UPDATED TREND AND DATA ANALYSIS
SAN JUAN BASIN WATER QUALITY ANALYSIS PROJECT
SAN JUAN BASIN, COLORADO

Submitted to:

Colorado Oil and Gas Conservation Commission
Denver, Colorado

Submitted by:

AMEC Geomatrix, Inc., Denver, Colorado

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Project No. 15244

AMEC Geomatrix

TABLE OF CONTENTS

TABLES

FIGURES

APPENDICES (provided on CD)

TREND AND DATA ANALYSIS UPDATE

San Juan Basin Water Quality Analysis Project
San Juan Basin, Colorado

1.0 INTRODUCTION

The Fruitland Formation of the San Juan Basin extends from southwestern Colorado into New Mexico and is the most productive coalbed methane (CBM) reservoir in the United States. In La Plata County, at the northern edge of the San Juan Basin, the Fruitland Formation rises steeply to the ground surface or near the ground surface. This approximately 50-mile long strip of land across La Plata County is referred to as the Fruitland Formation outcrop (Outcrop).

In 2000 the Colorado Oil & Gas Conservation Commission (COGCC) received a request from area operators to allow for an optional additional well to be drilled for production of Fruitland gas for certain 320-acre drilling and spacing units in the Ignacio-Blanco Field. As a result of that request the COGCC issued Orders No. 112-156 and 112-157 on April 25, 2000 (Orders). The Orders require routine water well sampling by operators for new CBM wells since 2000 to permit the additional gas well spacing. The analytical requirements for the water well samples are summarized as follows:

<table>
<tr><th>Monitoring Period</th><th>Analytical Requirements</th></tr>
<tr><td>Baseline (pre-drilling)</td><td rowspan="4">Major cations (Ca^{++}, Mg^{++}, K^{+}, Na^{+}), major anions (CO_3^{-}, HCO_3^{-}, Cl^{-}, SO_4^{--}), total dissolved solids, iron, manganese, nutrients (nitrates, nitrites, selenium), dissolved methane, pH, presence of bacteria, specific conductance, and field hydrogen sulfide.
<u>Methane ≥ 2ppm triggers compositional analysis for:</u>
δD (methane) and δ13C (methane).</td></tr>
<tr><td>One year post well completion</td></tr>
<tr><td>Three years post well completion</td></tr>
<tr><td>Six years post well completion</td></tr>
</table>

As of April 1, 2009, these data collection requirements have been extended to all coalbed methane basins in Colorado under Rule 608 – Coalbed Methane Wells.

Area operators have been submitting this data to the COGCC since 2000. The data is kept in an Access™ database in the Denver COGCC offices; the database currently includes records for 2,128 wells, a total of 7,074 samples, and over 132,000 analytical results for the San Juan Basin.

A detailed evaluation of methane in groundwater was conducted by the COGCC in 2004, however, a comprehensive evaluation of the entire database was not performed at that time. Therefore, in 2009-10, data quality review and trend and data analysis were performed for the San Juan Basin Water Quality Analysis (SJBWQA) Project (AMEC Geomatrix, 2010a; 2010b). The objectives of the SJBWQA Project are as follows:

- To assess potential long-term trends in general groundwater quality in the San Juan Basin based on data available in the COGCC database and to evaluate any identified trends for relevance to area CBM drilling and production;
- To review and update current COGCC data management and QA/QC procedures; and
- To add triggers and data flags to the current COGCC San Juan Basin water quality database to help facilitate long-term management of CBM related water quality monitoring data.

New data were added to the project database by the COGCC in 2010 and the trend and data analysis were updated in 2011. The remaining sections of this report describe the updated data and trend analysis.

2.0 TREND AND DATA ANALYSIS

Data and trend analysis were performed to assess the distribution and long-term changes in the groundwater quality in the San Juan Basin. It is important to note that the water quality database contains more than 132,000 records for 435 different water quality parameter names. The intent of the analysis was to identify any short or long-term trends that might indicate that oil and gas drilling and production activities are impacting domestic water wells in the San Juan Basin. Therefore, emphasis was placed on a subset of constituents that could indicate potential impacts from CBM drilling and production activities.

Water quality data and trend analysis were performed by geographic mapping, plotting data on time-concentration plots, performing Mann-Kendall trend analysis, and evaluating the results of compositional analysis of methane.

Most common statistical methods of analysis require at least four data points for the results of the statistical analysis to be considered reliable. Therefore, time-concentration plots and Mann-Kendall trend analysis were limited to data sets that included four or more results. For example, trend analysis was performed for each water well and for each target parameter that had four or more results in the water quality database. The isotope ratios were not included in the trend analysis. Based on this approach, a total of 3,872 data sets for 12 parameters in 560 wells were evaluated using time-concentration plots and Mann-Kendall trend analysis. Note that there were not enough data to perform trend analysis reliably for all 12 parameters in all 560 wells (the total number of possible analyses for all 12 parameters in 560 wells is 6,720).

