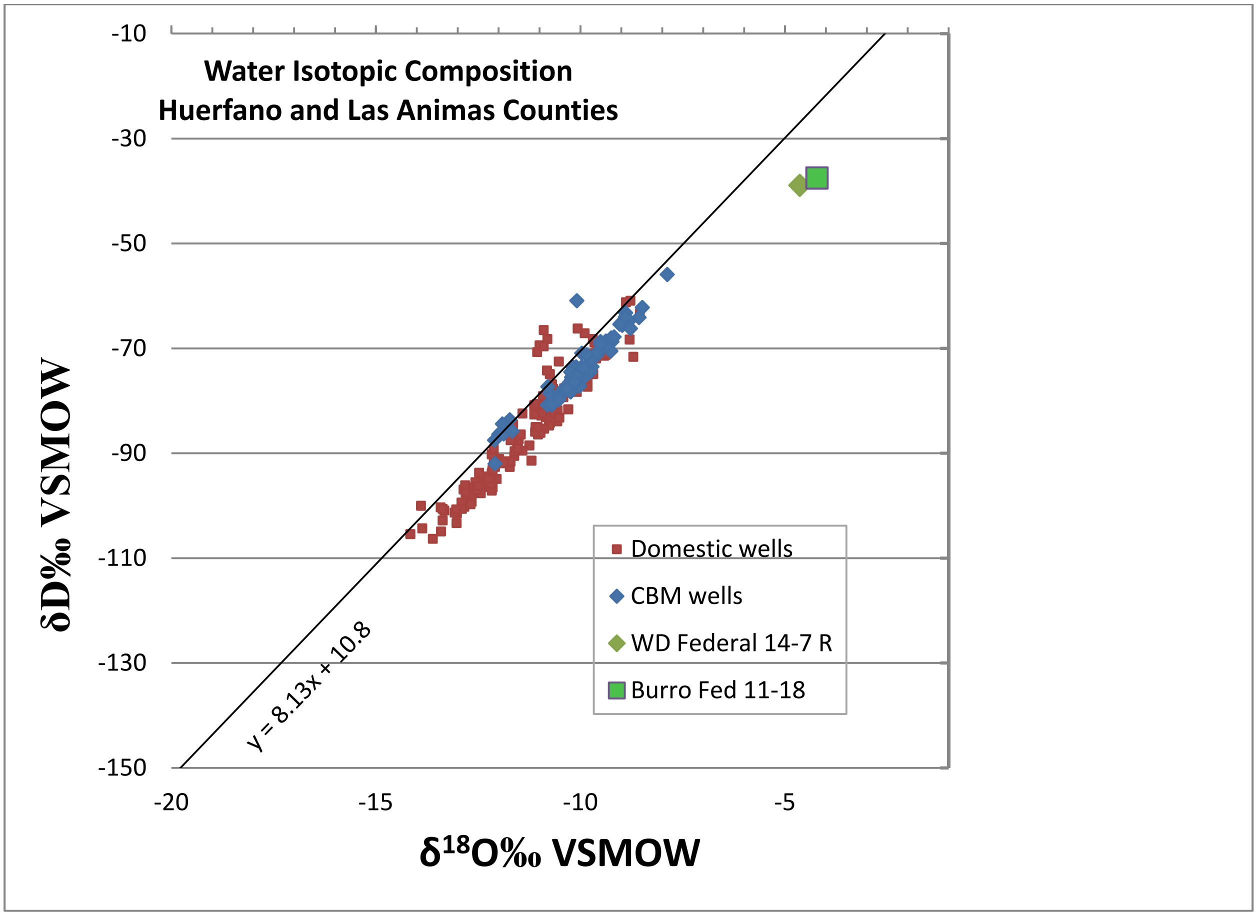

Figure 6. Water Oxygen and Hydrogen Isotopic Ratios of Raton Basin Groundwater Samples

The oxygen and hydrogen water isotope ratios of two specific produced waters are highlighted. Gas and water production from both the WD Federal 14-7 R and the Burro Fed 11-18 are from the coals of the Vermejo Fm. but the isotopic composition of produced water in each is not similar to that of any other CBM or domestic wells in the Basin for which we have data and which are plotted in Figure 5 above. The major ion composition of water produced from both of the highlighted CBM wells is also anomalous in that both are dominantly of sodium-chloride character with concentrations of dissolved solids, sodium and chloride far above the medians presented in Table 3 above. TBA has been detected in produced waters from both of these CBM wells and the gas composition and methane isotopic composition from samples collected from both wells will be discussed in more detail in a following section of this report. The significant differences in water isotopic composition from two of the six CBM produced waters with TBA detected could provide a potentially valuable tracer of mixing with other groundwaters in the Basin from spills or releases of produced water from these two wells.

Possible Sources of and Mechanisms of TBA Introduction into Raton Basin Groundwater and Criteria for Evaluation

The presence of TBA in groundwater accessed by CBM, monitoring wells or domestic wells was not well known or documented until recently. Analysis of numerous samples of groundwater collected prior to 2013 for determination of VOCs is available, but typically the analyte list reported by labs did not include results for TBA even though the labs may have been analyzing samples for TBA. Thus there is limited baseline information available on the presence or absence of TBA in groundwater from the Basin. What older data exist typically are present with detection limits 5 to 10 times higher (*e.g.*, 50μg/l) than provided with more recently analyzed VOC data.

The identification and evaluation of potential sources of TBA in groundwater is an integral part of this project. The identification of media that might be involved in migration of TBA away from any identified source(s) to receptors such as groundwater accessed by water well bores followed by evaluation of potential migration pathways from possible sources is another integral part of this project. The determination of the presence of TBA, the source(s) of TBA and the presence of media capable of transporting TBA and migration pathways from a source of TBA to a receptor of TBA are necessary parts of any forensic investigation designed to determine causes of any undesirable components present in groundwater. The presence of one chemical compound in a groundwater sample does not, in and of itself, prove the source of the chemical, the media for migration of the chemical or the existence of migration pathways of the chemical from its source to groundwater in a well as discussed above.

Ten potential sources of TBA have been identified previously and discussed in the TBA chemistry section and are summarized below in Table 4. Five potential sources in Table 4 are potentially linked to CBM drilling, completion and production operations including E&P waste disposal (sources 4, 5, 8, 9 and 10). Three of the potential sources are potentially linked to CBM operations (sources 5, 9 and 10) and also inherently define the media that could migrate to be produced water from the CBM wells. As part of this project, new produced water analytical data from 27 CBM wells were used to better define the chemistry of the fluids that could potentially migrate to domestic wells and potentially carry TBA to those domestic wells. A wide variety of produced water analytical data from more than 2,000 CBM wells are also present in the COGCC environmental database, with major ion chemistry summarized above in Table 3 and used in this study.

Two potential sources of TBA in Table 4 involve gas phases as media of input to or migration into as indirect (4) and direct (8) sources. Examination of water well and CBM well drilling reports show that use of compressed air as the drilling fluid is prevalent in the area. The presence of TBA was reported in the only analysis of a sample of compressed air used in drilling that was available for this study. Evaluation of compressed air as a potential source of TBA in this study is limited to the well drilled at that time because of limited analytical data. As discussed previously, methane as well as heavier hydrocarbon gases have been detected in samples from nearly 60% of the water wells for which data is available. As part of this study, analysis of gas composition and isotopic composition of methane was performed at all but a few of the 108 facilities/matrices for which TBA analyses are available. The COGCC records and environmental database have gas composition and isotopic composition analyses from more than 350 sampling events at more than 150 CBM wells and 200 domestic water wells as well as from more than 40 soil gas seeps to be used in a broader evaluation of potential source 4 in Table 4.

1 Direct	Household product containing TBA disposed to septic systems with infiltration to groundwater
2 Indirect	Spills of gasoline containing MTBE and isobutane with subsequent microbial degradation
3 Indirect	Spills of gasoline containing isobutane with subsequent microbial degradation
4 Indirect	Seeps or releases of natural gas containing isobutane with subsequent microbial degradation
5 Indirect	Use and breakdown of *tert*-butyl hydroperoxide in hydraulic fracture stimulations of oil and gas wells
6 Direct	Use of crosslinked polyethylene (PEX) pipe in wells with leaching of TBA
7 Direct	Use of other polyethylene pipes in wells with leaching of TBA
8 Direct	Use of products in drilling and constructing wells that may contain TBA (compressed air, foamers, Portland cement, bentonite and pipe thread sealants)
9 Direct	Use of products that may contain TBA in hydraulic fracture stimulations of oil and gas wells
10 Direct	Discharges to surface waters, infiltration from unlined permitted pits, infiltration of spills or releases of produced water containing TBA

Table 4. Potential Sources of TBA

As part of the evaluation of source, media and migration pathways, each of the potential sources listed above must be evaluated using all available data. Use and integration of all available chemical, geological and hydrologic data available must be done to evaluate potential sources, pathways and media that introduce TBA into the groundwater. Use and integration of process knowledge of drilling, completion and operations, including drilling and completion records of domestic and CBM wells, and records of products used in drilling and completions is also necessary to evaluate potential sources, pathways and media that may introduce TBA into the groundwater.

Site-specific information, including locations and volumes of spills/releases of E&P wastes and CBM production records, including water volumes produced and mechanism(s) of produced water disposal, is necessary to evaluate potential sources, media and migration pathways. Evaluation of the geologic units into which domestic wells are drilled and geochemistry of groundwater from those wells must be used in the evaluations described above. As an example, TBA has not been detected at this time in any shallow water wells with major ion composition characteristic of alluvial aquifers in the area. Alluvial groundwater accessed by shallow domestic wells would be a first receptor if flowback or produced water containing TBA is spilled or released at the surface. The apparent absence of TBA in alluvial groundwater sources in the Basin may be an indicator that these sources, media and migration pathway are not occurring at present. From sampling to date, TBA has not been detected in shallow wells with major ion chemistry similar to alluvial aquifers in the area. This absence of TBA indicates that this source, media and pathway of TBA introduction into shallow alluvial groundwater followed by subsequent migration to deeper groundwater is unlikely.

Use of Stiff diagrams to categorize similarities or differences in waters from different sources was introduced previously in this report. Evaluation of changes in major ion chemistry by Piper diagram and subsequent evaluation of possible mixing of two sources of water from Piper diagrams was also introduced previously. Both Stiff and Piper diagrams are tools to evaluate the media by which TBA migration might take place and to some extent evaluate pathways the media may have migrated through.

The remainder of the report will focus on evaluating potential sources of TBA, potential media of migration and potential pathways for migration of TBA to groundwater in each of the four geographic areas. The report will focus on a few wells in each area to illustrate the evaluation discussed above. In the sections of the report that follow, wells with higher concentrations of TBA or with better defined possible sources of TBA will be discussed, but all sources of groundwater with TBA detections were evaluated using similar processes.

Section 1: North Fork Ranch and Wet Canyon Area Summary

The NFR area was one of two Raton Basin areas in which the EPA collected multiple samples on four occasions as part of the Raton Basin retrospective case study portion of the national study. Norwest, on behalf of Pioneer Natural Resources collected split samples at many of the NFR sites on each of the four semi-annual sampling events conducted by the EPA between 2011 and 2013. COGCC staff or contractors collected split samples at many of the NFR sites during the same period. Samples from additional sites in this area were collected as part of this investigation. In all, analyses of samples from 31 sites in the NFR and Wet Canyon area were reviewed and incorporated in this discussion.

TBA was detected in 4 of 14 samples of groundwater from domestic wells in this area and in 2 of 10 samples of produced water from CBM wells. TBA concentration in the four domestic wells ranged from 5-64µg/l in recent sampling. Dissolved methane concentrations in groundwater from the four domestic wells in which TBA was detected are low to relatively high (0.5-30mg/l). The reported concentrations of TBA in the two CBM well produced water samples in this area ranged from 7-12µg/l in recent sampling. Dissolved methane concentrations in groundwater from the two CBM wells in which TBA was detected are relatively high (9-15mg/l). Isobutane as well as BTEX and other aromatic compounds were detected in the one Wet Canyon domestic well with TBA also reported as present. BTEX and other aromatic compounds and isobutane were not detected in the three NFR area domestic wells in which TBA was detected.

Groundwater from seven monitoring wells in this area was sampled and analyzed and TBA was detected in six of them. The concentrations of TBA reported in the six monitoring well samples range from 3.7-920µg/l in recent sampling. Dissolved methane concentrations in groundwater from five of the six monitoring wells in which TBA was detected are relatively high (6-19mg/l) and BTEX or other aromatic compounds have been historically detected in four of the six monitoring wells in which TBA has been detected. Isobutane has been detected in two of the six monitoring wells in which TBA has been detected.

Concentrations of TBA in water samples collected at the Sanchinator MW are the highest of any site discussed in this summary. Figure 7 below shows the variability in concentrations of TBA reported for individual sampling events at the Sanchinator MW. This variability may be attributed in part to sampling variability and in part to analytical uncertainty. Sampling variability is likely introduced since the Sanchinator MW cannot be purged in typical fashion due to slow water level recovery. This monitoring well only makes 10-30 gallons of water before the water level goes below the pump intake. Thus sampling by three parties has typically taken place over a week of more. One purge event in the week prior to sampling followed by two or three sampling events two to four days apart has been a typical schedule. Intra-laboratory and inter-laboratory variability are also components of the variability of TBA concentrations observed in Figure 7. Method-specific calibration criteria of up to ±20% may account for much of variability observed. Because of the combined sampling and analytical variability, it is difficult to state that any meaningful concentration trend upward or downward is observed in the period between the fall of 2011 and January 2014. Because the monitoring well has low recovery rate, it may not be possible to minimize or eliminate the variability due to sampling. The ranges of intralaboratory and interlaboratory analytical variability could be further evaluated by round-robin analysis of matrix matched samples spiked with TBA reference materials to known levels spanning the range of TBA concentrations seen in samples from the Basin. The effects on analytical results of different chemical preservatives (acid, base or simple refrigeration) should also be evaluated as possible sources of TBA analytical variability seen the data plotted in Figure 7.

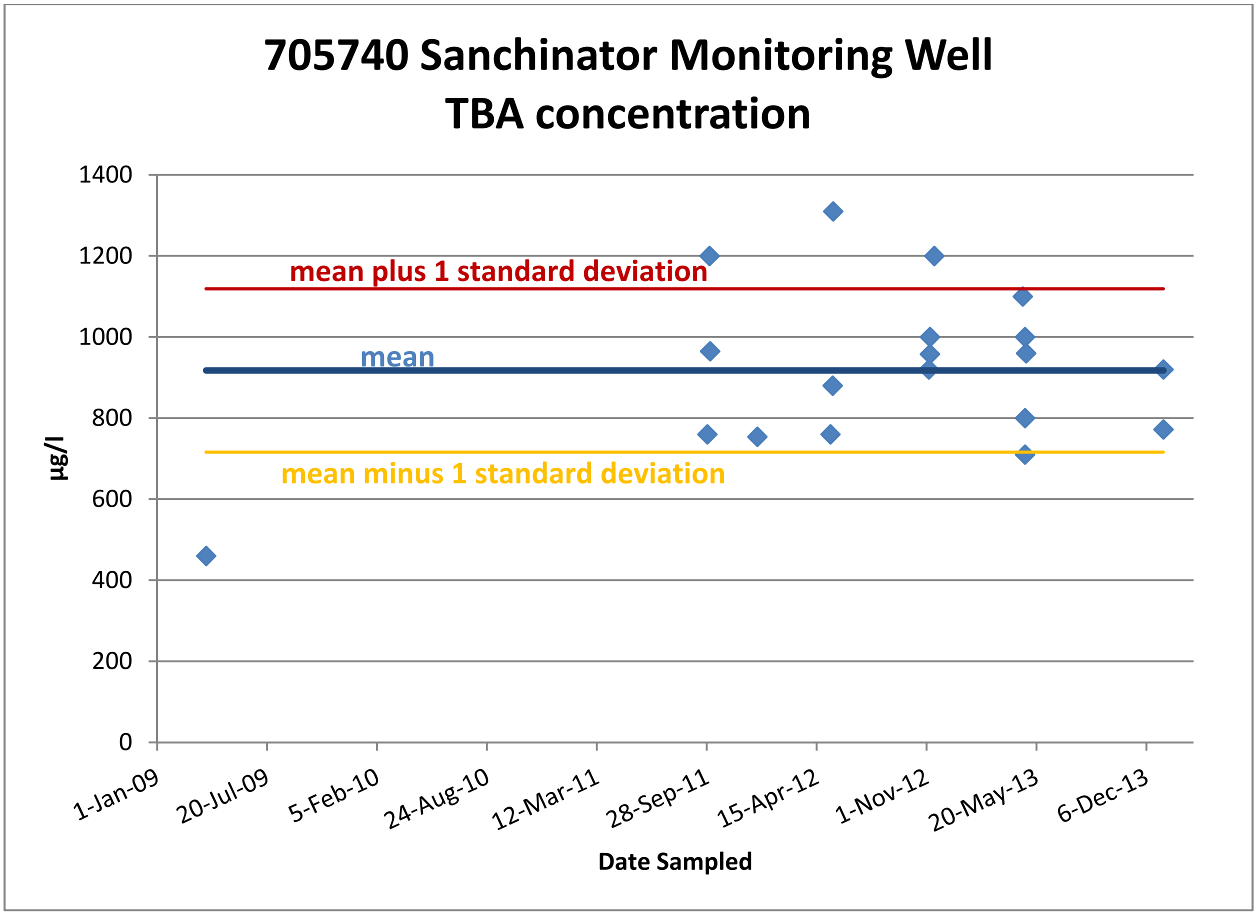

Figure 7. Concentration of TBA in Groundwater Collected at Sanchinator MW

Concentrations of toluene present in groundwater samples from the Sanchinator MW do show a pattern of input of toluene from anthropogenic sources with gradual decrease following the introduction as shown in Figure 8. Please note the vertical axis uses a logarithmic scale. The sampling events with the highest concentrations of toluene (September 2007 and September 2009) follow maintenance activities downhole in the monitoring well.

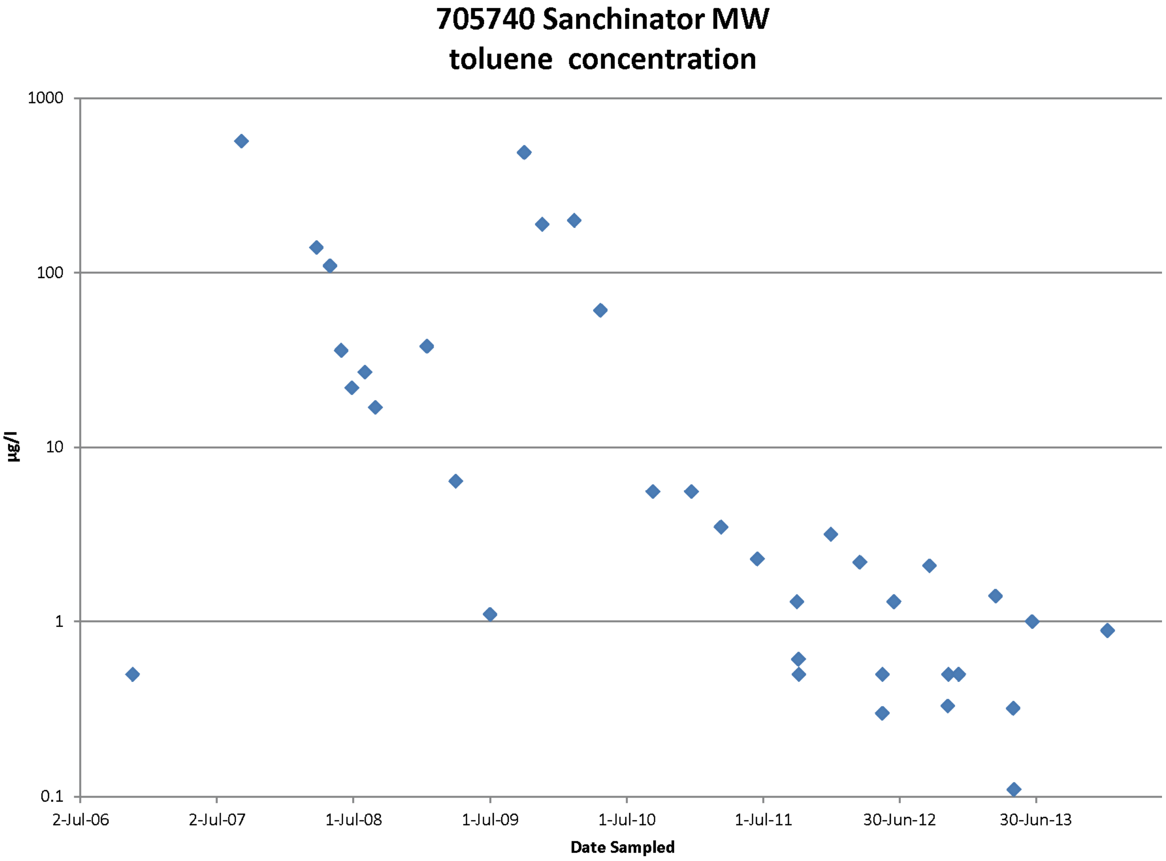

Figure 8. Concentration of Toluene in Groundwater Samples from the Sanchinator MW

An electric submersible pump was installed prior to the September 2007 sampling event and the pump was pulled and reinstalled prior to the September 2009 sampling event. The reported concentrations of other BTEX compounds did not follow the pattern observed for toluene. Benzene, ethylbenzene and xylene isomers were reported as not detected in the same sampling events in which the highest toluene concentrations were reported. COGCC staff members have observed elevated toluene without the presence of other BTEX compounds in groundwater samples from many parts of the state, particularly in new water wells or water wells with newly installed pumps.

COGCC staff members have not observed elevated toluene concentrations without other detectable BTEX compounds in samples of produced water or flowback from the Basin, so one can conclude that while the source of the toluene in this well is from an anthropogenic source, that source is not likely to be spills or releases of E&P wastes. Toluene is present in many adhesives (ATSDR, 2001). Two possible product sources containing adhesives that are used in installing pumps, where toluene is detected when analyzed as part of this project but other BTEX are not, will be discussed later in this report.

Chloroform has also been detected in groundwater samples collected from the Sanchinator MW. Reported concentrations of chloroform decrease from the first analysis for this compound in March 2009 as seen in Figure 9 below. Chloroform can be formed as a byproduct of chlorination disinfection processes. The presence of chloroform in groundwater from the monitoring well is most likely from one of two anthropogenic sources. Drillers may have used treated municipal water in drilling the well, or the well may have been shock chlorinated during or after the pump installation in 2007.

Chloroform was not detected in samples of flowback or produced water in data available for this report. As with the toluene present in groundwater pumped from this monitoring well, it is likely that the source of the chloroform in this well is from an anthropogenic source, but that anthropogenic source is not likely to be spills or releases of E&P wastes.

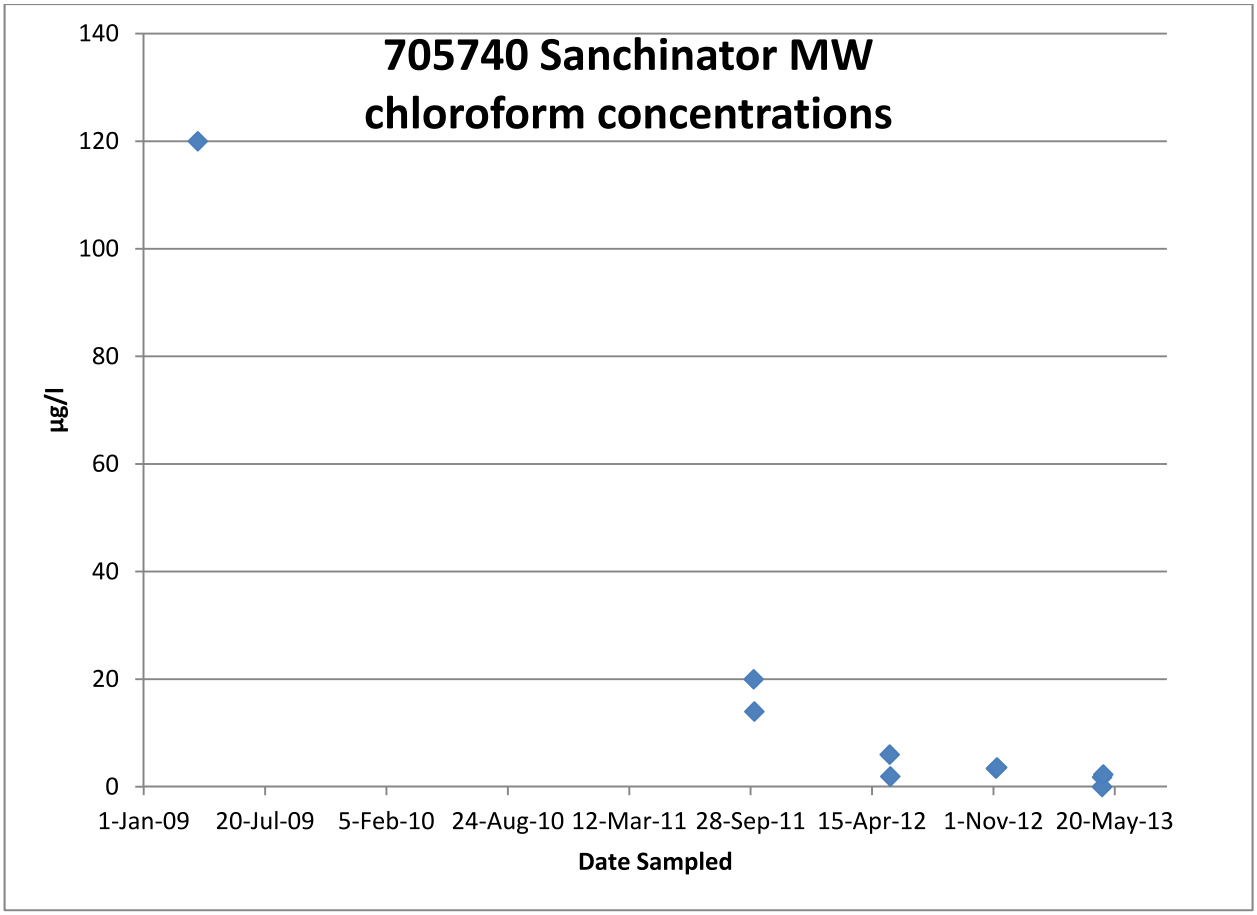

Figure 9. Chloroform Concentrations in Groundwater from the Sanchinator MW

Concentrations of chloride in samples of water from the Sanchinator MW have also changed since the well was first sampled in 2006. The increase in chloride concentration and ratio of chloride to bromide (Cl/Br) in water from this monitoring well is illustrated in the Figure 10. Chloride and bromide can be considered as conservative groundwater tracers in that once in solution in groundwater, there are few processes that will remove these anions. The chloride/bromide ratio has been used to understand mixing of different sources of water. One explanation for the observed changes is that a source of water that contained little chloride was introduced during drilling of the well and by early 2010 that water had mostly been removed from the well and subsequent samples are more representative of native groundwater around the well bore.

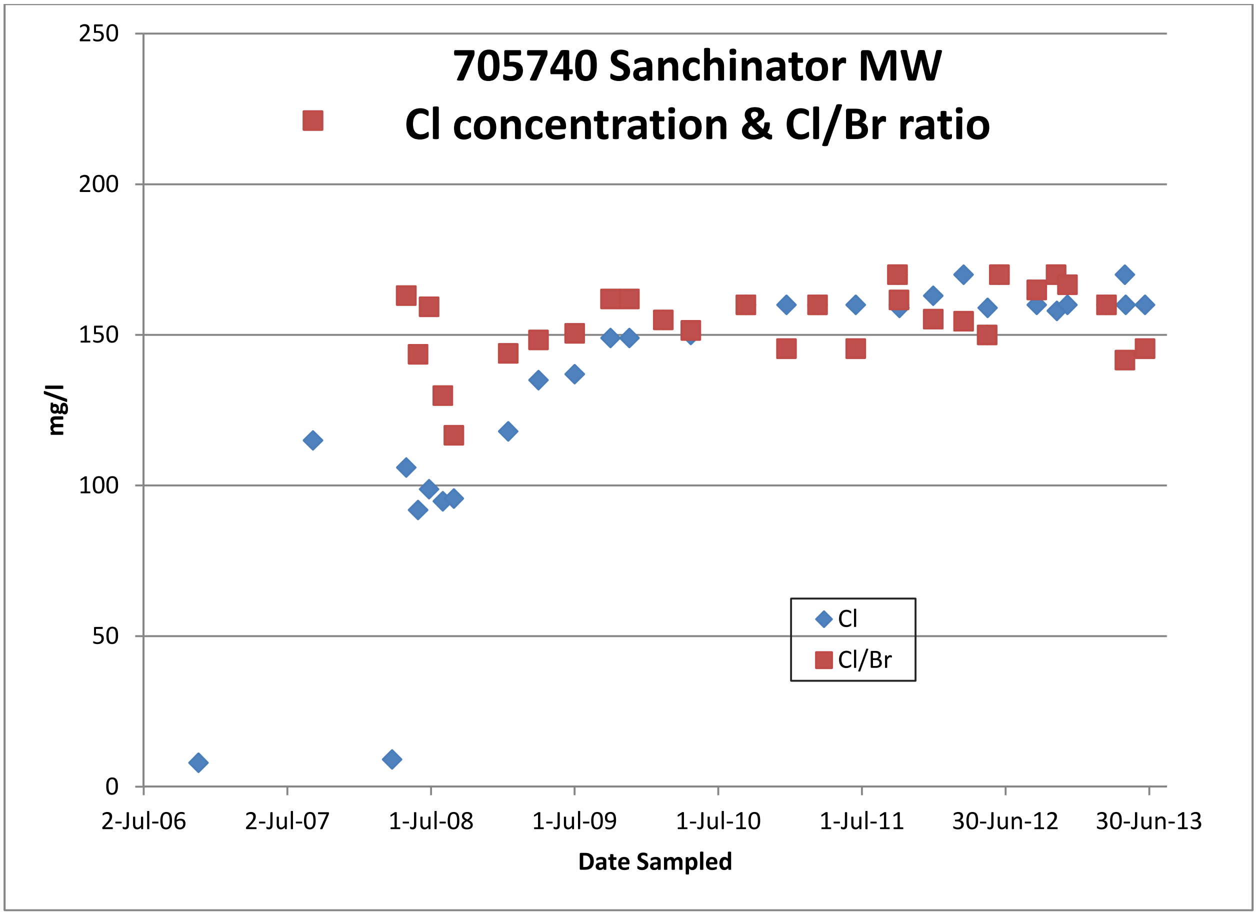

Figure 10. Changes in Chloride Concentration and Cl/Br Ratio in Groundwater from Sanchinator MW

The Piper diagram below (Figure 11) shows a trend in major ion composition of Sanchinator groundwater samples away from the major ion composition of produced water samples from CBM wells on the same location. This trend in major ion composition cannot be accounted for by mixing the monitoring well groundwater with produced water from the CBM wells on site.

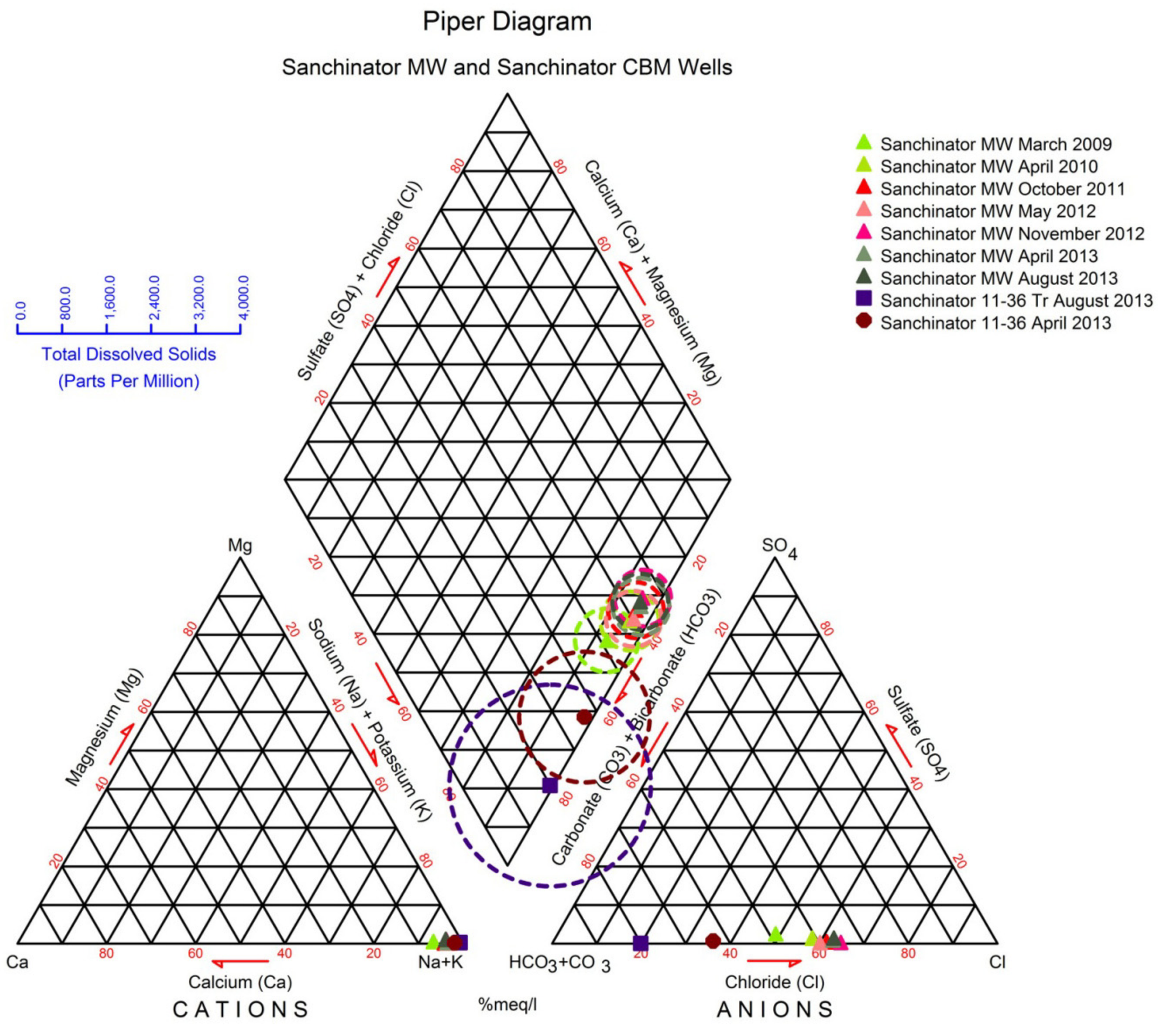

Figure 11. Piper Diagram of Samples from Wells Located on the Sanchinator Pad

TBA when detected in produced water from CBM wells in this area is at the same or lower concentrations than TBA detections in the monitoring wells and is at the same or lower concentration than in the domestic wells in which TBA has been detected. These results indicate that recent spills or releases of CBM produced water at the surface are not a likely cause of the TBA detected in the four domestic wells or in the six monitoring wells in the area. This assumes that present composition of produced water is reflective of past produced water composition, as demonstrated in Figure 12 and the discussion that follows below.