2.1 TARGET PARAMETERS

The scope of the data and trend analysis was limited to 14 target parameters that are considered to be indicators of possible impacts from CBM drilling and production activities. The 14 target parameters are as follows:

Methane	Alkalinity
Total dissolved solids	pH
Calcium	Carbonate
Magnesium	Bicarbonate
Potassium	Chloride
Sodium	Sulfate
δD (methane).	δ^{13}C (methane)

Cations, anions, alkalinity, TDS, and pH are considered to be reliable indicators of general water quality. These parameters are not related to specific regulatory actions contained in the Orders. As further described in Section 2.2, concentrations of methane and compositional analysis of methane trigger prescribed actions under the Orders.

2.2 MONITORING TRIGGERS

The Orders describe specific monitoring requirements and regulatory actions, or triggers. As specified in the Orders, if methane is detected in a water quality testing well at a concentration equal to greater or than 2 ppm then compositional analysis and carbon isotopic analysis of methane is required to determine the gas type. If the carbon isotope analysis of methane suggests that the methane has a thermogenic or intermediate signature then annual testing is required. However, if the carbon isotope analysis of methane suggests that the methane has a biogenic signature then no further isotopic testing is required. In addition, if methane concentrations increase by more than 5 ppm between sampling periods, or increases to more than 10 ppm, then an action plan is required to determine the source of the gas. These triggers provide the rationale for the data and trend analysis that are described in the Sections 2.3 through 2.6.

2.3 GEOGRAPHIC MAPPING

The geographic distribution of methane in water wells in the San Juan Basin was mapped using ArcGIS and results are shown on the maps on Figures 1 through 3. Analytical data for methane in groundwater are available for 2,038 water wells in the water quality database

(Figure 1). There are 301 water wells that had methane concentrations equal to or greater than 2 ppm (Figure 2) and there are 128 water wells that had methane concentrations equal to or greater than 10 ppm (Figure 3). Because the solubility of methane in water is between 28 and 30 ppm (USGS, 2006), analytical results that are greater than 30 ppm for methane in groundwater may indicate free gas in the sample.

Water wells at several of the locations shown on Figures 2 and 3 were previously identified by COGCC staff during either routine screening of incoming data, notification by the operator sampling the well, or by a complaint filed by a well owner. Investigations have either been completed, are ongoing or are pending at these locations.

2.4 TIME-CONCENTRATION PLOTS

Time-concentration plots were prepared for 3,872 data sets in 560 water wells. Wells are identified by IID numbers that are stored in the water quality database. Detected results are shown on the plots as closed circles at the measured concentration; non-detect results are shown on the plots as open circles at the detection limit. The time-concentration plots are presented as Appendix A. The time-concentration plots are provided in Excel format so that the individual data points can be reviewed and the plots are also compiled in PDF format for easier navigation.

Initially, the time-concentration plots were reviewed visually to evaluate changes in the long-term concentrations qualitatively. Note that qualitative interpretation of the long-term trends by visual methods is subject to some bias. The vertical axis on each time-concentration plot is scaled to show the full range of concentrations for the selected parameter on each plot. Long-term changes in the concentrations of a parameter in different wells may appear to be similar, however, the magnitude of the concentration on the vertical axis must be considered. For example, the methane concentrations in Well IID-14 range from 0.0005 to 0.0083 ppm whereas the methane concentrations in Well IID-18 range from approximately 20 to 29 ppm.

2.5 MANN-KENDALL TREND ANALYSIS

Mann-Kendall trend analysis was used to evaluate changes in the long-term concentrations using a quantitative approach. Mann-Kendall trend analysis is a non-parametric statistical technique that is routinely used to assess trends in groundwater. Non-parametric statistical methods do not assume any underlying distribution in the data whereas parametric statistical methods assume that a certain underlying distribution is present, such as a normal or log-normal distribution. Mann-Kendall was used for the SJBWQA Project for several reasons as follows:

- Mann-Kendall is particularly well-suited for small data sets that do not have enough data to establish the underlying distribution as required for most parametric statistical techniques. The individual data sets in this evaluation included between only four and 22 data points.

- Mann-Kendall is insensitive to missing data because the missing values are ignored and do not influence the result.

- Mann-Kendall is able to handle non-detects because the non-detect values are replaced with a common value that is less than the smallest detected concentration.

Mann-Kendall trend analysis is used to determine the presence or absence of a *statistically significant* trend in the data over time. Statistical significance is determined by comparing the S-statistic (***S***) for the number of data points (**n**) in the sample population to the table of null probability values (**α**) at the specified significance level. For this analysis, the statistical significance of the trend was evaluated at the 95 percent confidence level (**α** = 0.95**)** as follows:

$(1- \boldsymbol{\alpha}) < 0.05$	True (trend is significant)
$(1- \boldsymbol{\alpha}) > 0.05$	False (trend is not significant)

Mann-Kendall is also a test for zero slope of time-ordered data that is based on a nonparametric analog of linear regression. The slope of the data is determined using the S-statistic as follows:

$\boldsymbol{S} > 0$	Increasing trend
$\boldsymbol{S} = 0$	No trend
$\boldsymbol{S} < 0$	Decreasing trend

Results of the Mann-Kendall trend analyses are summarized in Table 1 and the complete results are presented in Appendix B.