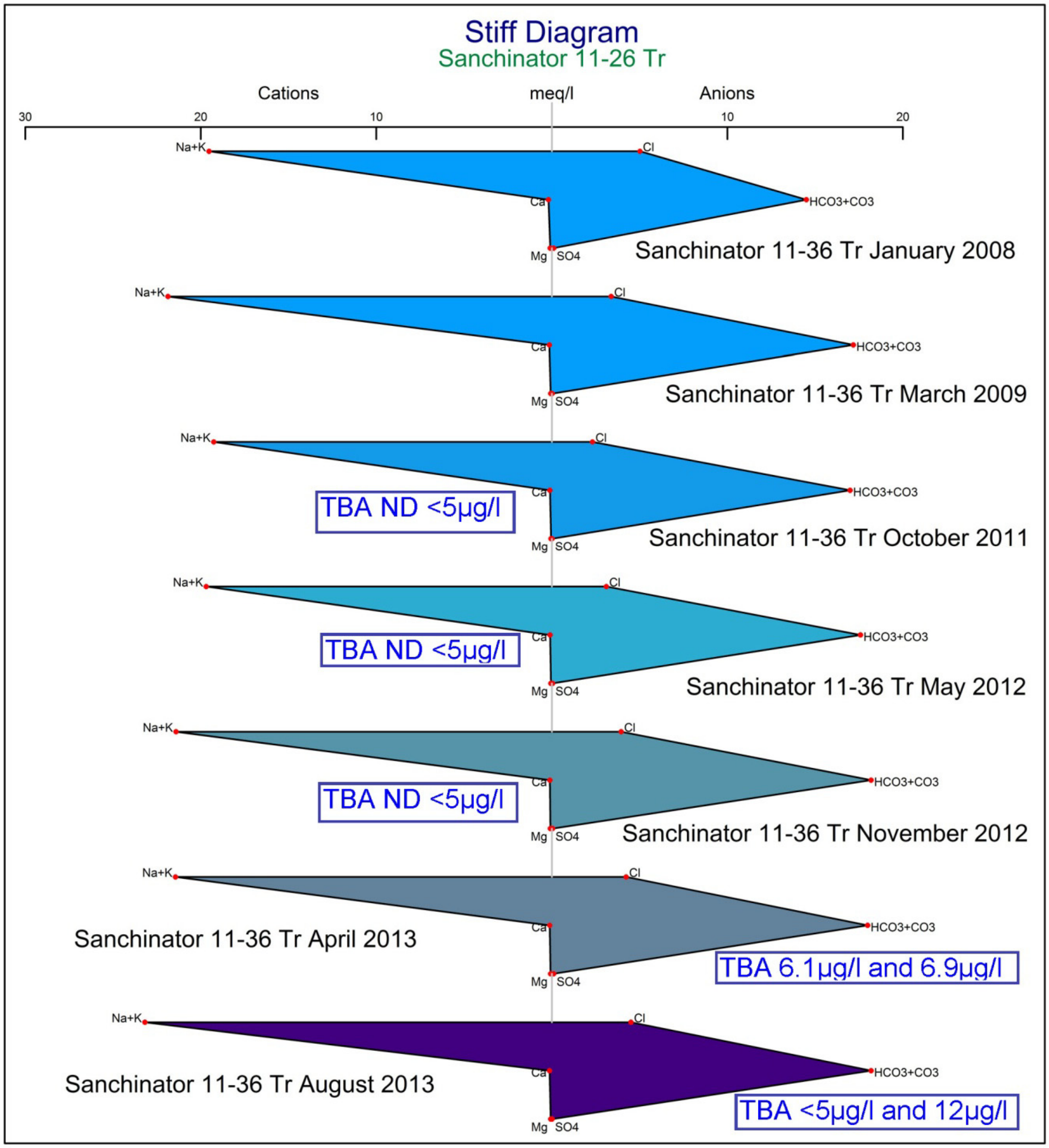

Figure 12. Stiff Diagram of Sanchinator 11-36 Tr Produced Water 2008-2013

The Sanchinator 11-36 Tr CBM well has been sampled multiple times over the last six years. The Stiff diagrams indicate little change in major ion composition over that time. Production started at the well in late 2007 with approximately 155,000 barrels of water produced and approximately 240,000 thousand cubic feet (MCF) of gas produced by the end of 2013. Also included on the Stiff diagram are results of sampling and analysis for TBA conducted as part of this project and as part of the EPA national study. No analysis of the Sanchinator 11-36 Tr produced water for TBA was conducted prior to 2011. TBA was first detected in the well in April 2013 after approximately 160,000 barrels of water had been produced from the CBM well according to monthly production reports submitted to COGCC by the operator. The reported volume of frac fluids used in stimulating and completing the Sanchinator 11-36 Tr CBM well in 2007 were 1,141 barrels of nitrogen foam frac fluids. By April 2013, more than 160 times the frac volume of produced water had been removed from the well. Chemicals present in products reported used in completions by the same operator since 2006 were known to include other chemicals that were part of the EPA study sampling and analysis plan. These chemicals include 2-butoxyethanol, glycols and alcohols such as ethanol and isopropyl alcohol. None of the individual organic chemicals listed in the 2006 frac were reported as present above detection limits in any of the CBM or monitoring wells on or near the Sanchinator pad.

TBA was not detected (<5µg/l) in the frac flowback samples from the one CBM well collected in 2013 in this area. Review of frac composition used by the operator in this area since 2006 do not indicate the use of *tert*-butyl hydroperoxide gel breakers but do instead record the use of enzymatic gel breakers. Therefore, the source of TBA present in the four domestic wells and six monitoring wells in this area is unlikely to be from fluids and products used in hydraulic fracture stimulation of CBM wells in the area. Assuming the fluids sampled are representative of fluids used in typical hydraulic fracture stimulation, analysis of the 2013 frac flowback fluid sample indicates that frac fluids currently in use in the area are not likely to be a source of TBA in groundwater.

Potential anthropogenic sources of toluene and chloroform present in samples collected from the Sanchinator MW have been identified, but those sources are not associated with CBM exploration, production or waste disposal activities. The mechanism by which these organic compounds reached groundwater accessed by this well is emplacement directly in the well and not transport and migration in produced water from CBM wells on the location.

No potential anthropogenic source of the TBA present in groundwater pumped from the Sanchinator MW has been identified. No mechanism of transport or migration of TBA into groundwater accessed by the Sanchinator MW involving produced water as the migrating media was identified. Major ion composition and water isotopic composition indicate there is no reason to conclude that such migration of E&P wastes into the groundwater accessed by the Sanchinator MW has occurred.

TBA was also detected in the shallow source of groundwater (≈80 feet depth) found during drilling of the PXD-2 MW in 2013. A potential anthropogenic source of TBA was determined to be compressed air used in drilling this well. The mechanism by which this organic compound reached groundwater accessed by the PXD-2 MW is likely to be emplacement directly in the well during drilling and not transport and migration in produced water from CBM wells on the location. Major ion composition and water isotopic composition indicate there is no reason to conclude that migration of E&P wastes into the groundwater accessed by the PXD-2 MW has occurred.

Section 2: Rancho la Garita and Arrowhead Ranchettes Area Summary

In response to landowner concerns, two domestic wells approximately 900 feet apart and located on property of one landowner were sampled by the EPA during their study in the Rancho la Garita and Arrowhead Ranchettes area in the Las Animas County portion of the Basin. The EPA did not sample any other sources of groundwater within 7 miles of these sites. TBA was detected in groundwater from one of the two domestic wells sampled as part of the EPA study. Groundwater from a third water well in the area was known to COGCC from previous sampling to have TBA present. Staff of COGCC and CDPHE determined that better definition of the presence of TBA was needed in this area. During the COGCC investigation, COGCC and CDPHE requested permission to sample approximately 15 domestic wells in this area in August 2013 and received permission to access 8 domestic wells, which were sampled and analyzed in the fall of 2013. By the conclusion of sampling and data collection, analyses of groundwater from 15 domestic wells, produced water from 12 CBM wells, flowback following hydraulic fracture stimulation of 1 CBM well and four discharge points were available from this area and are shown on Map 3.

TBA was detected in six of the domestic well groundwater samples with reported concentrations ranging from 10-480µg/l. TBA was not detected in any of the produced water samples from 12 CBM wells in this area. TBA was not detected in a flowback sample from the Panther 33-5 CBM well collected in 2011, nor was TBA detected in produced water samples collected from the Panther 33-5 CBM well in 2014. TBA was not detected in samples collected at four permitted discharges of produced water in this area. The analytical data indicate that at present there are no known sources of TBA associated with CBM drilling, completion, operations or waste management practices in this area. All detections of TBA to date in this area have been solely in groundwater sources accessed by domestic wells.

COGCC plotted the data from the six domestic water well samples with TBA present on the Stiff diagram shown as Figure 13 for evaluation. Three of the six domestic well samples in which TBA was detected have similar major ion character (sodium-bicarbonate) with little chloride (10% or less of the anions) and are shown in shades of green in the figure. The major ion character of three of the six are unusual for the area in that chloride concentrations are higher than in the other nearby domestic wells (30-50% of the anions) and are shown in shades of blue in Figure 13.

Concentrations of dissolved solids in the six domestic well groundwater samples in which TBA was present range from 400-1000mg/l. Dissolved solids concentrations of

CBM produced water samples in the area range from two to five times greater than the concentrations reported in the domestic well groundwater samples.

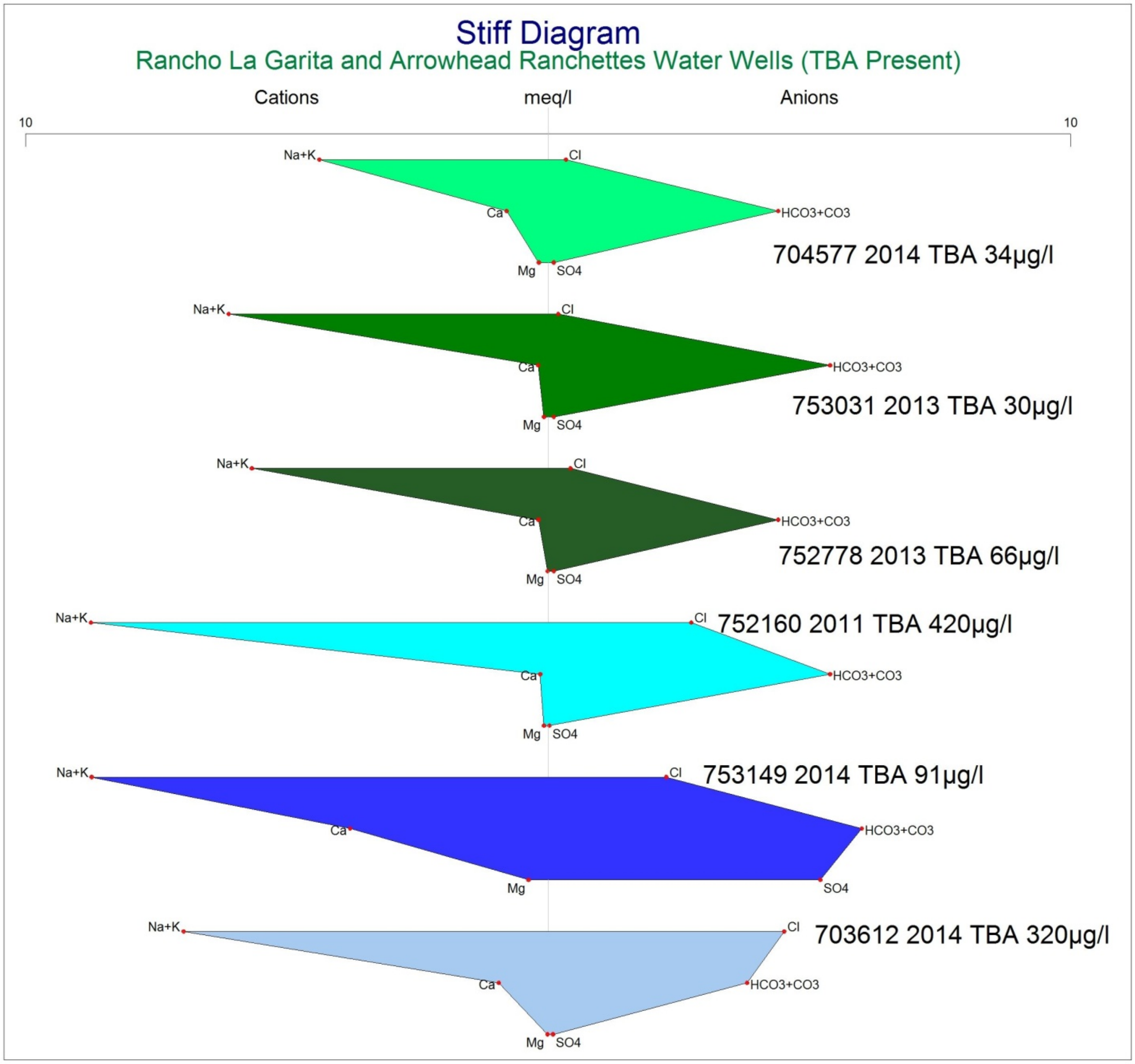

Figure 13. Groundwater Major Ion Composition (TBA Detected) in the Rancho la Garita and Arrowhead Ranchettes Area

Concentrations of dissolved methane in the domestic well groundwater samples in this area with TBA detected range from 2.3-38mg/l. The isotopic composition of methane present from 6 domestic well samples in which TBA was detected and from 12 CBM produced water samples in this area are plotted on Figure 14 below. The isotopic composition of methane from five groundwater samples and all of the CBM produced water samples plot in a linear trend typical for Raton Basin CBM from mature thermogenic to immature thermogenic sources. The isotopic composition of methane from one domestic well plots above the linear trend of the other 17 samples from the area. The isotopic composition data indicate that the methane present in the one sample not on the linear trend line has perhaps been microbially oxidized and may have originally been from a thermogenic source.

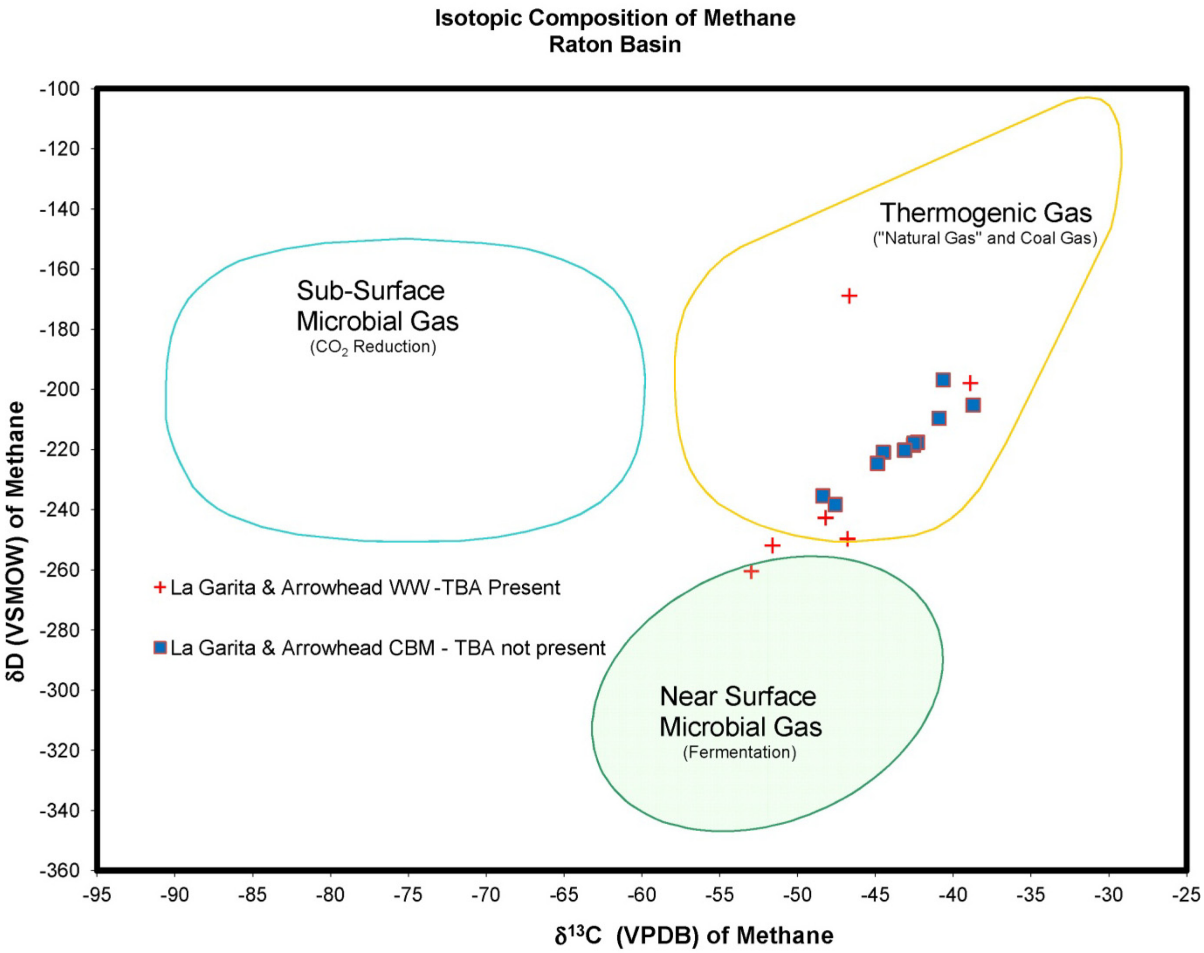

Figure 14. Isotopic Composition of Methane from Rancho la Garita and Arrowhead Ranchettes Samples

Analysis of oxygen and hydrogen isotopes in the water from each of the samples discussed above indicate slight to moderate differences in water sources between domestic groundwater wells and CBM wells. Figure 15 is a plot of the isotopic composition of oxygen and hydrogen in water from groundwater samples from the Rancho la Garita and Arrowhead Ranchettes area plotted against the global meteoric water line (GMWL). The water isotopic composition reflects temperature of the area as influenced by elevation and latitude as well as sources of water vapor in precipitation in the area. Water isotopic composition was determined for all samples in which

TBA has been detected and in general for most of the groundwater samples discussed in this report. The water isotopic data can be used to evaluate mixing of two sources of water such as a spill of produced water reaching a groundwater source. Water isotopic data can also be used to evaluate changes in source of water such as seasonal influxes of meltwater or rainwater to shallow wells. There is little overlap between the water isotopic ratios of produced water in this area with the isotopic composition of water from domestic wells in this area in which TBA was detected.

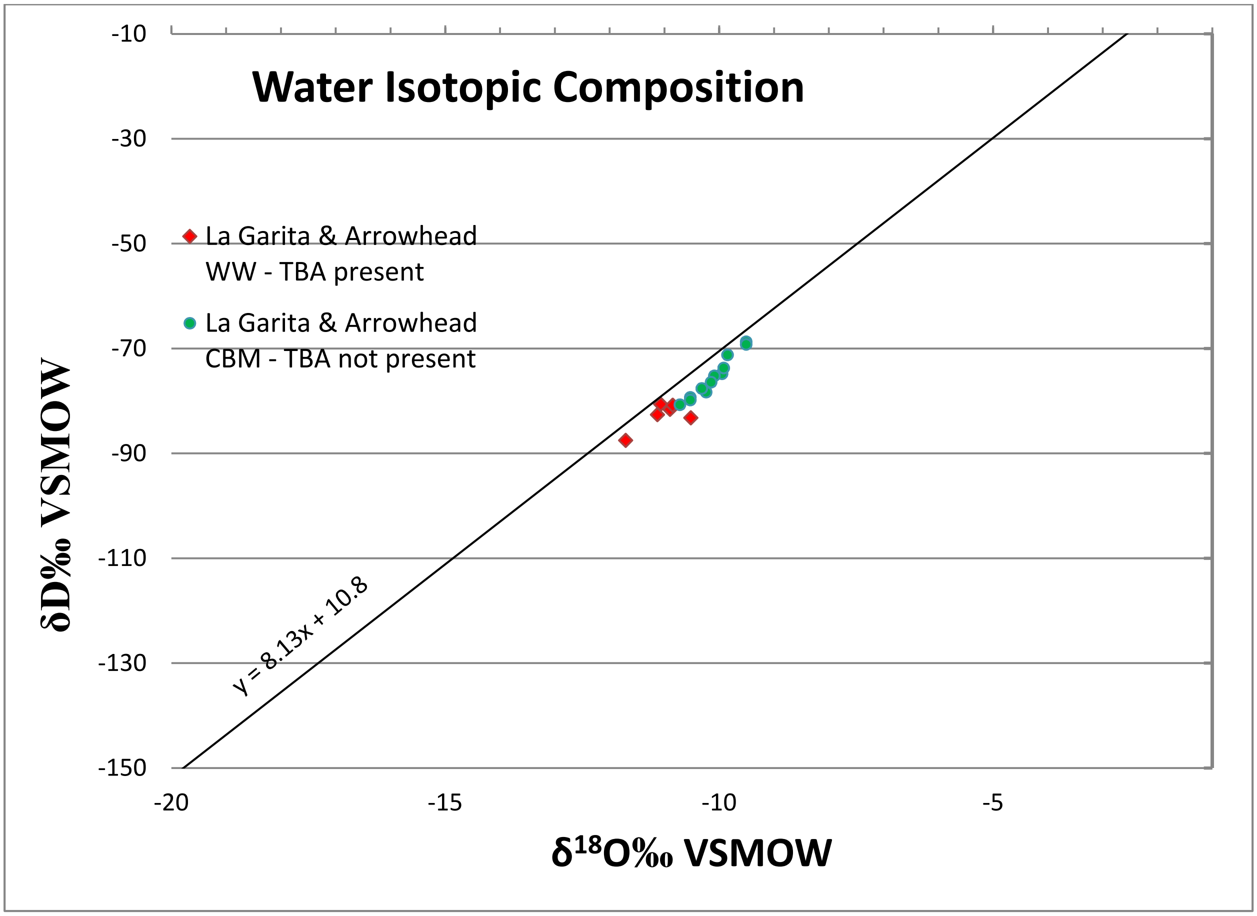

Figure 15. Water Isotopic Composition from Rancho la Garita and Arrowhead Ranchettes Samples

The isotopic composition of carbon in dissolved inorganic carbon (DIC) in typically shallower domestic groundwater is negative and generally reflects soil carbon dioxide isotopic compositions. The isotopic composition of carbon in DIC from produced water at generally deeper CBM wells typically is a positive (heavier) ratio reflecting longer residence times of water and processes such as sulfate reduction and methanogenesis. Figure 16 indicates the predicted trends of carbon isotope composition of DIC are generally observed in the samples from this area with two exceptions. The water well with positive $\delta^{13}C$ of the DIC is the deepest water well of those sampled and is 830 feet deep. The DIC carbon isotopic ratio in this deep domestic well likely reflect processes more similar to nearby CBM wells than to processes in the other shallower water wells (≈150-400 feet deep) in this area in which TBA was detected. Water from 753149 contained DIC with anomalously negative $\delta^{13}C$ and particularly anomalous in comparison to $\delta^{13}C$ of DIC in groundwater from nearby well 703612. Facility 703612 is approximately 600 feet east of 753419 and review of geologic maps indicates both are drilled in the Poison Canyon Fm. The anomalously light DIC carbon may indicate that microbial processes including methane degradation are more active in groundwater accessed by this well than in nearby 703612, but we have not yet had an opportunity to better define the microbial population at this well.

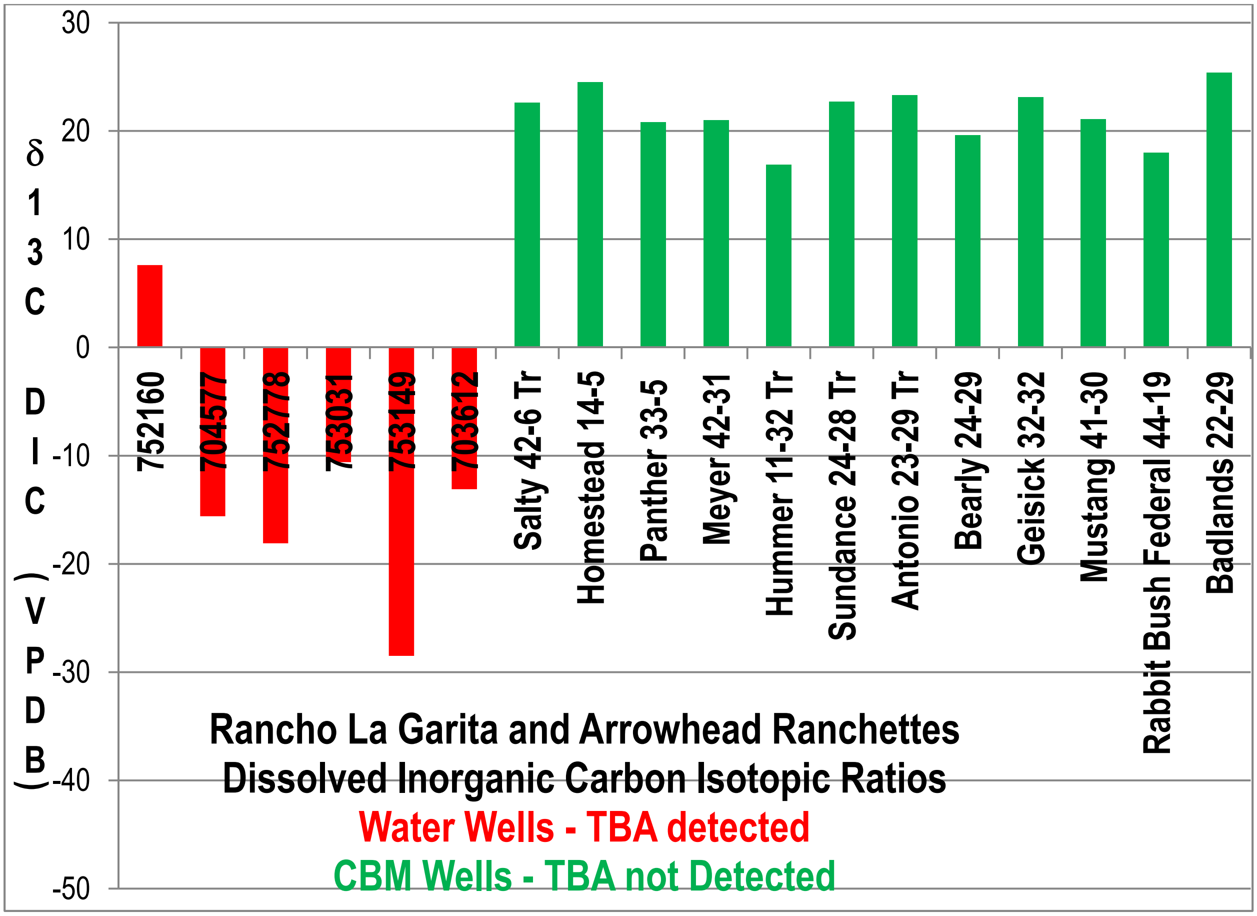

Figure 16. Carbon Isotopic Composition of Dissolved Inorganic Carbon from Rancho la Garita and Arrowhead Ranchettes Samples

At one domestic well (facility 703612) in which groundwater was sampled in 2014 and TBA was detected at 320µg/l and 470µg/l, there is a record of major ion composition (but not TBA analysis) of the groundwater dating to a United States Geological Survey

(USGS) sampling event in 1981. CBM operations were not present in the area until the mid-1990s; therefore, the 1981 sampling event provides a true baseline. The major ion composition of groundwater pumped from that well is the same within analytical uncertainty between the 1981 and 2014 sampling and analyses. The water chemistry from facility 703612 is of distinctly different major ion character than produced water from four nearby CBM wells as shown on the Piper diagram in Figure 17, below.

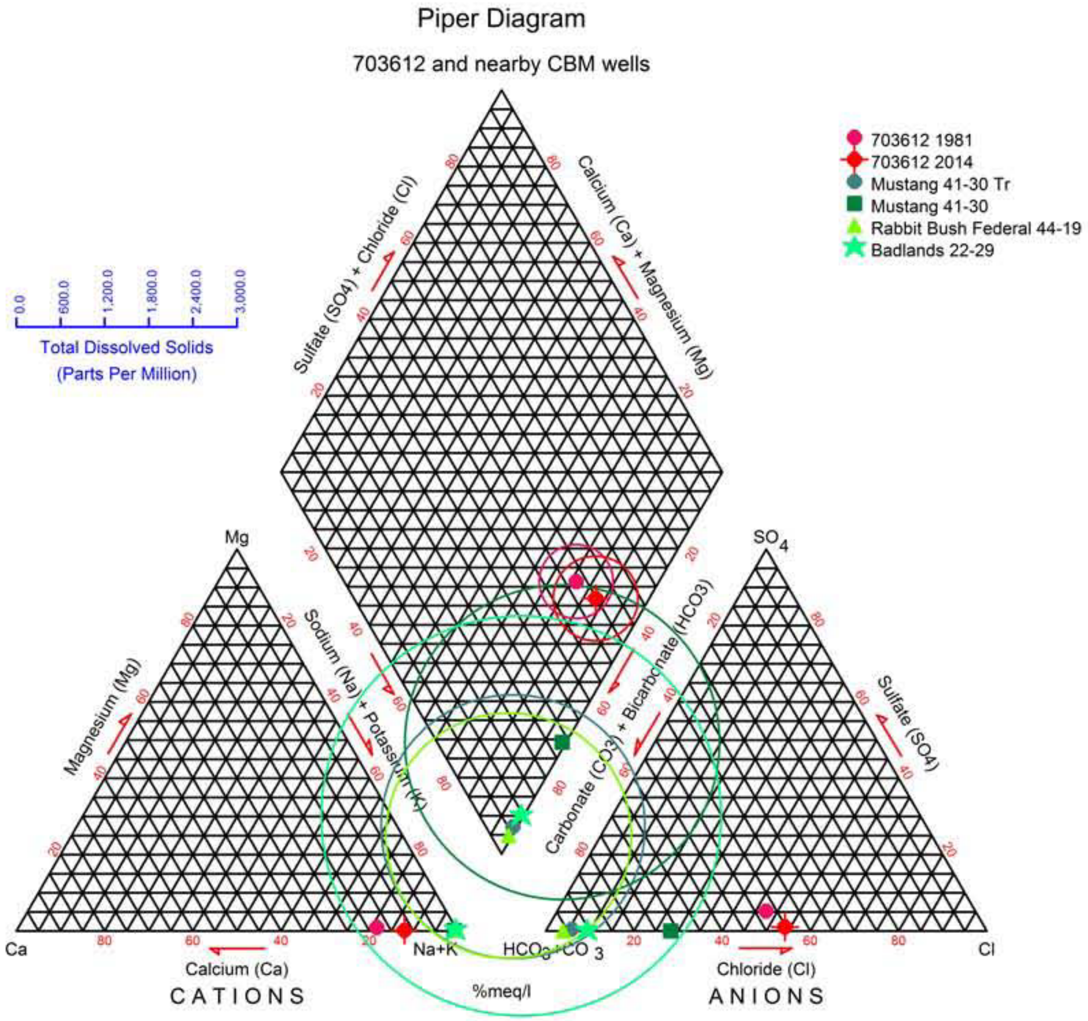

Figure 17. Piper Diagram of Major Ion Composition of 703612 and Nearby CBM.

In this instance the relative percentage of chloride in the anion fraction of groundwater at 703612 has stayed at approximately 50% between 1981 and 2014. Since the relative fraction of chloride in the anions present in the four produced water samples is considerably less than 50% of the anions, the plot illustrates that there is no significant mixing of CBM produced groundwater with the groundwater pumped from the domestic well 703612.

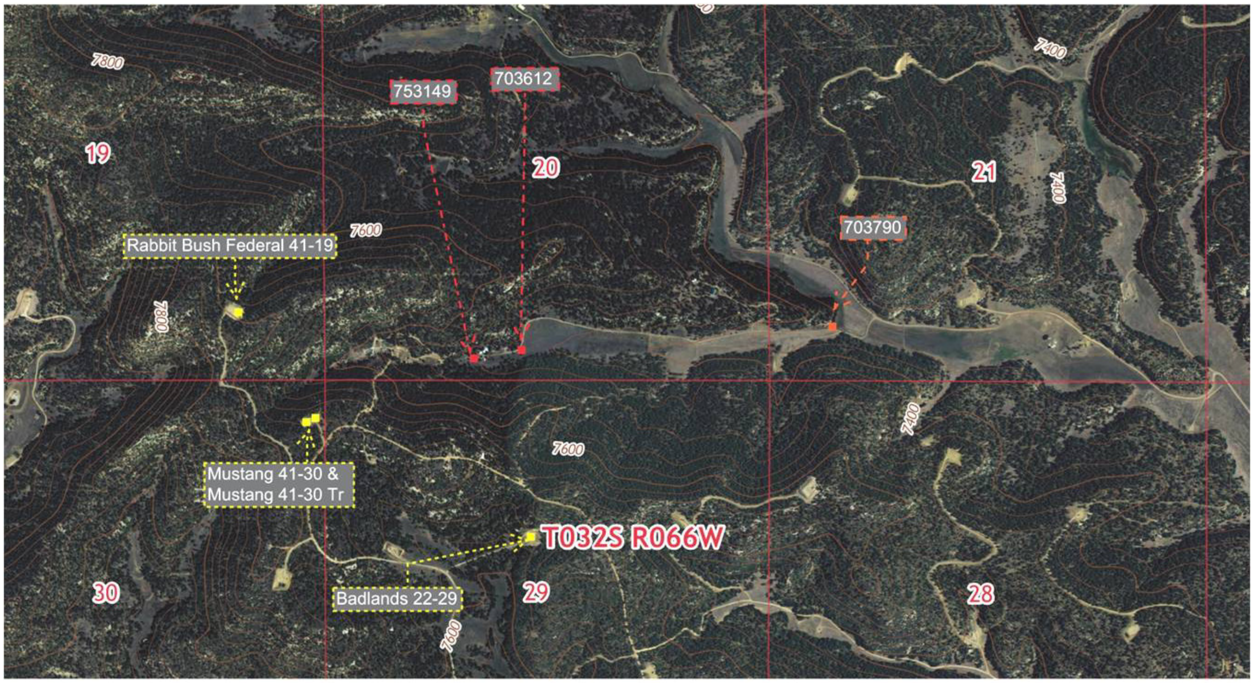

Figure 18. Water wells and CBM wells located near 703612 on 2011 aerial base with topographic contours.

The closest CBM well to 703612 is the Badlands 22-29 (2,230 feet distant), which is located in a different drainage from the water well, so it is improbable that any spills at the surface would flow towards 703612, as shown on a 2011 aerial photo with topographic contours in Figure 18. The red lines are section lines and are approximately 1 mile apart with north to the top of the aerial. The Mustang and Rabbit Bush Federal CBM wells are located at the headwaters of the drainage valley in which 703612 is located but are more than 2,500 and more than 3,400 feet, respectively, from the 703612 well.

Facility 703612 is drilled and completed in the Poison Canyon Fm. with estimated horizontal hydraulic conductivity of 55 feet/year (Norwest Corporation *et al.*, 2010). Subsurface migration from the closest CBM well to 703612 would be expected to take 40 years or more. The earliest CBM well in the drainage (Mustang 41-30) was spud in 2001. TBA was detected in water samples from the cistern at this property in 2011 or only 10 years after initial CBM operations in the drainage valley where 703612 is located.

COGCC database contains no reports of spills from the Rabbit Bush Federal location and records of four spills of produced water at the Mustang location. Approximately 215 barrels of produced water spilled in those incidents with the longest spill path reported as 250 feet. Surface migration can proceed very rapidly in comparison to the estimated groundwater flow time above. A surface flow path of 250 feet shortens the estimated groundwater flow time between the Mustang location and 703612 from 47 years to 42 years. The time estimate for groundwater flow between 703612 and nearby CBM wells in conjunction with the stable major ion chemistry of 703612 indicate that spills of produced water are very unlikely to be a source of TBA in groundwater pumped from 703612.

As there is no demonstrated change in major ion composition at 703612 in the 33 years since first sampled, any input of TBA would arguably have to be entering the system as pure or nearly pure TBA with no carrier CBM produced water. Alternatively, the TBA could be produced by microbial processes in the groundwater near the well, as isobutane was detected in samples from this well, could be entering groundwater from products used in the well, or could be directly or indirectly introduced from fuel spills, as BTEX and other aromatic compounds are present in samples from this well.

TBA was reported in groundwater from another domestic well (facility 704577) in this area as early as June of 2006. The closest CBM well in 2006 to this water well was more than 2,200 feet distant and that well was drilled and completed in January 2005. If that CBM well was the source of the TBA found in the domestic well in 2006, then groundwater flow rates of 1,500 feet per year would have been required. Review of regional geologic maps as compiled by Topper *et al.,* (2011) indicates the domestic well 704577 is drilled and completed in the upper portions of the Raton Fm. The horizontal hydraulic conductivity rate in the upper units of the Raton Fm. was estimated at 37.5 feet per year in models submitted into evidence during rulemaking on the tributary/non-tributary status of produced water in the Central Raton Basin (Norwest Corporation *et al.*, 2010). Estimated time for groundwater to migrate from the nearest CBM operations to this water well is more than 58 years at the horizontal hydraulic conductivity of the upper portions of the Raton Fm. cited above, so groundwater migration from CBM drilling, completion and production operations cannot be viewed as potential source of TBA in groundwater at facility 704577. The earliest CBM wells drilled in this area are less than 30 years old and as each of those is even further from 704577 there is little likelihood of those older CBM wells being a source of TBA by groundwater migration to 704577.

During a 2005 sampling event at facility 704577, COGCC staff observed water flowing back downhill into the well from the approximately 400 feet of plastic pipe (thought to be polyethylene) connecting the well to the house, as check valves were apparently not used in the installation. Access to sample this well in 2013 as part of this investigation was not granted to COGCC/CDPHE despite repeated requests. Therefore, further investigation of this occurrence of TBA in groundwater from a domestic well has not been possible and COGCC cannot eliminate the plastic delivery pipe as a potential source of TBA in the earlier samples collected from this domestic well.

TBA was not detected in produced water from any of the 12 CBM wells sampled in the Rancho la Garita and Arrowhead Ranchettes area. TBA was not detected in frac flowback samples from one CBM well collected in 2011 in this area. These results indicate that spills or releases of CBM produced water at the surface are not a likely cause of the TBA detected in the six domestic well groundwater samples.

Review of frac composition used in this area since 2006 does not indicate the use of *tert*-butyl hydroperoxide gel breakers. Records do indicate the use of enzymatic gel breakers (not known to contain TBA or the possible precursor *tert*-butyl hydroperoxide). TBA was not detected in analyses in 2011 of flowback following hydraulic fracture stimulation of the Panther 33-5 in this area, confirming that there was not a source of TBA in the fluids used during the completion of the CBM well. The records and the analytical data available from flowback indicate that frac fluids are not a likely source of TBA in this area.

Section 3: Burro Canyon, Reilly Canyon and Colorado Canyon Area Summary

Wells in this area were not sampled as part of the EPA retrospective case study. The locations of four Burro Canyon CBM wells and four water wells east of Burro Canyon sampled as part of this investigation are shown on Map 4. The CBM wells produce from the coal bearing Vermejo Fm. The three easternmost water wells (off Colorado Canyon) are also most likely developed in the Vermejo Fm. and are approximately 2.5 to 3 miles east of the closest CBM well. The water well in the center of the map east of Reilly Canyon is developed in the Raton Fm. and is approximately 0.5 mile east of the closest CBM well.