2.6 COMPOSITIONAL AND CARBON ISOTOPE ANALYSIS OF METHANE

As described in Section 2.2, compositional and carbon isotope analysis of methane is required when methane is detected at a concentration equal to or greater than 2 ppm. The additional analysis of methane includes the carbon and hydrogen isotopes, $\delta^{13}C$ (methane) and δD (methane), respectively. Analytical results for both of these isotopes are available for 428 water samples that were collected in 188 wells in the San Juan Basin where methane was detected at a concentration equal to or greater than 2 ppm.

Whiticar (1999) presented concentration ranges of the $\delta^{13}C$ (methane) and δD (methane) isotopes for various natural and artificial sources of methane (Figure 4). The ratios of the $\delta^{13}C$ (methane) and δD (methane) isotopes in the San Juan Basin are compared to the ranges presented by Whiticar (1999) for various sources of methane in Figure 5. The geographic distribution of isotopic results for the water samples is shown on Figure 6.

3.0 RESULTS

Results of the updated data and trend analysis are summarized as follows:

- The updated database contains 25 new wells; 12 new wells had datasets eligible for Mann-Kendall analysis.
- Analytical results for methane in groundwater are available for 2,038 water wells throughout the San Juan Basin (Figure 1).
- Methane was detected in 301 water wells at a wide range of concentrations that are equal to or greater than 2 ppm generally throughout the entire San Juan Basin (Figures 2 and 3).
- Mann-Kendall trend analysis was performed for 3,872 data sets including 12 water quality parameters and 560 wells (Table 1). Based on the results of Mann-Kendall trend analysis, 166 data sets in 111 wells have increasing trends that are statistically significant, 265 data sets in 182 wells have decreasing trends that are statistically significant, and 694 data sets in 354 wells have no trend.
- Statistical analysis for methane concentrations in 547 wells identified increasing trends that are statistically significant in10 wells and decreasing trends that are statistically significant in 34 wells (Table 1). Mann-Kendall results for methane in the remaining 503 wells were either not statistically significant or have no trend.
- Results of analysis for $\delta^{13}C$ (methane) and δD (methane) for 253 samples in 117 wells were interpreted to have biogenic sources and results for 175 samples in 71 wells were interpreted to have thermogenic sources.
- No geographic patterns or clusters were identified by the results of the data and trend analysis outside of known historic areas such as Bondad and the Pine River Ranches.

4.0 REFERENCES

AMEC Geomatrix, 2010a, Technical Memorandum: Data Quality Review Summary, San Juan Basin Water Quality Analysis Project, 6 January 2010.

AMEC Geomatrix, 2010b, Trend and Data Analysis, San Juan Basin Water Quality Analysis Project, 8 June 2010.

US Geological Survey, 2006, Methane in West Virgina Groundwater, Fact Sheet 2006-3001, 2006.

Whiticar, M.J, 1999, Carbon and Hydrogen Isotope Systematics of Bacterial Formation and Oxidation of Methane, Chemical Geology, Vol. 161, p. 291-314, 1999.