Data from a 2012 sampling of produced water from one CBM well in the Burro Canyon area indicated the presence of TBA. That CBM well and one other nearby CBM well were sampled in 2013 as part of the COGCC investigation to confirm the presence of TBA in Vermejo Fm. groundwater in this area. TBA was detected in produced water samples collected from these adjacent CBM wells at concentrations between 20-100µg/l. Produced water from two nearby CBM wells was sampled in 2014 and TBA was not detected in these CBM wells. The closest water well to these CBM wells is more than 1 mile away.

TBA was detected at 2µg/l in samples from one domestic well east of Colorado Canyon and approximately 3 miles from the closest CBM well. TBA was not detected in samples of groundwater from the other three water wells in this area for which we have data.

As shown earlier in this report, produced water from two CBM wells sampled in the Burro Canyon area is unusual for produced water from coals in the Basin. As apparent on the Stiff diagram (Figure 19) showing the major ion character of produced water from these two wells, both CBM wells produce water of sodium-chloride character and both also have concentrations of dissolved solids in the 20,000mg/l range. Most CBM produced waters are of sodium-bicarbonate character with dissolved solids concentrations 5-15 times lower.

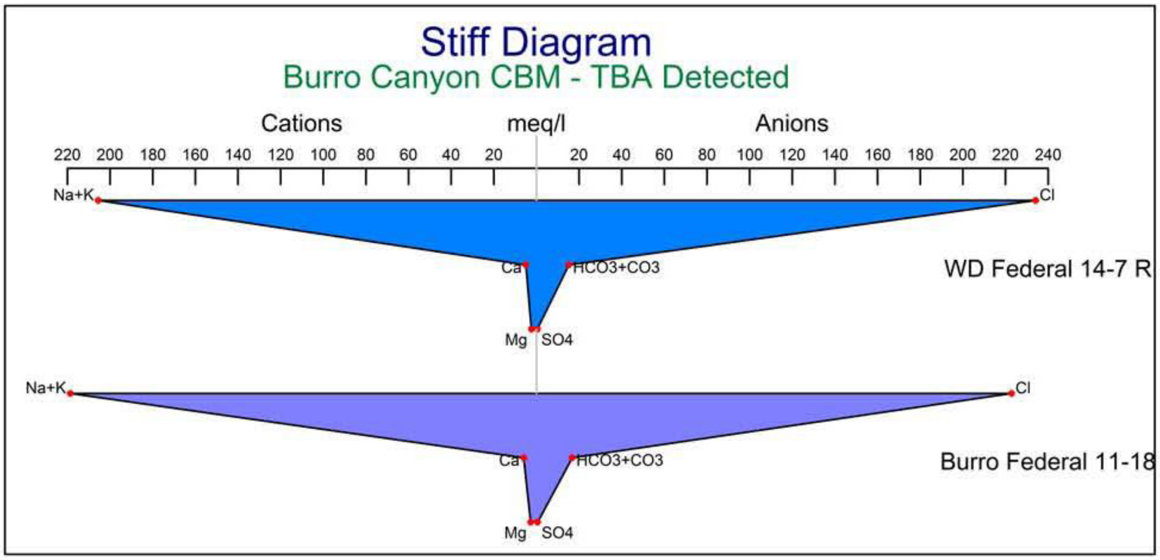

Figure 19. Stiff Diagram Vermejo Fm. CBM in Upper Burro Canyon

The domestic well in which TBA was detected was drilled in August 2012 by air rotary method. No pump had been installed before the sampling event in the spring of 2013. A three-hour pump test was performed at the time of drilling using bailer and air lift. For this study, a licensed local pump installer was contracted to install a temporary pump in the well in order to collect groundwater samples. Toluene and TBA were detected in water samples collected from this well during the one sampling event for which data is available.

As part of the COGCC investigation, samples were collected of two products used in the temporary installation of the pump at facility 753153. Both products are routinely used in domestic wells. With the cooperation of the pump installer, samples of green waterproof electrical tape and samples of pipe thread sealant product were collected and submitted to a lab for the following procedure and analysis. Aliquots of each product were weighed into volatile organic analysis (VOA) vials used for sampling of water. The aliquots of tape and pipe dope were immersed in volatile-free blank water and sealed. The product samples were stored for six days to mimic immersion of these products in groundwater and to determine if VOC leach from the products used during the initial contact of the products with groundwater.

Analyses of the water samples in which the tape and pipe dope were immersed are summarized in Table 5 below. Toluene and acetone were present in water in contact with each product and at relatively high concentrations. Use of VOC such as acetone and toluene in adhesives is documented in literature. The lab reported that TBA was not detected in either sample at elevated detection limits and those results are from analysis of samples that were diluted due to high concentrations of other volatile compounds. Review of the analytical data package does indicate the presence of TBA in water in contact with the pipe thread sealant product but at a level just below the lab's established limit of detection (LOD) for TBA in water samples.

Toluene was detected in groundwater samples collected from the well (10µg/l) in which the tape and thread sealant were used as well as in VOC free water exposed to the products at the lab. Other than toluene, no BTEX compounds were detected in these groundwater samples or in water exposed to the products in the lab. TBA was detected at low concentration in the groundwater samples from the well (2µg/l). TBA was present in the water exposed to the pipe thread sealant product. Although the sample result was below the lab's established LOD, the LOD was elevated due to dilution of the sample for high concentrations of other VOC and the presence was confirmed by review of spectral match and retention time match. The estimated concentration of TBA of approximately 300µg/l in water in contact with the pipe thread sealant indicates the product is a possible source of TBA present in groundwater in domestic wells when this product has been used in pump installation.

Sample	Analyte	Dilution	Result µg/l	Flag
water with underwater electrical tape (40ml to 6.71g)	toluene	5000	29000	
	methyl methacrylate	100	2100	
	acetone	5000	16000	J
water with pipe thread sealant (40ml to 11.02g)	acetone	2000	120000	
	chloroethane	10	17	
	vinyl acetate	10	130	
	2-butanone	10	39	J
	toluene	10	7.3	J
	tert-butyl alcohol	10	(≈300)	below LOD
J = below the lab's established reporting threshold with estimated concentration				

Table 5. VOC Detected in Water Exposed to Two Products

The Colorado Canyon domestic well in which TBA was detected is located updip of and approximately 3 miles from the closest CBM well. It is improbable that CBM operations could be the source of TBA in this domestic well due to distance, groundwater transport rates and to a lesser extent because the domestic well's location is updip of CBM activities. Review of the well construction report and regional geologic maps indicate the well is completed in the lowermost conglomerates of the Raton Fm. or sandstones within the Vermejo Fm. Horizontal hydraulic conductivity in the Raton Fm.

conglomerates was estimated at 0.4-5.9 feet per year in models submitted into evidence during rulemaking on the tributary/non-tributary status of produced water in the Central Raton Basin (Norwest Corporation *et al*., 2010). Horizontal hydraulic conductivity in the underlying Vermejo Fm. was estimated at 10 feet per year in models submitted into evidence during rulemaking on the tributary/non-tributary status of produced water in the Central Raton Basin (Norwest Corporation *et al.,* 2010). Estimated time for groundwater to migrate from the nearest CBM operations to this water well is more than 1,500 years at the greater hydraulic conductivity of the Vermejo Fm. cited above.

Although it is possible that the presence of toluene and TBA in groundwater from this well is because one or both are naturally occurring in the groundwater, the most likely explanation is that both compounds are present as artifacts of the pump installation process due to the confirmed presence of toluene and TBA in products used in the pump installation.

Section 4: Gulnare Area Summary

Wells in the Gulnare area were not sampled as part of the EPA study. Groundwater from three domestic water wells and produced water from two CBM wells were sampled and analyzed during this investigation. Two of the water wells sampled were located approximately 5 miles southeast of the other three sampling sites in this area, as shown on Map 5. TBA was not detected in the two remote domestic water wells, but was detected in the two CBM wells and the nearby domestic water well. These TBA detections are discussed in more detail below.

In March 2014, COGCC received a general landowner complaint requesting baseline sampling of a domestic water well located in this area. Sampling and analysis conducted as part of the complaint investigation indicated presence of TBA in groundwater accessed by the domestic water well. Subsequently the domestic well was resampled and produced water samples from two CBM wells near the domestic well with TBA detected in shallow groundwater were collected for evaluation as potential sources of TBA.

The reported concentrations of TBA in the domestic water well sample were 78 and 96µg/l while the TBA concentrations reported as present in produced water from the CBM wells was between 2-3µg/l. The water well is likely completed in the coal bearing Raton Fm. and the two nearby CBM wells comingle production of gas and water from coals in both the Raton Fm. and the underlying Vermejo Fm. The major ion composition of all three samples is primarily a sodium-bicarbonate character with higher levels of dissolved solids in the CBM produced water. In contrast the CBM wells also have minor chloride character (200-300mg/l) and the water well has very low chloride concentration (<20mg/l). Methane was detected at elevated concentrations (10-22mg/l) in the three Gulnare area samples in which TBA was detected. The plot in Figure 20 below illustrates differences in isotopic composition of the methane in the water well in comparison to methane present in the CBM wells. The differences in major ion composition together with different possible sources of methane as indicated by the isotopic composition in Figure 20 indicate the domestic well and the CBM wells have different sources of water and methane. The 20-30 times greater concentration of TBA reported in groundwater from the domestic well in comparison to the TBA concentrations in the CBM produced groundwater indicates that the source of the TBA in the domestic well groundwater is not likely reported or unreported surface spills or releases of CBM produced water to the groundwater accessed by the shallower domestic well.

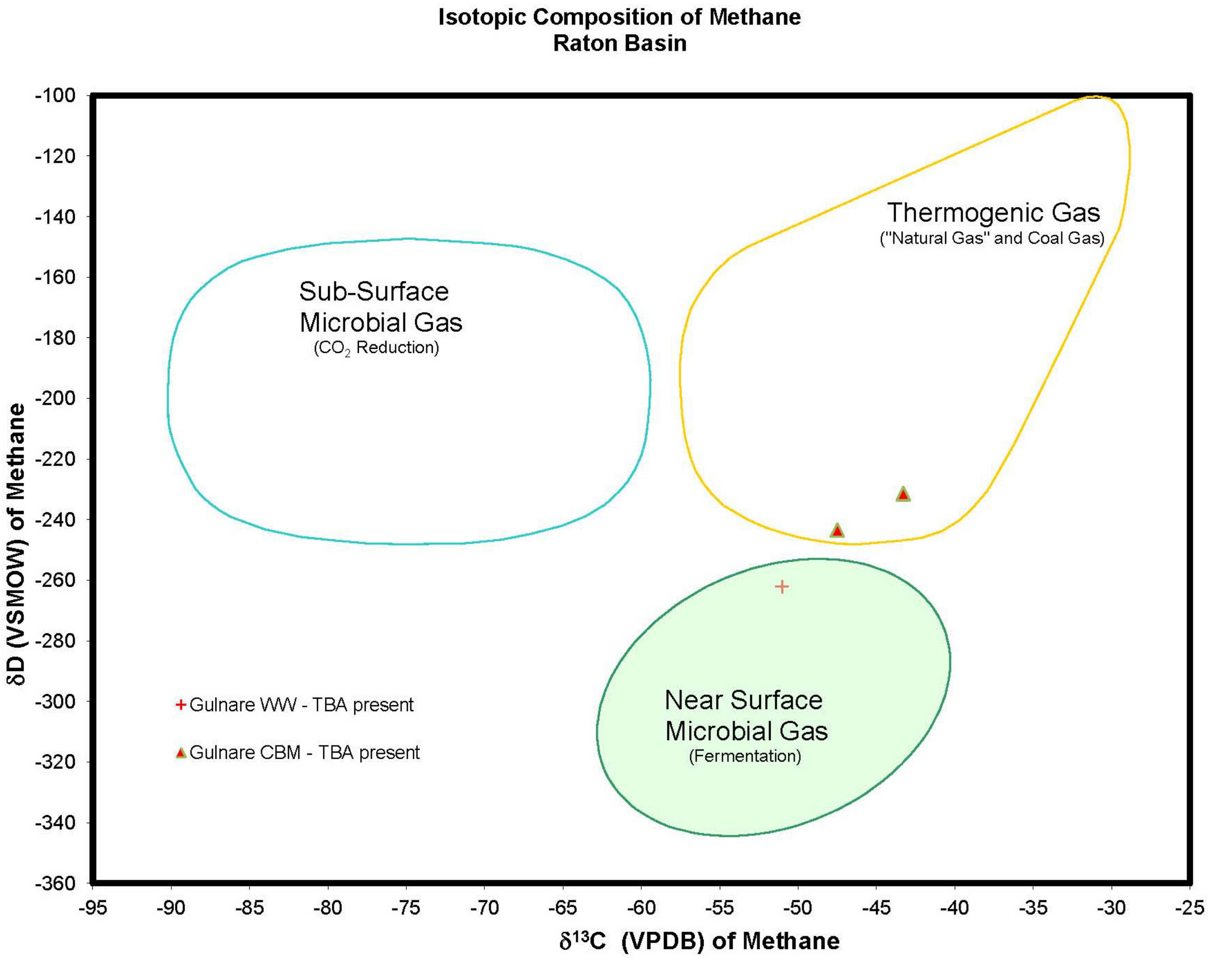

Figure 20. Gulnare Area Methane Isotopic Composition

Discussion

The data collected and reviewed as part of this study do not indicate a source of TBA in flowback fluids collected shortly after hydraulic fracture stimulation analyzed in 2011 and 2013, as TBA was not detected in samples of these flowback fluids. Review of MSDS of products used in hydraulic fracture well completions in this area since at least 2006 do not list TBA as a component of any of the products used in the completions.

One potential source of TBA in groundwater accessed by domestic wells was discovered to be pipe thread sealant used to seal threads on PVC drop pipes during pump installation. A second possible source of TBA in groundwater accessed by CBM and domestic wells was discovered to be compressed air used to aid cuttings removal during drilling of wells with air as the drilling fluid.

Discharge to waters of the state of produced water from CBM operations has been the major means of disposal of this E&P waste in the Basin. TBA was not detected in 13 samples collected at permitted outfalls at which produced water from CBM wells is discharged to the surface. This sampling indicates that the permitted discharge to waters of the state of these wastes is currently not a likely source of TBA in shallow alluvial groundwater or in deeper sources of groundwater that may be recharged from shallower sources.

TBA was detected at a slightly lower percentage in groundwater samples from CBM wells (22%) than from domestic water wells (24%). The slight difference is not likely statistically significant. When detected, TBA concentrations in water wells were generally greater than in CBM wells in which TBA was detected. For example, in the Rancho la Garita/Arrowhead Ranchettes area in which TBA was detected in 6 of 15 water wells sampled, TBA was not detected in groundwater from any of 12 nearby CBM wells sampled at the time of this report. Spills of produced water in this area cannot be considered a very likely source of TBA in water wells when concentrations of TBA are less (or not detected) in produced water from CBM wells than TBA concentrations in groundwater from generally shallower domestic water wells. Apparent absence of TBA in shallow alluvial character groundwater also indicates that spill or releases of exploration and production wastes are not likely sources of TBA detected in water or monitoring wells.

The groundwater samples from the Basin discussed in this review are mostly from rural residential subdivisions and all are remote from commercial gasoline sales and storage operations, though there are reports of moderate size private fuels storage tanks scattered in the area. Many homeowners may have small quantities of gasoline at their homes for use in lawn and garden equipment or all-terrain vehicles. Both types of homeowner gasoline storage tanks are potential sources of aromatic compounds and isobutane in groundwater samples which contain the similar aromatic compounds, short chain hydrocarbons including isobutane and TBA.

Diesel fuel is present on CBM locations during drilling and completion operations and is used to power compressors, generators or drilling equipment. Diesel fuel is a refined cut of hydrocarbons that is considered in EPA method SW-846 8015 to start at a 10 carbon chain length but may contain limited amounts of octane (eight carbon length). Because of its generally heavier (longer chain hydrocarbon) composition diesel fuel is not considered a potential source of short chain hydrocarbons such as isobutane, propane and ethane observed in a number of wells in which TBA and those short hydrocarbons have all been detected.

MTBE has not been detected in groundwater from any of the sampling locations summarized in this review, so it is unlikely that MTBE is the source of TBA present in some groundwater in the Basin.

Three of the groundwater samples from domestic wells in which TBA has been detected also contain elevated levels of BTEX compounds, which could be indicative of fuels spills impacting the groundwater. Depth to water sources reported by drillers in the three domestic wells with elevated BTEX are between 90-115 feet, 232-451 feet and deeper than 700 feet, respectively. Coliform bacteria have been detected in water samples from one of the three domestic wells with elevated BTEX and TBA present. The presence of coliform bacteria in groundwater samples may indicate a likely downward migration pathway along the water well bore for water and possibly any entrained contaminants from the surface that could include BTEX and TBA.

The methane to ethane ratio from these three wells (38-82) is unusually low and lower than the C_1/C_2 ratios of any CBM production gases for which we have data as shown in Figure 2. Concentrations of isobutane in these three wells are also greater than the concentrations of isobutane in any gas produced from CBM wells for which we have composition analyses. Kaplan *et al.*, (1997) indicated that propane was typically the lightest gas present at low, but measureable, levels in gasoline they analyzed. Isobutane was reported in approximately 10 times greater concentrations than propane in gasolines tested. The presence of ethane in gasoline fuels was not reported (Kaplan *et al.*, 1997). The source of methane and ethane in these three samples is thermogenic as interpreted by methane and ethane isotopic compositions, but the gas composition as indicated from the low C_1/C_2 ratios suggests a gas source other than what is produced nearby from CBM wells.

TBA and elevated concentrations of BTEX were also detected in groundwater sampled from one CBM well (WD Federal), but it seems unlikely that the source of the BTEX and TBA in the CBM well could be from a surface fuel spill. The shallowest perforation in the CBM well with elevated produced water BTEX concentrations is at a depth of 1,318 feet and completion records for this well indicate good cement coverage on the surface casing to 273 feet and good cement coverage along the production casing from 4 feet to 1,717 feet. In the absence of a short circuit path along the well bore, the migration from surface of BTEX and TBA would take a prohibitive amount of time to travel to 1,318 feet depth or greater. This CBM well was drilled in August 2011 and completed in October 2011 and water produced from the well contained BTEX and TBA when sampled in February 2012.

The produced water from this well (WD Federal) and a nearby CBM well (Burro Federal) have major ion chemistry unusual for the area as discussed above. The methane to ethane ratio from the WD Federal gases (148) is unusually low in comparison to the C_1/C_2 ratios of gases produced from coals in the Basin as shown in Figure 2. The concentrations of isobutane detected in WD Federal gases are also greater than any other coal bed methane gas from the Basin for which we have data.