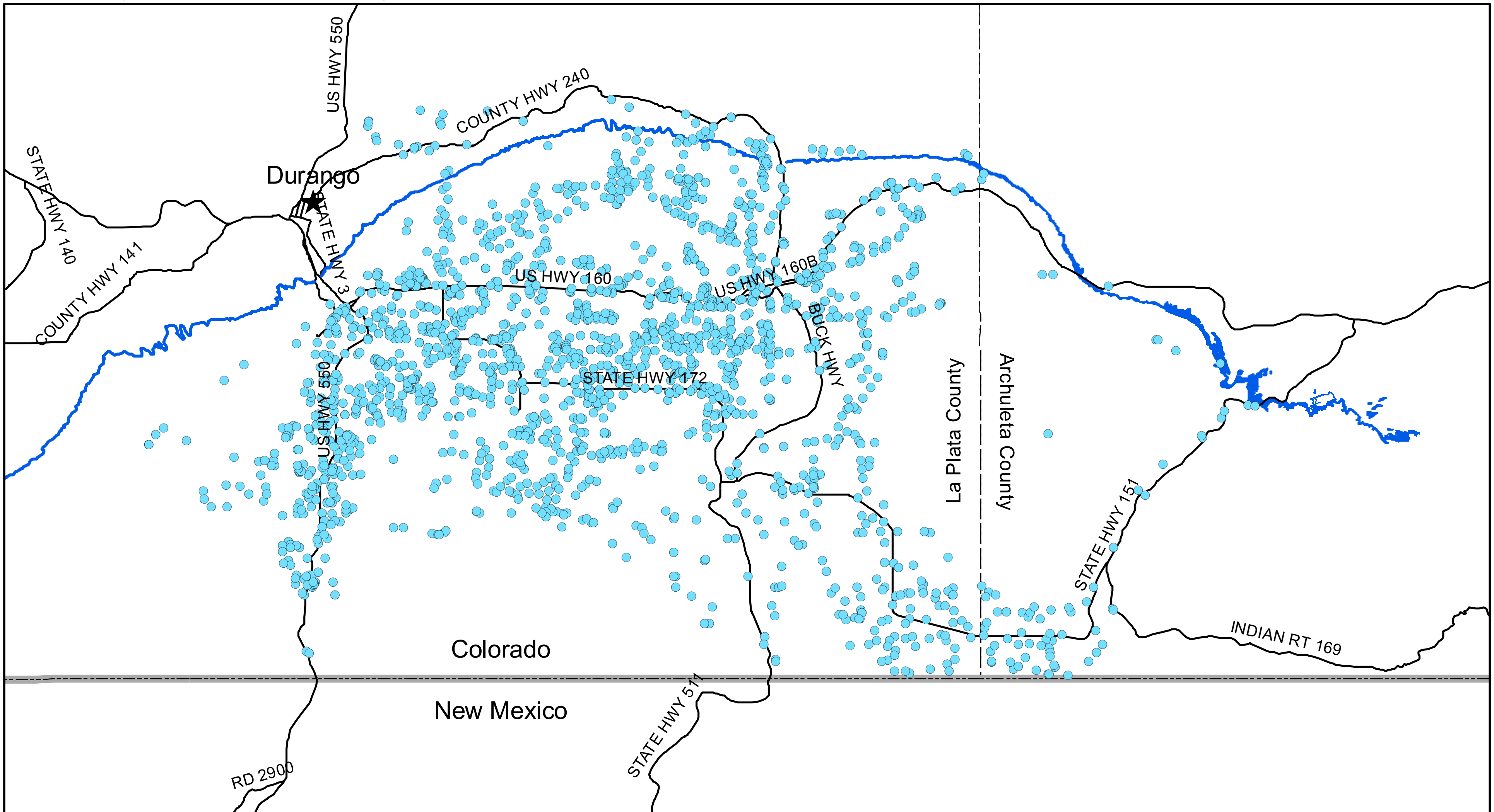
TABLES

TABLE 1
MANN-KENDALL RESULTS SUMMARY
San Juan Basin Water Quality Analysis Project

Parameter	Increasing Trend		Decreasing Trend		No Trend	No. Wells / Analysis
	Statistically Significant	Not Statistically Significant	Statistically Significant	Not Statistically Significant		
Alkalinity	5	34	12	31	13	95
Ca	27	137	24	132	53	373
Cl	20	122	18	117	35	312
CO3	0	19	1	39	64	123
HCO3	14	50	17	50	15	146
K	11	138	13	158	56	376
Methane	10	163	34	200	140	547
Mg	17	125	18	120	93	373
Na	23	119	22	161	50	375
pH	9	96	31	177	60	373
SO4	14	103	40	170	53	380
TDS	16	108	35	178	62	399
No. Analyses	166	1214	265	1,533	694	3,872
No. Wells	111	435	182	438	354	

FIGURES

File path: K:\Projects\COGCC_15244\GIS_Maps\Fig_1_Locations.mxd



N

0 2.5 5 7.5 10
Miles

Legend

Methane Samples (2038 wells)

Fruitland Outcrop

Locations of Methane Results
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