The two samples also have distinctly different water isotopic ratios compared to hundreds of other groundwater samples in the Basin, as discussed previously and shown in Figure 6. The water isotopic composition of groundwater from the WD Federal and Burro Federal CBM wells, as seen in Figure 6, indicates sources of water from different history compared to sources of water from any other wells for which we have data. This is further evidence of a lack of connection between shallow sources of groundwater and the perforated zones producing groundwater in these two CBM wells.

Table 6 below is included to better illustrate the quantities of water used in hydraulic fracturing in these two wells with water volumes produced after completion and also to calculate the concentration that would be needed to result in the current measured concentration if the TBA had been introduced to the local groundwater in fluids used to hydraulically fracture stimulate the two wells. The frac volumes for the WD Federal and the Burro Federal CBM wells were less than 2,000 barrels of water. Records indicate both wells have produced more than 100 times more water than used in the frac jobs since initial production. If TBA was introduced into the coals around the WD Federal well bore in one event (hydraulic fracture stimulation), the necessary concentration in the 1,950 barrels of fluid would have to be a minimum of 103 times greater than currently observed, due to the volumes of water produced from the CBM well since completion and assuming a linear decrease over time. TBA was not detected in frac flowback samples collected in 2011 at the Panther CBM well (<50µg/l). The calculations in Table 6 indicate that if frac fluid was the sole source of TBA in the WD Federal, the concentration would have been more than 240 times greater than the reported non-detection in actual flowback from a CBM well drilled and completed in the same time frame (Panther 33-5) and completed using the same products used at the fracture stimulation of the Panther.

Well	Date of Completion	Produced Water Since Initial Production (bbl) to September 2014	Frac Volume (bbl)	Number of Frac Volumes of H_2O Since Production	TBA Conc. (µg/l)	Conc. in Frac Fluid (µg/l) if Frac Were Sole Source of TBA
WD Federal 14-7 R	10/16/2011	202,286	1,950	103	120	12,360
Burro Federal 11-18	07/23/2002	292,833	1,344	218	22	4,796

Table 6. Comparison of Frac Volumes with Subsequent Produced Water Volumes

For CBM wells such as WD Federal and Burro Federal, most of the sources/mechanisms outlined in the previous section on TBA chemistry and occurrences can be ruled out from data presented above. The only potential source of TBA not ruled out from data presented above is the possibility of in situ microbial oxidation of naturally occurring isobutane to TBA by methanotrophic bacteria.

Groundwater samples from several selected sites discussed above were submitted for microbial identification using one or both of two analytical techniques as part of the special project and also from samples collected by COGCC during EPA sampling. Identification and quantification of bacteria from methanogenic phylogenetic groups (methane producing) and from methanotrophic phylogenetic groups (methane consuming) was performed by quantitative polymerase chain reaction (PCR) techniques. PCR was also used to identify the presence of genetic markers indicative of the presence (or absence) of benzene and toluene degrading bacteria. Identification of general types and proportions of classes of bacteria present was performed by phospho-lipid fatty acid (PLFA) analysis. The bacterial analyses were performed on groundwater samples from wells in which TBA was detected and also from wells in which TBA was not detected.

Methanotrophic bacteria and methanogenic bacteria were detected in groundwater samples from each of 14 sites submitted for PCR analysis between October 2012 and

August 2013. Estimates of the number of methanotrophic bacteria present were between 10^6 and 10^8cells/ml. Estimates of the number of methanogens present in these groundwater samples ranged from less than 1cells/ml to greater than 10^6cells/ml.

The PCR-based concentrations of methanotrophs were high in samples collected in both Huerfano and Las Animas counties. For example, three samples from Huerfano County domestic wells were analyzed and contained greater than 10^7 methanotrophic cells/ml. Gas composition and methane isotopic composition have changed over time in these wells as shown in the figures below. Figure 21 illustrates isotopic changes in methane present in one domestic well that are illustrative of microbial oxidation of methane. The isotopic composition of methane from three nearby CBM wells sampled and analyzed in 2007 is also shown for comparison to the water well sample results. Microbial oxidation of isotopically lighter (more negative) methane is favored with resulting heavier methane still present.

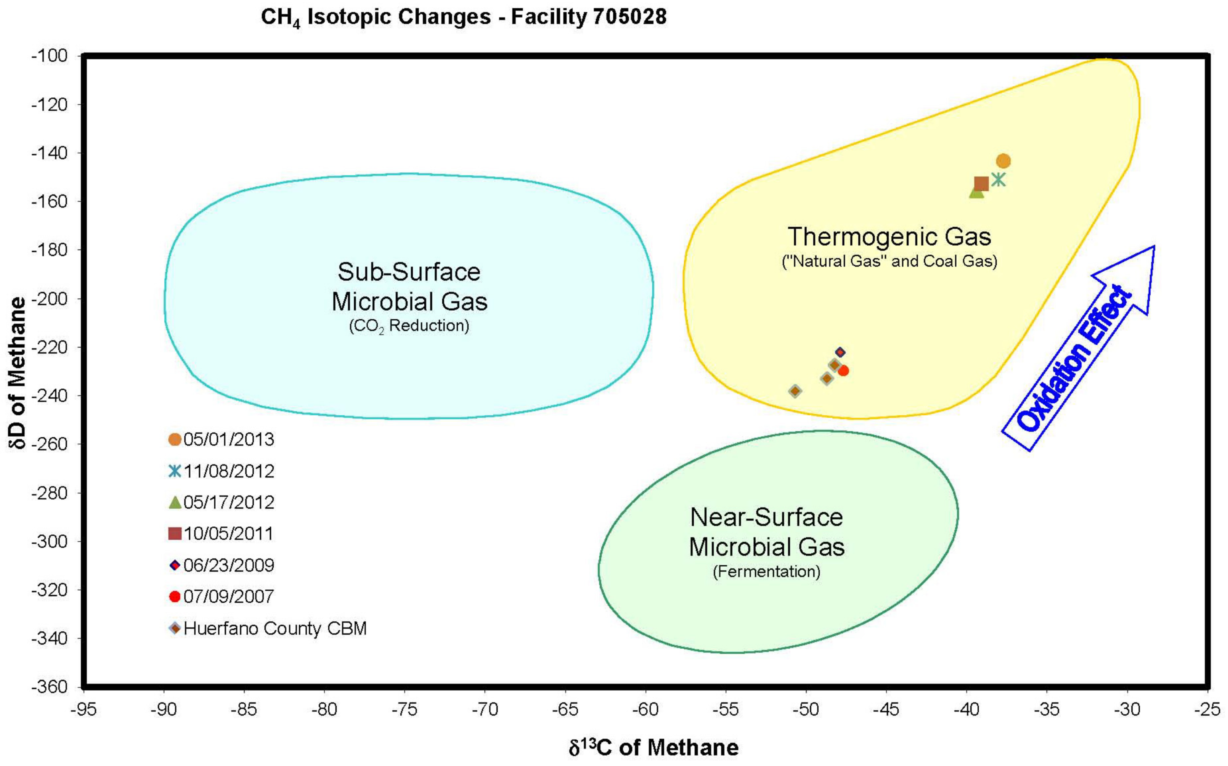

Figure 21. Changes in Methane Isotopic Composition (Facility 705028) Since 2007

Changes in compositional ratios of gases dissolved in groundwater may also take place if microbial oxidation is present. Figure 22 below illustrates the ratio of methane to ethane (C_1/C_2) from the facility 705028 plotted versus carbon isotope ratio of the methane in the same samples. The isotopic composition of methane and C_1/C_2 ratios from four nearby CBM wells sampled and analyzed in 2007 is also shown for comparison to the water well sample results. The gas composition ratios are plotted on a logarithmic scale. The plot illustrates that while the methane carbon isotope ratios change due to microbial oxidation, there is not a significant related change in gas composition. The lack of change in C_1/C_2 ratios while active microbial oxidation is underway indicates that ethane and perhaps all of the short chain hydrocarbons present are being degraded at relatively the same rate as methane present in the groundwater. So while microbial oxidation of methane and presumably other light hydrocarbons can be demonstrated at facility 705028 in Huerfano County, TBA was not detected in multiple sampling and analysis events at this water well.

Data available in the COGCC database indicate that gases from CBM wells in the Basin typically have methane to ethane ratios of greater than 1,000 and sometimes as high as 25,000 and are in general all considered as dry gases (Lillis *et al.*, 2008 and Tissot and Welte, 1984). The available data indicate typically very low concentrations of isobutane are present if detected at all. The typical detection limit for isobutane in the analyses discussed is 0.0001 mole percent (mol%) of the gases present. For example, isobutane was detected in only one of seven samples collected since 2007 from facility 705028.

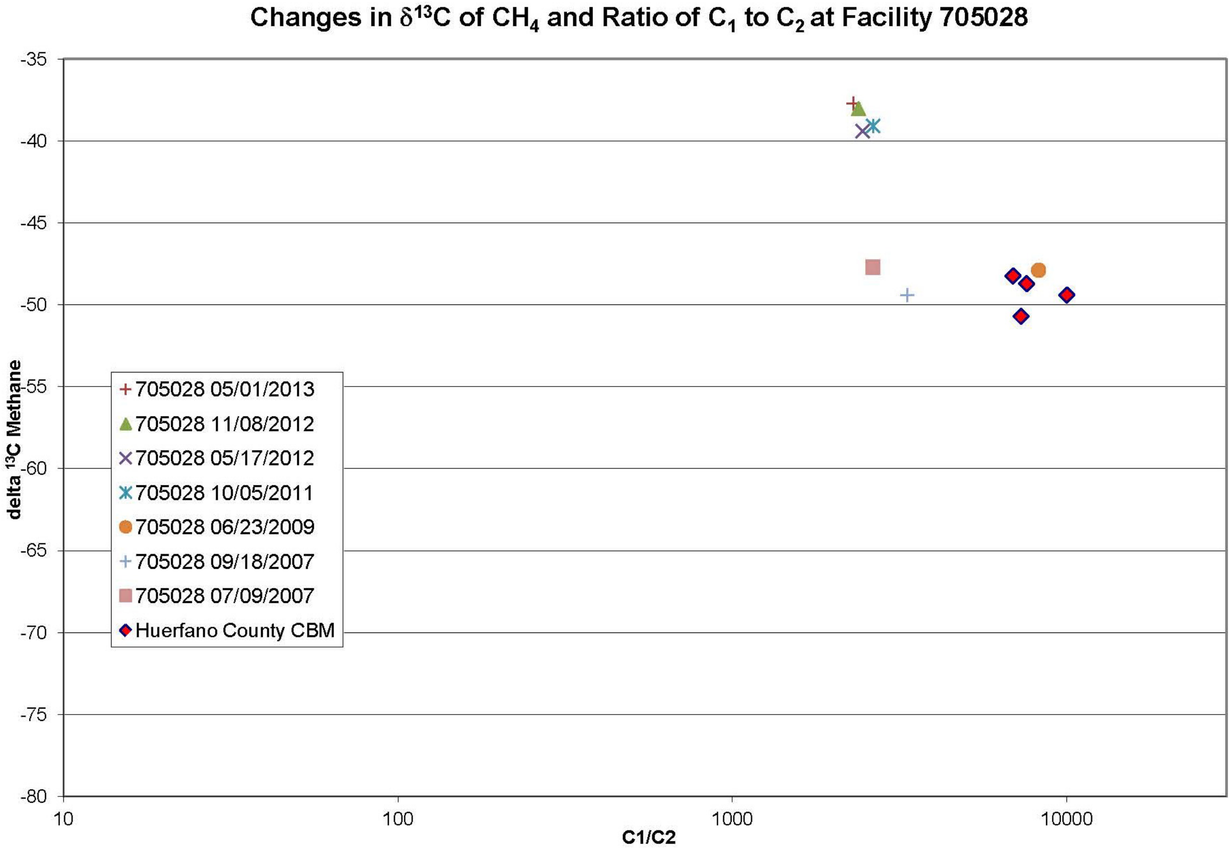

Figure 22. Changes in Methane Carbon Isotopic Composition Versus Ratio of Methane to Ethane

In comparison to the dry gas observed in Huerfano County wells, significantly wetter gas composition from seven samples from the Las Animas County portion of the Basin is illustrated below in Figure 23. Gas composition and carbon isotopic ratio for methane from five groundwater samples from domestic wells and two groundwater samples produced from CBM wells are included. The two CBM wells included in the graph produce from Vermejo Fm. coals and are located in upper Burro Canyon. The water wells included on the Figure 23 are completed in the Raton Fm.

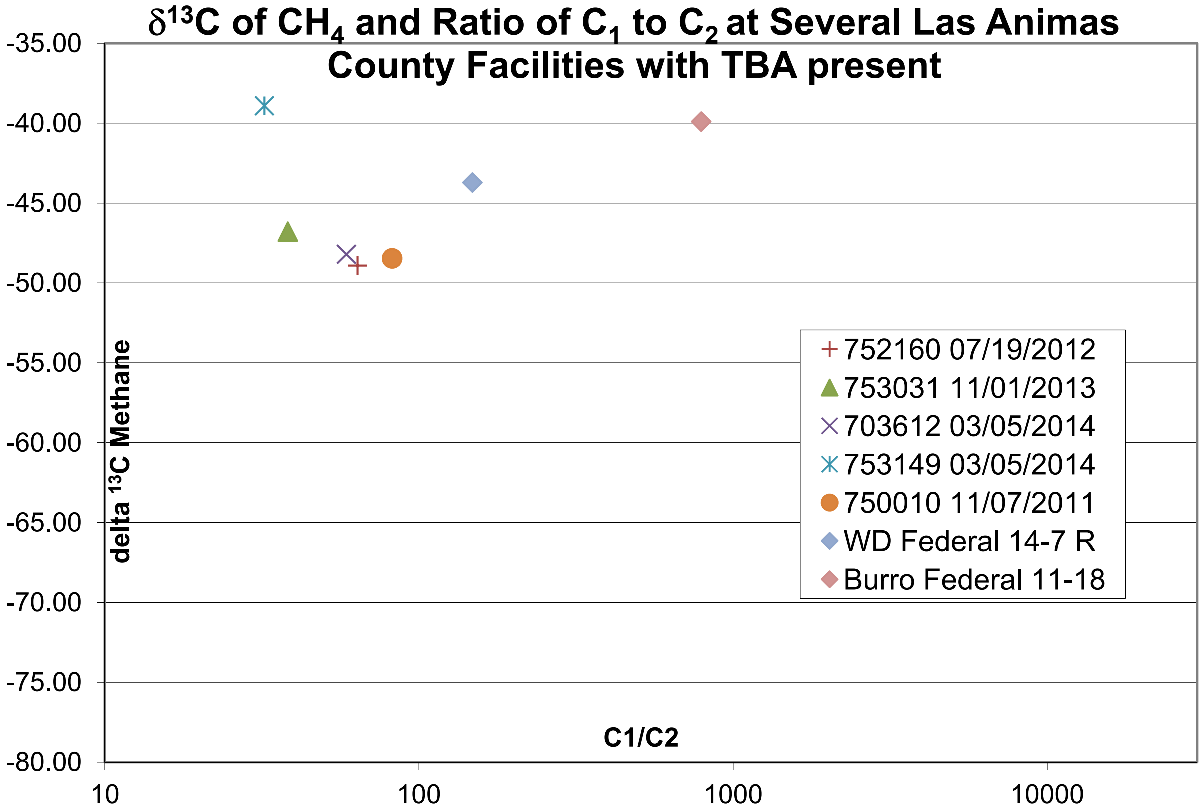

Figure 23. Gas Composition and Methane Carbon Isotopic Ratios from Several Las Animas County Wells with TBA Present

Figure 23, above, illustrates methane to ethane ratios of several samples with TBA present, but the presence or absence of isobutane (a possible TBA precursor) cannot be shown on such a graph. Table 7, below, includes measured gas composition in mol% for the seven samples included in Figure 23. Isobutane is present in all seven samples with concentrations between 0.0026 and 0.3250 mol% of the gases present in the groundwater from the wells. For comparison to the Las Animas county samples discussed here, the gas composition of groundwater from facility 705028 in Huerfano County discussed above is shown. Isobutane if present in the Huerfano County domestic well (705028) would be, at a minimum, 25 times less than in the Las Animas county sample listed with the lowest concentration of isobutane. Therefore, with isobutane detected in the seven Las Animas County samples in Figure 23 and Table 7, a microbial degradation pathway to produce TBA may be possible.

Facility	Date Sampled	methane (mol%)	ethane (mol%)	propane (mol%)	isobutane (mol%)	TBA (µg/l)
752160	11/11/2011	90.68	0.63	0.51	0.1120	420
753031	11/01/2013	87.89	2.30	1.08	0.3250	30
703612	03/05/2014	68.71	1.17	0.03	0.0645	320
753149	03/05/2014	20.35	0.63	0.11	0.0051	91
750010	11/07/2011	90.31	1.10	0.11	0.0342	450
WD Federal 14-7 R	08/21/2013	70.22	0.48	0.23	0.0700	96
Burro Federal 11-18	01/29/2014	58.22	0.0736	0.0131	0.0026	19
705028 (Huerfano)	05/01/2013	56.78	0.0247	0.0007	<0.0001	<5

Table 7. Methane (C_1) to Isobutane (iC_4) Gas Composition of Water from Eight Sources

Methanotrophic bacteria, if present in groundwater with detectable isobutane from the Las Animas county wells listed in Table 7, could potentially be a source of TBA in groundwater from these wells. Groundwater samples from one water well and one CBM well listed in Table 7 were submitted for microbial identification using two analytical techniques as part of this special project. Identification and quantification of bacteria from methanogenic and from methanotrophic phylogenetic groups was performed by PCR techniques. PCR was also used to identify the presence of genetic markers indicative of the presence (or absence) of benzene and toluene degrading bacteria. Identification of general types and proportions of classes of bacteria present was performed by PLFA analysis.

Estimates of the number of methanotrophic bacteria present were between 10^6 and 10^7cells/ml. Estimates of the number of methanogens present in these groundwater samples ranged from less than 5cells/ml (750010) to greater than 10^6cells/ml (WD Federal) based on phylogenetic group PCR analysis. Benzene and toluene were present in groundwater from both of these wells and PCR analyses of functional genes indicated the presence of benzene and toluene oxidizing bacteria at concentrations estimated to be less than 10^3 cells/ml. PLFA analysis was used to estimate the relative proportions (community structure) of different groups of bacteria. Proteobacteria were determined to be about 46% of the bacteria in the WD Federal groundwater and approximately 71% of the bacteria in groundwater from 750010 when sampled in 2013. The majority of hydrocarbon utilizing bacteria are proteobacteria.