By: JLM	Date: 6/20/2011	Project No. 15244

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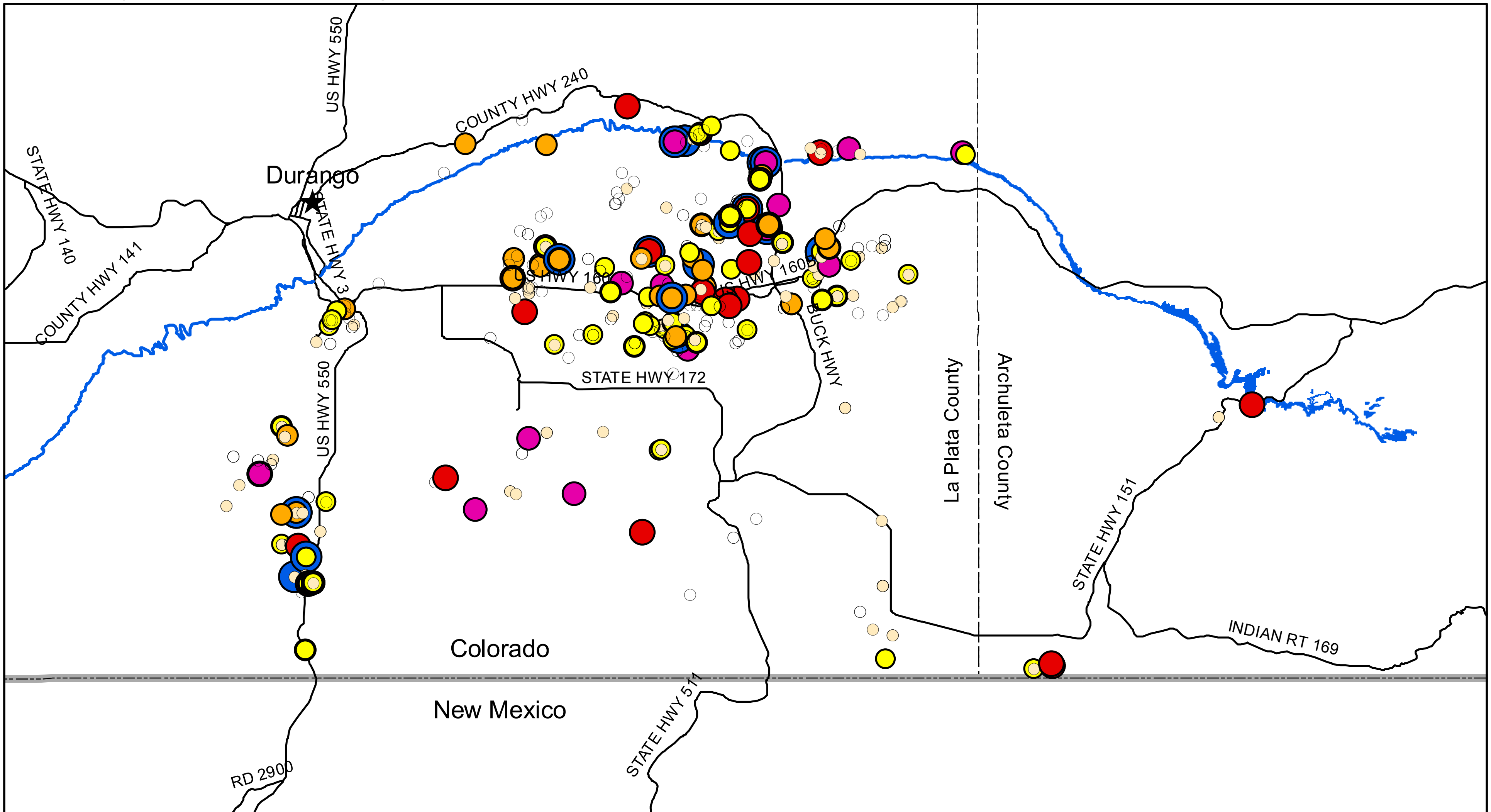
Figure 1

File path: K:\Projects\COGCC_15244\GIS_Maps\Fig_2_meth_2ppm.mxd



Legend

Fruitland Outcrop

Methane Concentration (ppm)

2.00 - 5.00
5.01 - 10.00
10.01 - 15.00
15.01 - 20.00
20.01 - 25.00
25.01 - 30.00
> 30.00

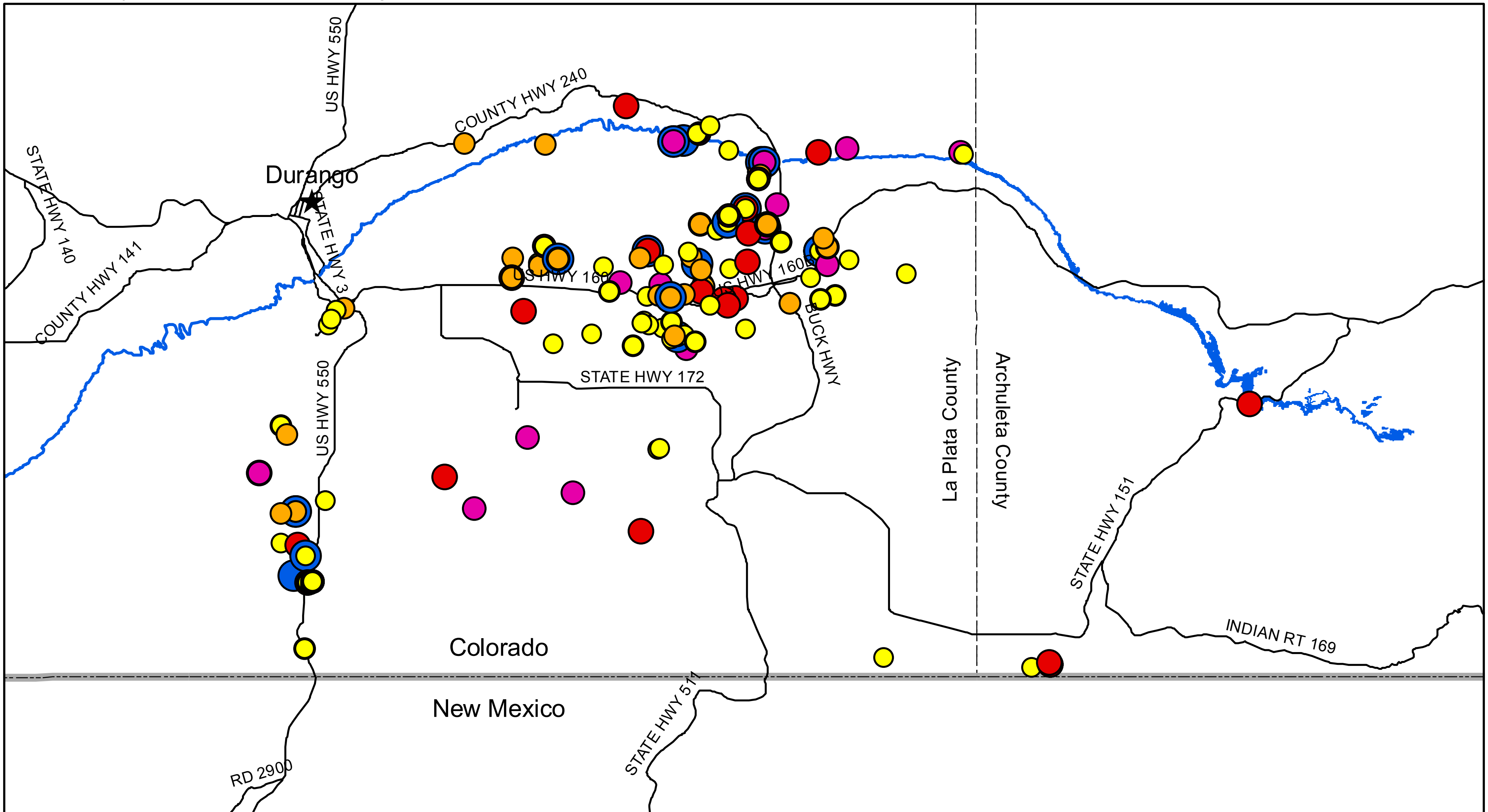
Locations of Methane Results ≥ 2 ppm
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

By: JLM	Date: 6/20/2011	Project No. 15244

AMEC Geomatrix

Figure 2

File path: K:\Projects\COGCC_15244\GIS_Maps\Fig_3_meth_10ppm.mxd



N

0 2.5 5 7.5 10 Miles

Legend

Fruitland Outcrop

Methane Concentration (ppm)

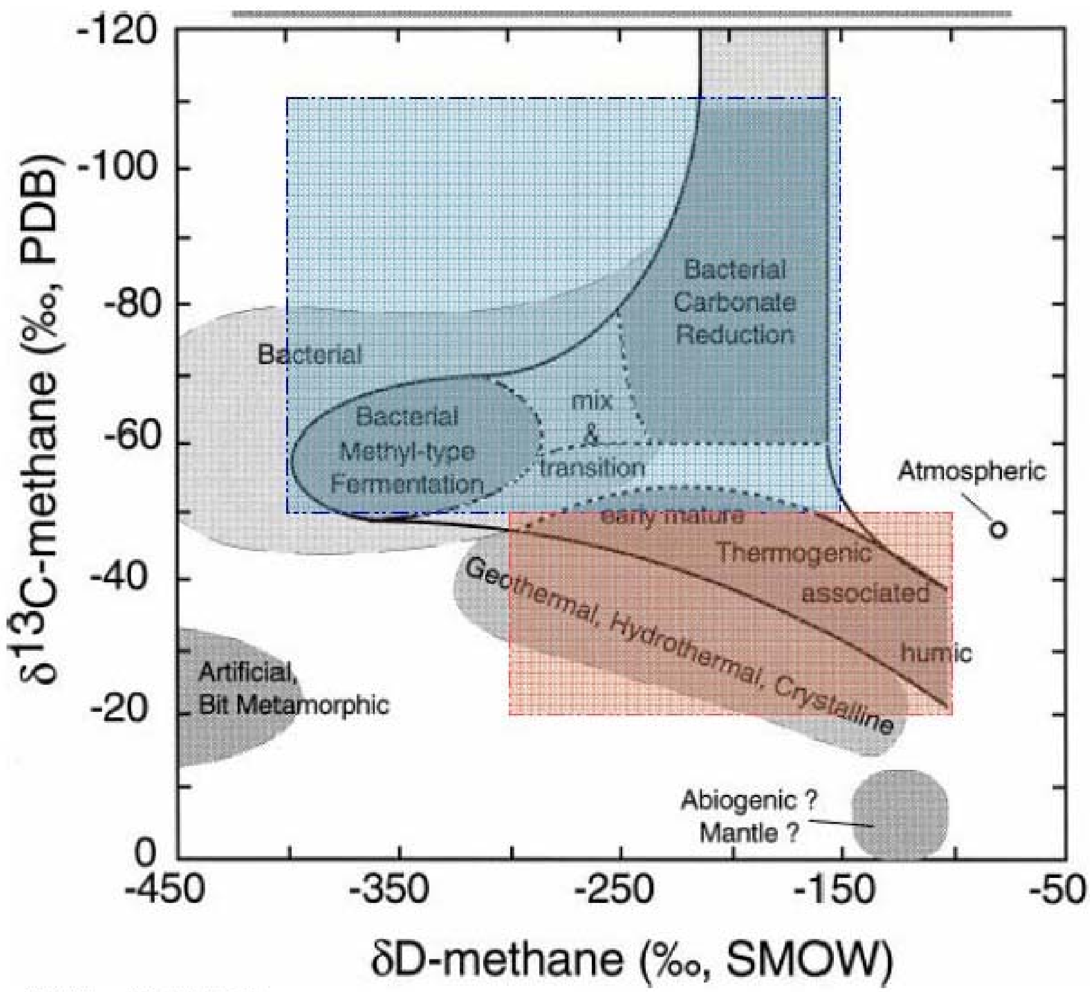
10.01 - 15.00
15.01 - 20.00
> 30.00
20.01 - 25.00
25.01 - 30.00