Groundwater samples from 753031 collected in 2013 and 2014 also contain TBA and several BTEX compounds. PCR analysis of samples from this well (2014) indicate the presence of methane oxidizing bacteria at greater than 10^5 cells/ml and the presence of toluene oxidizing bacteria at 10^3 cells/ml. Groundwater sampled from this well was also analyzed by a sequencing technique in an effort to determine phylogenetic classes of bacteria present to identify bacteria to the genus level. Gammaproteobacteria were identified as approximately 50% of the bacteria in the sample from 753031 with two methanotrophic genera making up approximately 47% of the Gammaproteobacteria (*Methylmicrobium spp*. and *Methylomonas spp*.). Genera of Betaproteobacteria were also identified in samples from 753031. One of the Betaproteobacteria genera (*Hydrogenophaga spp*.) was identified as being capable of degrading TBA (personal communication, Hyman 2014). Two genera of Actinobacteria (*Gordonia spp*. and *Mycobacterium spp*.) were present in groundwater samples from 752778 in which TBA was present, but BTEX and related compounds were not detected. Both genera of Actinobacteria present in groundwater from this well are known to degrade TBA (personal communication, Hyman 2014).

Facility 752778 is approximately 2,650 feet northeast of 753031 and both are in the Rancho la Garita and Arrowhead Ranchettes area. Bacteria that are known to be capable of producing TBA are present in samples analyzed. Bacteria that are known to be capable of degrading TBA are present in the same samples. The presence of the genera of bacteria capable of producing and genera of bacteria capable of degrading TBA does not prove that either process is actively taking place but does indicate that microbial production or degradation of TBA is possible. The presence of the genera of bacteria capable of producing and genera of bacteria capable of degrading TBA indicate it is possible in some groundwater systems in the Basin that both degradation and production of TBA is occurring simultaneously which could result in a steady state concentration of TBA but this cannot be proven with the data presently available.

The presence of BTEX and related aromatic compounds in many of the Raton Basin groundwater samples in which TBA was detected was mentioned previously in this report. In general, the groundwater samples from the Basin with the highest concentrations of TBA and BTEX typically contained gases with lower methane to ethane ratios than groundwater samples in which TBA was not detected. The methane to ethane ratio of dissolved gases in 23 of 24 groundwater samples in which TBA was detected are plotted versus carbon isotopic composition of methane in the samples in Figure 24 below. The groundwater sample from the PXD-2 investigation well did not contain high enough methane concentration for isotopic analysis to be performed and thus cannot be plotted on the graph.

The number beside each point plotted on Figure 24 is a count of the number of aromatic compounds detected in groundwater from that site. In general the groundwater samples with wetter gases (lower methane to ethane ratios) also have more aromatic compounds reported as present. Thermal maturation of organic source rocks such as the coals in the Basin can produce hydrocarbons other than methane and ethane as discussed previously (Waples, 1983, Rice, 1993). Thermal maturation of coals has produced aromatic hydrocarbons in the Powder River Basin (Orem *et al.*, 2007) and in the San Juan Basin and Raton Basin (Dahm *et al.*, 2011). Raton Basin groundwater samples that have TBA present and C_1/C_2 ratios lower than 200 have more aromatic compounds present than the groundwater samples with TBA present but ratios of C_1/C_2 greater than 200, as seen in Figure 24. The groundwater samples with wetter gas composition and more aromatic compounds present also have higher concentrations of TBA, in general, than the groundwater samples with higher C_1/C_2 ratios and fewer aromatic compounds present.

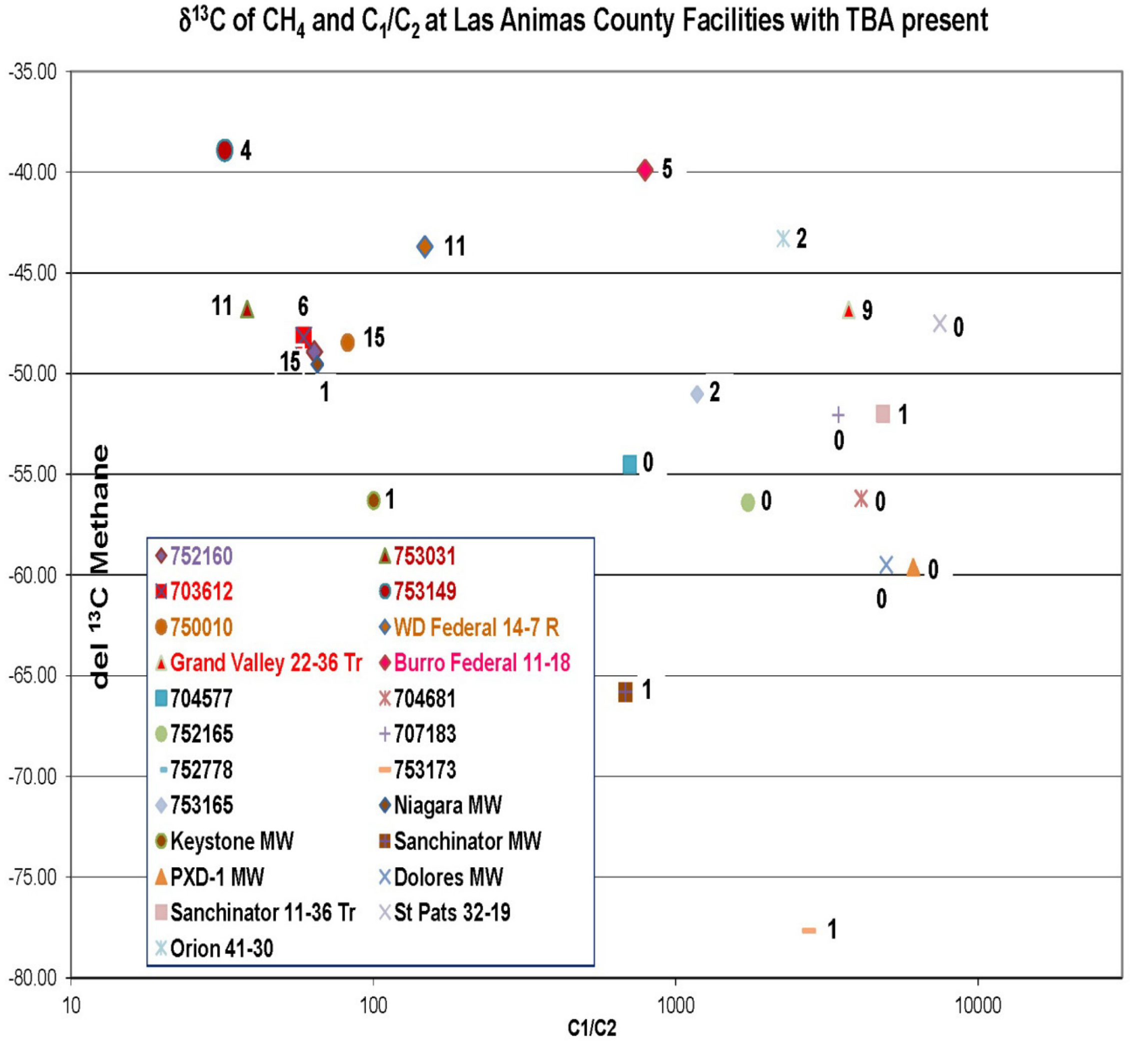

Figure 24. Methane to Ethane Ratio Versus Carbon Isotopic Ratio of Methane from Raton Basin Groundwater Samples in which TBA Has Been Detected

Investigation of Occurrence of *tert*-Butyl Alcohol in Raton Basin Groundwater

The existence and possible sources of wetter gases in produced water sampled from the WD Federal 14-7 R was discussed previously in this report. Groundwater from this CBM well has wetter gas composition, several aromatic compounds present and the highest concentration of TBA of CBM produced water samples collected to date. The wetter gas in this well is produced from the Vermejo Fm. coal seams in which the well is completed. The two sources of production gas in the Basin for which we have data with C_1/C_2 ratios under 200 (Figure 2) other than the WD Federal are gas wells completed in the Pierre and Niobrara formations which underlie the Vermejo Fm. Groundwater from the WD Federal also has a source of water (Figure 6) and major ion composition (Figure 19) different from the majority of other groundwater samples in the Basin. One hypothesis that might explain the unusual gas composition and the presence of aromatic compounds, unusual water source and unusual major ion composition is possible migration of gases and water from the underlying formations. Higley (2007) hypothesized that open fracture or open fault systems could also have contributed gas from deeper source rocks as suggested above.   Methanotrophic bacteria that produce soluble methane monooxygenase are present in samples from the WD Federal and this type of methanotroph has been shown in the lab to degrade isobutane to TBA (Patel *et al.,* 1982). The only potential source of TBA in produced water from the WD Federal CBM well that is considered possible from the 10 sources postulated in Table 4 is in situ microbial degradation of isobutane.

Summary and Conclusions

TBA was present in groundwater samples from 24% of the domestic water wells sampled. TBA was present in produced water from 22% of the CBM wells sampled. None of the samples collected from CBM produced water discharges contained TBA. TBA was not reported as detected in the two samples of flowback fluid collected shortly after hydraulic fracture stimulations of CBM wells. The reported composition of fluids used in the last 10 years in hydraulic fracture completions in the Basin do not include products known to contain TBA and do not indicate use of products that contain potential TBA precursor compounds such as *tert*-butyl hydroperoxide.

The sampling and analysis of 108 facilities/matrices evaluated as part of this study has not led to definitive identification of the source(s) of the TBA. However, the composition of frac fluids currently used in the area does not constitute a potential source of TBA as supported by the absence of TBA in two recent flow back samples collected from CBM wells. Furthermore, the data available indicate that the occurrence of TBA in the domestic water wells is not related to recent spills or discharges of produced water at the surface. In several instances the concentrations of TBA in groundwater from domestic water wells is higher than the concentration of TBA in water produced from proximal CBM wells.

Constituents of products used in Raton Basin hydraulic fracture CBM well completions known from both product review and analysis of flowback fluids include 2-butoxy ethanol, glycols, ethanol and isopropanol. None of these compounds were detected above established reporting thresholds by labs utilized by EPA in the four rounds of sampling done as part of their Raton Basin retrospective case study in data tabulations provided to COGCC by EPA. Based on all data available to this investigation, there is no indication that the source of TBA in the domestic water wells is recent CBM drilling, completion or production operations.

The presence of TBA in the immersion sample of pipe sealant used in water well drilling, construction and pump installation together with the detection of TBA in the Colorado Canyon domestic water well located approximately 3 miles from CBM wells in which the pipe sealant was used, indicates that this pipe sealant product is one potential anthropogenic source of TBA. The fact that one or more of toluene, ethylbenzene and xylenes were present in 63% of the samples that contained TBA may also be an indicator of impacts related to products used during well construction in cases where toluene is detected at elevated concentrations but other BTEX are present at much lower concentrations if detected at all, as supported by the concentration of toluene derived from the electrical tape immersion sample. The presence of several aromatic organic compounds (not toluene alone) in 63% of the samples in which TBA was detected could be indicators of fuels spills or indicators of natural processes such as thermal maturation of organic rich source rocks (*e.g.*, coals or organic rich shales which lie beneath the coals). The absence of MTBE in any of the 108 samples collected indicates that degradation of MTBE is an unlikely source of TBA in groundwater in the Basin.

The presence of methane at moderate to high concentrations in all but one of the samples that contained TBA may be an indication of a natural occurrence whereby methanotrophic bacteria may be able to oxidize methane and other hydrocarbons including isobutane.

Analyses of 19 groundwater samples from the Basin for the presence and concentration of methanotrophic bacteria were conducted during or prior to this project. Methanotrophic bacteria were reported as present in all 19 samples submitted for analysis. The estimated concentrations of methanotrophs present were between 10^4 and 10^9 cells/ml. Samples from CBM, monitoring wells and domestic wells all contained significant numbers of methanotrophs. The presence of soluble methane monooxygenase producing bacteria was determined in four samples. This specific class of methanotrophs capable of degrading isobutane to TBA were analytically determined as present at concentrations of approximately 10^2 to 10^4 cells/ml in the four samples all of which have TBA present.

Microbial degradation of isobutane, if present, could be producing the equivalent length branched chain alcohol (TBA). The presence of the five-carbon equivalent of TBA (TAA) was reported in several of the samples with the highest TBA concentrations. The presence of TAA may be another indicator of microbial oxidation of short branched hydrocarbons in samples in which it is present.

At first glance, the absence of TBA in the Huerfano County samples with relatively high methane concentrations and in which active microbial oxidation processes were documented does not seem to support a microbial oxidation source of TBA in groundwater in the Basin. However, differences in gas composition with relatively lower amounts of available isobutane in the Huerfano County wells may limit formation of TBA as a metabolic breakdown product.

Based on the results of this investigation, there is no data indicating that recent oil and gas activity related to the drilling, completion of or operation of CBM wells is the source of TBA in the domestic water wells in the Raton Basin. Anthropogenic sources of TBA in groundwater may result from immersion of products commonly used in well construction such as pipe sealant or from compressed air used during air percussion drilling of wells. Lastly, natural occurrences of TBA in groundwater may result from the oxidation of isobutane (when present) by methanotrophic bacteria which were present in groundwater from each well tested for presence of methanotrophs.

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Appendix 1. Types and Locations of COGCC facilities with TBA Analytical Data Evaluated in This Report

COGCC facility	Type of Facility	Map Area	EPA frac study identifier	Latitude	Longitude	TBA detected
217459	CBM well produced water Burro Fed 11-17 (API 05-071-06236)	4		37.17702	-104.719	Yes
217466	CBM well produced water Northcut 33-12 (API 05-071-06243)	4		37.18421	-104.7275	No
217520	CBM well produced water Geisick 32-32 (API 05-071-06297)	3		37.21813	-104.7988	No
256373	CBM well produced water Meyer 42-31 (API 05-071-06891)	3		37.21611	-104.8136	No
258602	CBM well produced water Mustang 41-30 (API 05-071-07108)	3		37.23536	-104.8131	No
259593	CBM well produced water Palomino 34-12 (API 05-071-07261)	4		37.18049	-104.727	No
259930	CBM well produced water Dakota 42-28 (API 05-071—07318)	2		37.23082	-104.8864	No
273234	CBM well produced water Rabbit Bush Federal 44-19 (API 05-071-08149)	3		37.23894	-104.8161	No
273504	CBM well produced water Bearly 24-29 (API 05-071-08177)	3		37.22372	-104.8044	No
274520	CBM well produced water Salty 42-6 Tr (API 05-071-08238)	3		37.20104	-104.8135	No
276198	CBM well produced water Casablanca 11-28 Tr (API 05-071-08314)	2		37.23573	-104.9014	No
285478	CBM well produced water Kauai 23-36 Tr (API 05-071-08834)	2		37.21262	-104.9469	No
285485	CBM well produced water Molokai 13-36 (API 05-071-08838)	2		37.21193	-104.9536	No
285562	CBM well produced water Sanchinator 11-36 Tr (API 05-071-08846)	2	RBPW01	37.21975	-104.9551	Yes
285563	CBM well produced water Sanchinator 11-36 (API 05-071-08847)	2	RBPW03	37.22	-104.9552	No

COGCC facility	Type of Facility	Map Area	EPA frac study identifier	Latitude	Longitude	TBA detected
285611	CBM well produced water Grand Valley 22-36 Tr (API 05-071-08849)	2		37.2169	-104.9499	Yes
286132	CBM well produced water St Pats 32-19 (API 05-071-08912)	5		37.33284	-104.7111	Yes
286289	CBM well produced water Keystone 11-35 (API 05-071-08938)	2	RBPW02	37.22067	-104.9732	No
286432	CBM well flowback J & P 33-12R (API 05-071-08956)	2		37.18431	-104.9442	No
288074	CBM well produced water Orion 41-30 (API 05-071-09089)	5		37.32109	-104.7076	Yes
288884	CBM well produced water Hummer 11-32 Tr (API 05-071-09159)	3		37.22037	-104.8086	No
289018	CBM well produced water Badlands 22-29 (API 05-071-09164)	3		37.23158	-104.804	No
289198	CBM well produced water Homestead 14-5 (API 05-071-09192)	3		37.19643	-104.8084	No
289941	CBM well produced water Antonio 23-29 Tr (API 05-071-09230)	3		37.22677	-104.8067	No
299153	CBM well flowback Panther 33-5 (API 05-071-09671)	3		37.19906	-104.8026	No
299153	CBM well produced water Panther 33-5 (API 05-071-09671)	3		37.19906	-104.8026	No
415081	CBM well produced water Sundance 24-28 Tr (API 05-071-09791)	3		37.22319	-104.7884	No
422582	CBM well produced water Larissa 32-35 (API 05-071-09856)	2		37.21499	-104.9616	No
423097	CBM well produced water WD Federal 14-7 R (API 05-071-09862)	4		37.18152	-104.7211	Yes
704634	CDPS permitted water discharge	2		37.241157	-104.8917	No
752872	CDPS permitted water discharge	2	RBSW03	37.19582	-104.9473	No
753477	CDPS permitted water discharge	2		37.17761	-104.888	No

COGCC facility	Type of Facility	Map Area	EPA frac study identifier	Latitude	Longitude	TBA detected
753478	CDPS permitted water discharge	2		37.20982	-104.8886	No
753479	CDPS permitted water discharge	1		37.08238	-104.7926	No
753480	CDPS permitted water discharge	1		37.07623	-104.832	No
753481	CDPS permitted water discharge	2		37.16409	-104.8695	No
753482	CDPS permitted water discharge	3		37.18061	-104.7976	No
753483	CDPS permitted water discharge	3		37.17715	-104.7751	No
753484	CDPS permitted water discharge	4		37.22109	-104.6502	No
753485	CDPS permitted water discharge	4		37.22753	-104.6974	No
753486	CDPS permitted water discharge	3		37.24179	-104.7383	No
753487	CDPS permitted water discharge	3		37.278744	-104.8092	No
704682	monitoring well PXD-1 MW	2	RBMW02	37.212338	-104.9574	Yes
705578	monitoring well Petroglyph Recovery 3	1	RBMW05	37.549124	-104.8821	
705737	monitoring well Dolores MW	2		37.213772	-104.9589	Yes
705738	monitoring well Keystone MW	2		37.219556	-104.9726	Yes
705739	monitoring well Niagara MW	2		37.214167	-104.9692	Yes
705740	monitoring well Sanchinator MW	2	RBMW03	37.219556	-104.9553	Yes
705741	monitoring well Anna MW	2	RBMW01	37.22175	-104.9645	No
708216	monitoring well Masters WW	1	RBMW04	37.53691	-104.8855	No
753035	monitoring well PXD-2 MW	2		37.219265	-104.9552	Yes
752873	surface water	2	RBSW02	37.19787	-104.8792	No
752874	surface water	2	RBSW01	37.17757	-104.9554	No
753475	surface water	1		37.17236	-104.4983	No
753476	surface water	1		37.17247	-104.5031	No
753488	surface water	4		37.21337	-104.695	No
753489	surface water	4		37.12217	-104.709	No
701407	water well	3		37.249553	-104.806	No