Locations of Methane Results ≥ 10 ppm
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

By: JLM	Date: 6/20/2011	Project No. 15244

AMEC Geomatrix

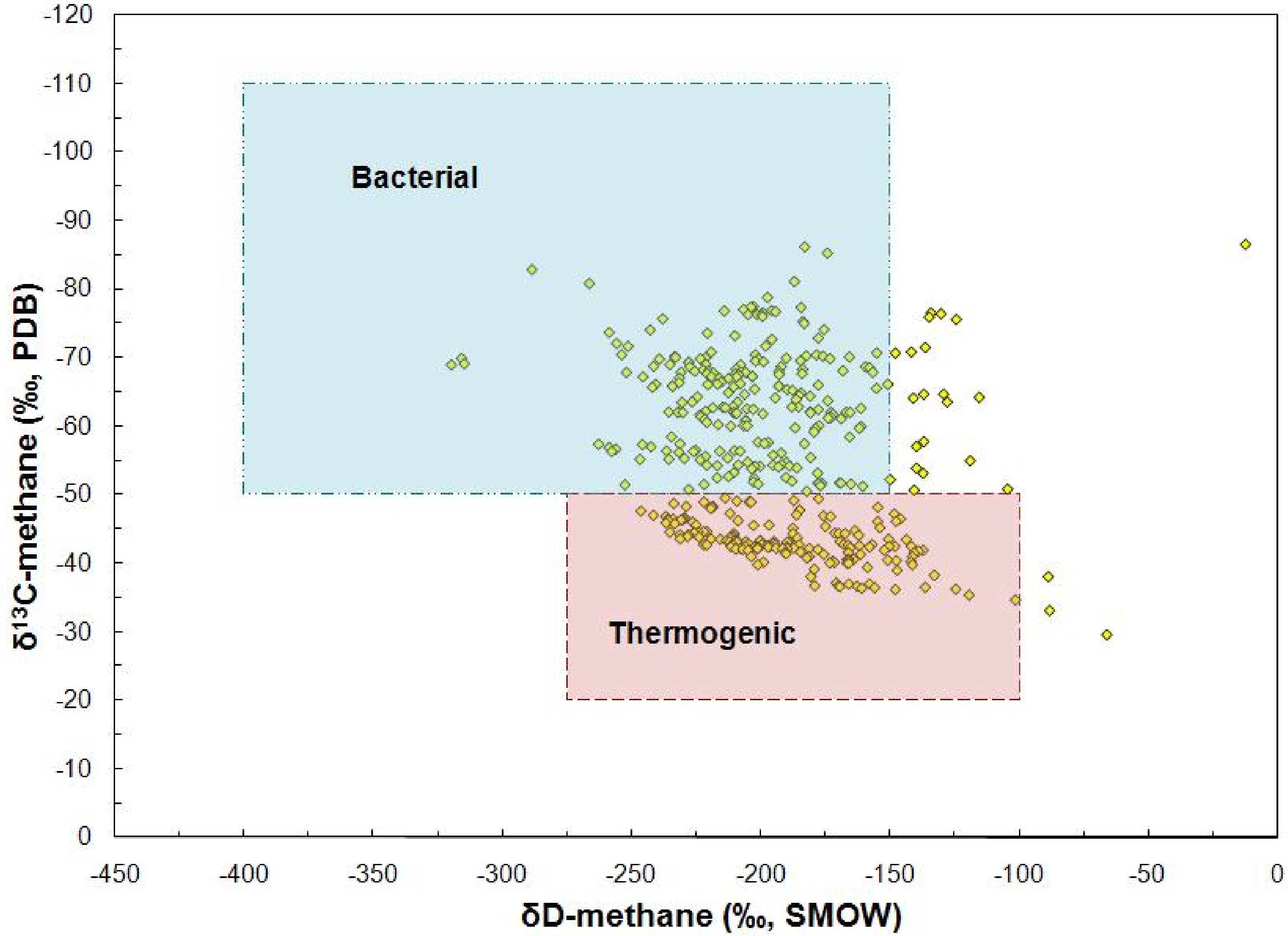
Figure 3



(Whiticar, M.J. [1999])