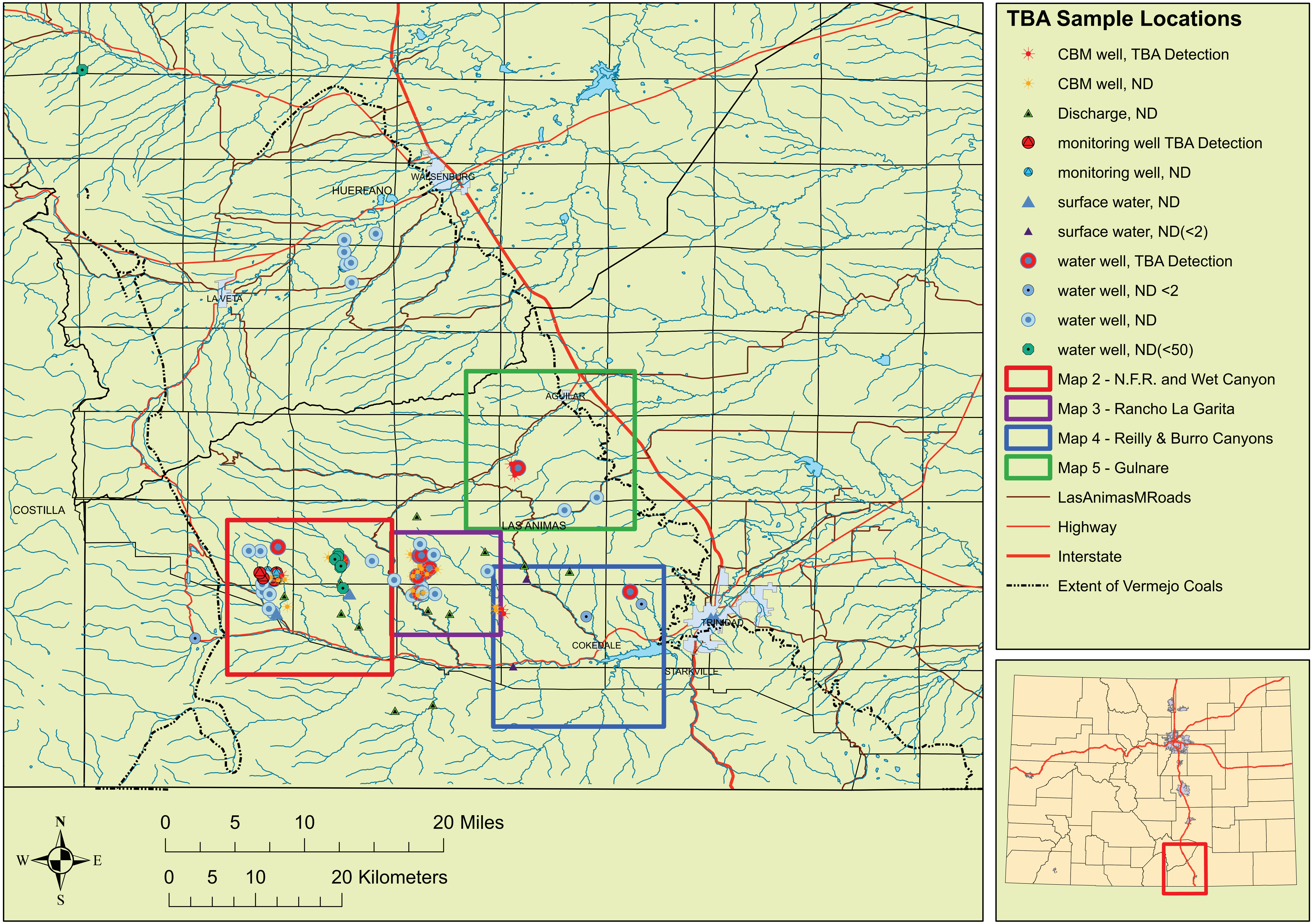
COGCC facility	Type of Facility	Map Area	EPA frac study identifier	Latitude	Longitude	TBA detected
701420	water well	3		37.218333	-104.803	No
703612	water well	3		37.237721	-104.8044	Yes
703745	water well	5		37.28475	-104.6555	No
703790	water well	3		37.238368	-104.7917	No
703906	water well	2		37.239249	-104.891	No
704235	water well	3		37.204433	-104.8041	No
704577	water well	3	RBDW11	37.198472	-104.8065	Yes
704681	water well	2		37.213122	-104.9582	Yes
705008	water well	1	RBDW06	37.521747	-104.8771	No
705028	water well	1	RBDW10	37.553389	-104.8848	No
705167	water well	1	RBDW08	37.540917	-104.8825	No
705286	water well	1	RBDW09	37.542222	-104.8778	No
705317	water well	5		37.298028	-104.622	No
705322	water well	2	RBDW02	37.215306	-104.966	No
705323	water well	2	RBDW05	37.197403	-104.9625	No
705325	water well	2		37.242222	-104.972	No
705509	water well	2		37.203694	-104.8862	No
705595	water well	2	RBDW04	37.207875	-104.9702	No
705596	water well	2	RBDW13	37.182167	-104.9631	No
705732	water well	2		37.225361	-104.8889	No
707182	water well	2		37.242528	-104.9841	No
707183	water well	2		37.246389	-104.9538	Yes
707184	water well	3		37.197654	-104.7903	No
707354	water well	2	RBDW01	37.178571	-104.9588	No
708217	water well	3	RBDW12	37.1988	-104.8034	No
750010	water well	2		37.231806	-104.8882	Yes
750011	water well	2		37.230306	-104.8863	No
750013	water well	2		37.236118	-104.8914	No
750014	water well	2		37.226687	-104.8882	No
750015	water well	2		37.233688	-104.8945	No
752160	water well	3		37.224551	-104.7962	Yes
752165	water well	2		37.212942	-104.9623	Yes
752513	water well	1	RBDW14	37.566044	-104.8848	No
752778	water well	3		37.2203	-104.801	Yes
752787	water well	3		37.200009	-104.8085	No
752788	water well	2		37.21213	-104.8328	No
752793	water well	2		37.23194	-104.856	No
752831	water well	3		37.19608	-104.8141	No
752871	water well	1	RBDW07	37.5725	-104.8519	No

COGCC facility	Type of Facility	Map Area	EPA frac study identifier	Latitude	Longitude	TBA detected
752874	water well	2	RBDW03	37.19972	-104.9697	No
753031	water well	3		37.21622	-104.8085	Yes
753149	water well	3		37.237336	-104.8064	Yes
753162	water well	4		37.187088	-104.5755	No
753163	water well	4		37.19796	-104.5878	No
753164	water well	4		37.174055	-104.6329	No
753165	water well	5		37.328703	-104.704	Yes
753172	water well	2		37.15141	-105.04	No
753173	water well	4		37.19989	-104.5873	Yes
753582	water well	1		37.74295	-105.1574	No
753596	water well	3		37.22138	-104.7357	No

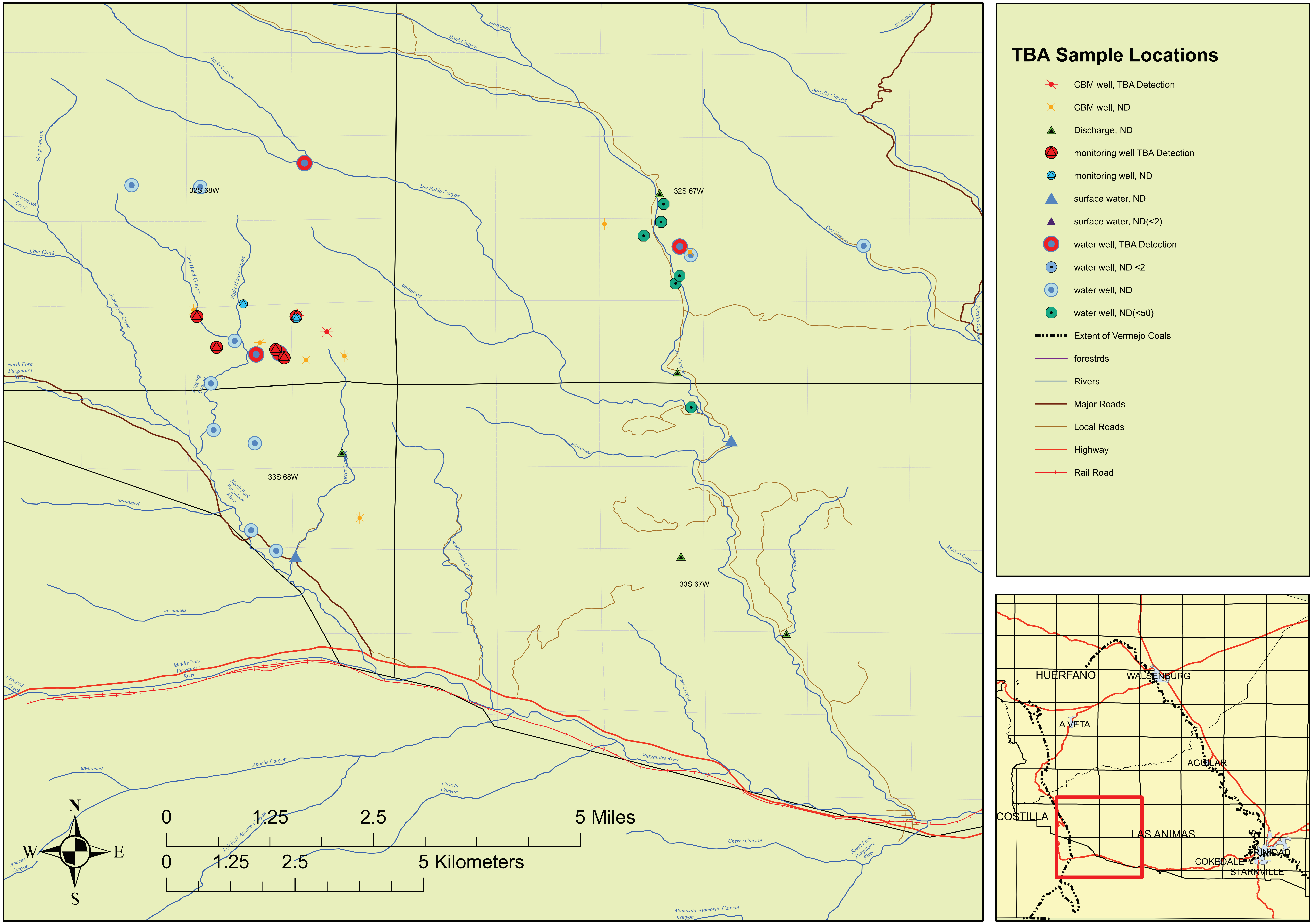
Appendix 2. Related Projects and Documents on COGCC website

COGCC Special Project	Description
2104	Fall 2011 Frac Study Analytical Reports
2110	Spring and Fall 2012 Frac Study Analytical Reports
2122	Spring 2013 Frac Study Analytical Reports
2130	TBA Study Analytical Reports and Documents
2009	NFR Monitoring Reports
2092	Raton Basin Products Used
1594	Raton Baseline Phase 1
COGCC Library web pages	Raton Baseline Phase 2

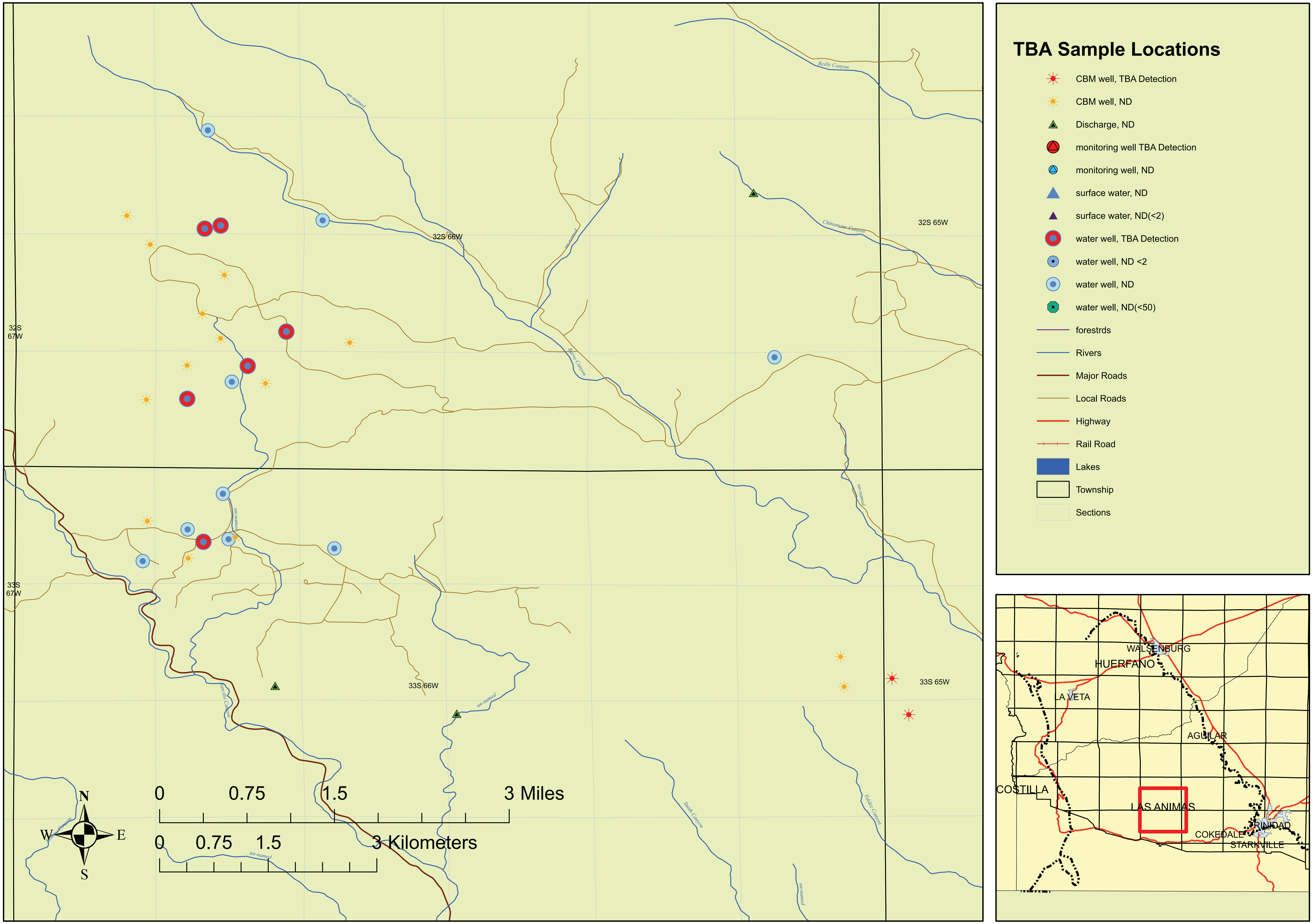
Map 1 TBA Sample Locations Raton Basin



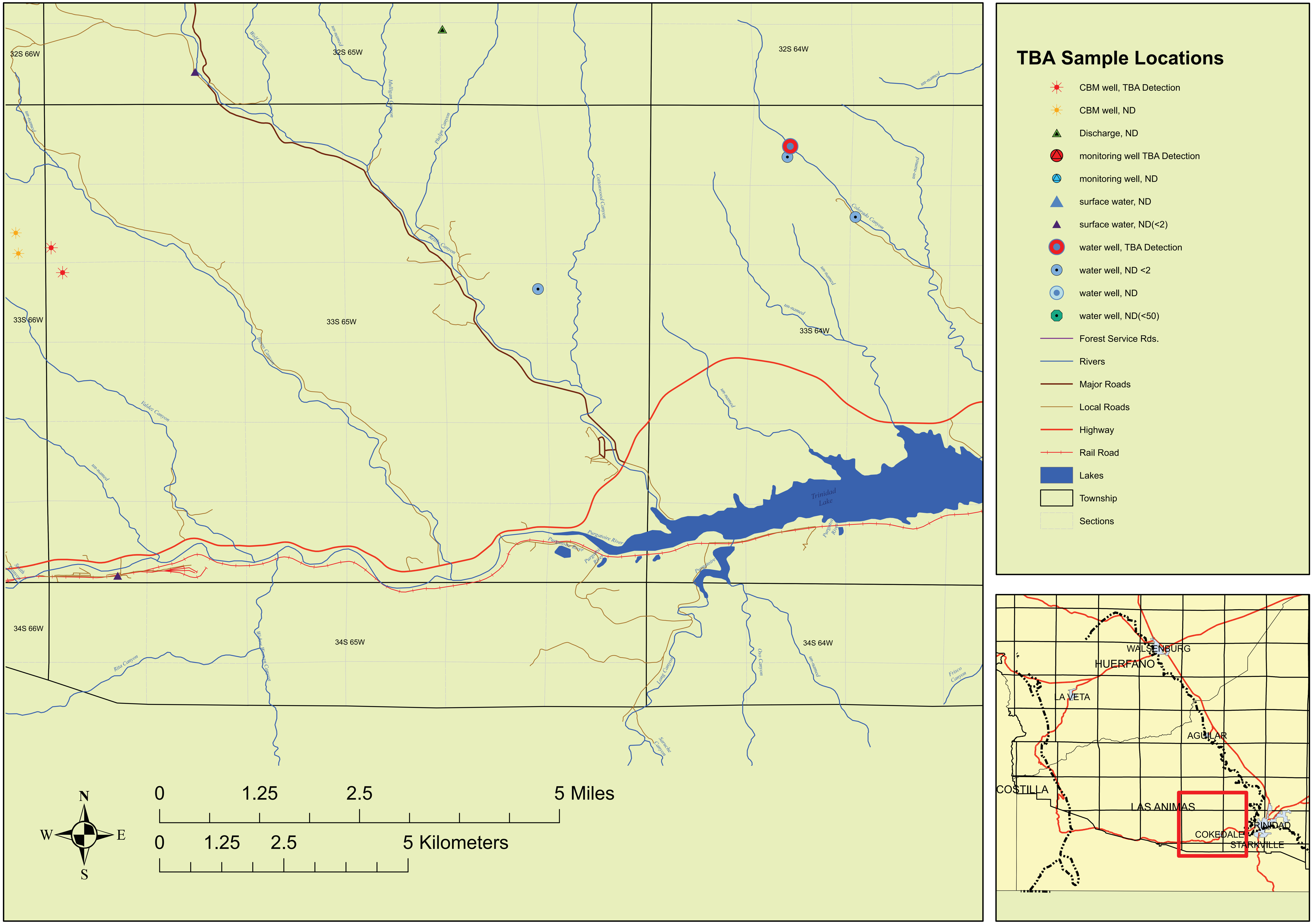
Map 2 TBA Sample Locations NFR and Wet Canyon



Map 3 TBA Sample Locations Rancho La Garita and Arrowhead Ranchettes



Map 4 TBA Sample Locations Reilly and Burro Canyons



Map 5 TBA Sample Locations Gulnare