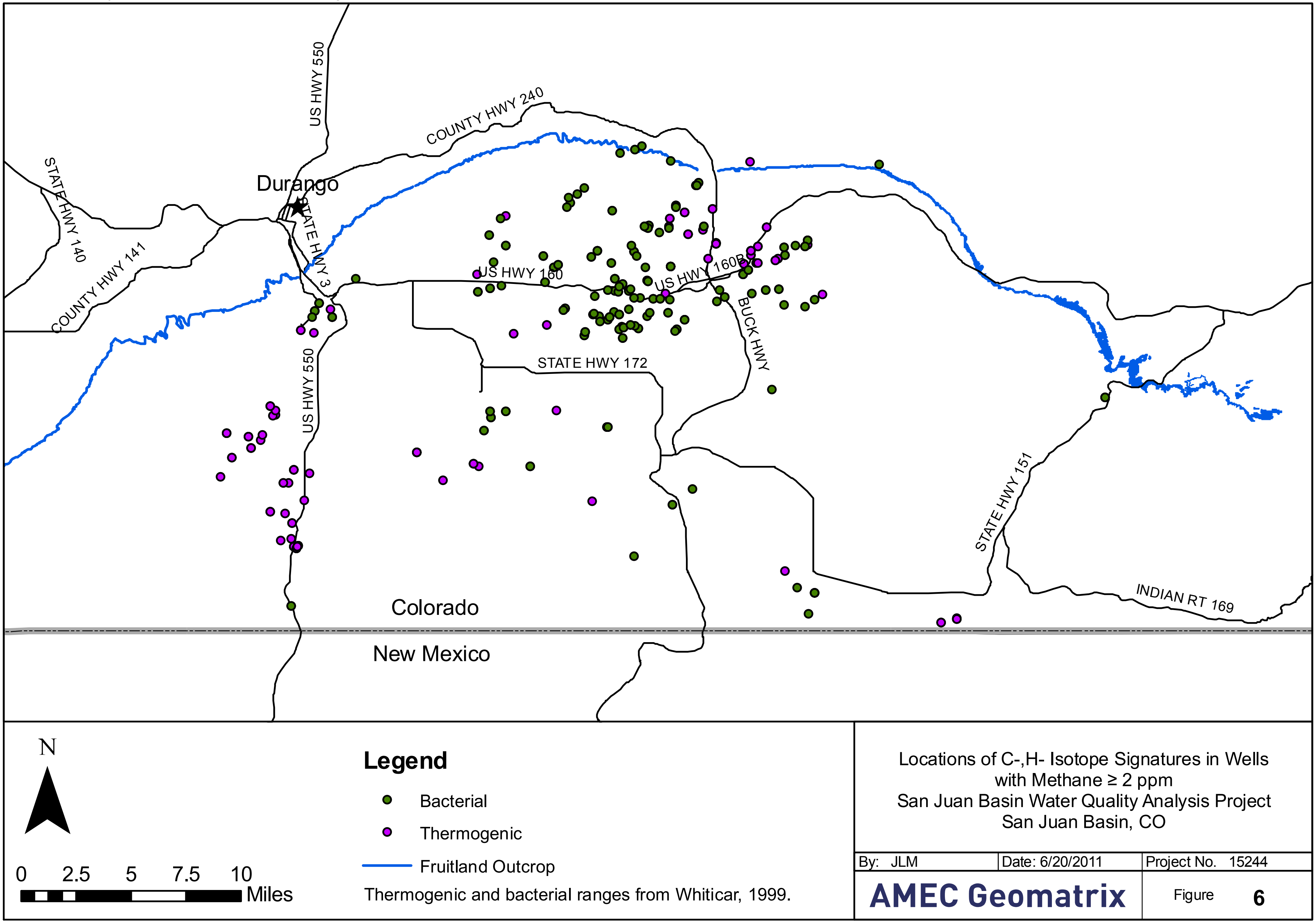
C-, H-Isotope Signatures of Methane Sources
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

By: JLM	Date: 6/20/2010	Project No. 15244
AMEC Geomatrix		Figure 4



AMEC Geomatrix	C, H - ISOTOPE SIGNATURES IN WELLS WITH METHANE ≥ 2 PPM San Juan Basin Water Quality Analysis Project San Juan Basin, CO	Project No. 15244 Figure 5

File path: K:\Projects\COGCC_15244\GIS_Maps\Fig_6_Isotopes.mxd



Legend

- Bacterial
- Thermogenic
- Fruitland Outcrop

Thermogenic and bacterial ranges from Whiticar, 1999.

Locations of C-,H- Isotope Signatures in Wells with Methane ≥ 2 ppm
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

By: JLM	Date: 6/20/2011	Project No. 15244
AMEC Geomatrix		Figure 6

APPENDICES

(Digital copy provided on CD)