TRENDS 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 Foster Wheeler Environment & Infrastructure, Inc.
Denver, Colorado

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Project No. 32820023

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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.

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^{2+}, Mg^{2+}, K^{+}, Na^{+}), major anions (CO_3^{2-}, HCO_3^{-}, Cl^{-}, SO_4^{2-}), total dissolved solids (TDS), iron, manganese, nutrients (nitrates, nitrate, selenium), dissolved methane, pH, presence of bacteria, specific conductance, and field hydrogen sulfide.

Methane ≥ 2 parts per million (ppm) triggers compositional analysis for δD (methane) and $\delta^{13}C$ (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 a SQL database in the Denver COGCC offices; the database currently includes records for 2,188 wells, a total of 8,178 samples, and over 150,000 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 (AMEC Geomatrix, 2011). Since 2011, the COGCC has continued to add data to the project database and the trend and data analysis were updated in 2015. 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 150,000 records for 305 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. Non-detect results with no recorded detection limit were not included in the Mann-Kendall analysis and time-concentration plots as no value could be assigned to the result. Non-detect results excluded from the analysis are presented in Appendix A. The isotope data (δD and $\delta^{13}C$ of methane) were also excluded from the trend analysis.

Using this approach, a total of 6,204 data sets for 12 parameters in 688 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 688 wells (the total number of possible analyses for all 12 parameters in all 688 wells is 8,256).

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 (TDS)	pH
Calcium	Carbonate
Magnesium	Bicarbonate
Potassium	Chloride
Sodium	Sulfate
δD (methane)	$\delta^{13}C$ (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 isotopes 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 well at a concentration equal to or greater than 2 ppm then compositional and isotopic analysis of methane is required to determine the gas type. If the isotope analysis suggests that the methane has a thermogenic or intermediate signature then annual testing of isotopes is required. However, if the isotope analysis suggests that the methane has a biogenic (i.e. bacterial origin) signature then no further isotopic testing is required. In addition, if methane concentrations increase by more than 5 ppm between sampling periods, or concentrations increase to more than 10 ppm, 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 Sections 2.3 through 2.6.

2.3 GEOGRAPHIC MAPPING

The geographic distribution of methane in water wells in the San Juan Basin is shown on Figures 1 through 3. Analytical and field data for methane in groundwater are available for 2,064 water wells in the water quality database (Figure 1). There are 298 water wells that had methane concentrations equal to or greater than 2 ppm (Figure 2) and there are 132 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 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 6,204 data sets in 688 water wells. Wells are identified by FacilityID 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. Non-detect results without detection limits were excluded as they could not be assigned a value to plot. The time-concentration plots are presented in Appendix B. The time-concentration plots are provided in Excel format so that individual data points can be reviewed. The plots are also compiled into a PDF document.

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 concentration 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 FacilityID 700537 range from non-detect to 0.025 mg/L whereas the methane concentrations in FacilityID 703461 range from approximately 0.27 to 10.41 mg/L.

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 normal or log normal distribution. Mann-Kendall was selected for the SJBWQA Project for the following reasons:

- 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 four and 22 data points;

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

- Mann-Kendall is able to handle non-detects because the non-detect values can be replaced with a common value that is less than the smallest detected concentrations. However, if no detection limit was recorded for a non-detect result, then the result was excluded from the analysis as it could not be assumed that the non-detection occurred at a value less than the smallest detected concentrations.

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 ($\alpha = 0.95$) as follows:

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

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

$S > 0$	Increasing trend
$S = 0$	No trend
$S < 0$	Decreasing trend

Results of the Mann-Kendall trend analyses are summarized in Table 1 and the complete results are presented in Appendix C. Wells with datasets for which Mann-Kendall analysis was performed are shown in Figure 4.

2.6 COMPOSITIONAL AND ISOTOPIC ANALYSIS OF METHANE

As described in Section 2.2, compositional and isotopic analysis of methane is required when methane is detected at a concentration equal to or greater than 2 ppm. The isotopic analysis of methane includes the carbon and hydrogen isotopes $\delta^{13}C$ and δD. Analytical results for both of these isotopes are available for 454 water samples that were collected in 198 wells in the San Juan Basin where methane was detected at a concentration equal to or greater than 2 ppm.

Whiticar (1999) presented ranges of $\delta^{13}C$ and δD isotope ratios for various natural and artificial sources of methane (Figure 5). The ratios of the $\delta^{13}C$ and δD isotopes in the San Juan Basin are compared to the ranges presented by Whiticar (1999) for various sources of methane in Figure 6. The geographic distribution of isotopic results for the water samples is shown on Figure 7.

3.0 RESULTS

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

- The updated database contains 25 new wells; one new well had datasets eligible for Mann-Kendall analysis (i.e. one new well had 4 or more sampling events in the database).
- Analytical results for methane in groundwater are available for 2,064 water wells throughout the San Juan Basin (Figure 1).
- Methane was detected in 298 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). Since the 2011 update, 32 methane results in 23 wells have exceeded a concentration of 2 ppm (Table 2). Of these 23 wells, 18 had methane results that exceeded 2 ppm prior to this data analysis and five had no methane results prior to this data analysis.

- Mann-Kendall trend analysis was performed for 6,204 data sets including 12 water quality parameters and 688 wells (Table 2). The addition of data acquired since the 2011 update resulted in eligibility of 2,332 more data sets for Mann-Kendall analysis. Of these 2,332 new data sets, 128 are from wells which did not have data sets eligible for analysis in 2011 (Figure 4).

- Based on the results of Mann-Kendall trend analysis, 236 data sets in 154 wells have increasing trends that are statistically significant, 387 data sets in 241 wells have decreasing trends that are statistically significant, and 1,235 data sets in 537 wells have no trend.

- Statistical analysis for methane concentrations in 561 wells identified increasing trends that are statistically significant in nine wells and decreasing trends that are statistically significant in 30 wells. Of the nine identified increasing trends, two were classified as thermogenic and one as biogenic using $\delta^{13}C$ and δD results. Both of the thermogenic wells had methane results above 2 ppm. Mann-Kendall results for methane in the remaining 522 wells were either not statistically significant or have no trend.

- Results of analysis for $\delta^{13}C$ (methane) and δD (methane) for 239 samples in 114 wells were interpreted to have biogenic sources and results for 179 samples in 73 wells were interpreted to have thermogenic sources (Figure 6). Twenty-two results in 14 wells had intermediate signatures (i.e. one isotope had a biogenic signature while the other had a thermogenic signature), and neither a biogenic, themogenic, nor intermediate signature could be determined for 14 results in 11 wells. Four of these results had themogenic $\delta^{13}C$ signatures and δD signatures that resemble that of atmospheric methane.

- 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.

AMEC Geomatrix, 2011. Updated Trend and Data Analysis, San Juan Basin Water Quality Analysis Project, 20 June 2011.

US Geological Survey, 2006, Methane in West Virginia 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	33	172	34	175	58	472
Ca	31	202	47	206	69	555
Cl	28	155	23	169	45	420
CO3	0	75	2	130	247	454
HCO3	38	168	37	187	64	494
K	11	183	21	247	85	547
Methane	9	130	30	206	186	561
Mg	22	184	22	180	134	542
Na	16	169	39	242	91	557
pH	16	169	32	205	83	505
SO4	17	153	59	251	73	553
TDS	15	172	41	216	100	544
No. Analyses	236	1,932	387	2,414	1,235	6,204
No. Wells	154	569	241	595	537	

TABLE 2
NEW METHANE RESULTS ≥ 2 PPM
San Juan Basin Water Quality Analysis Project

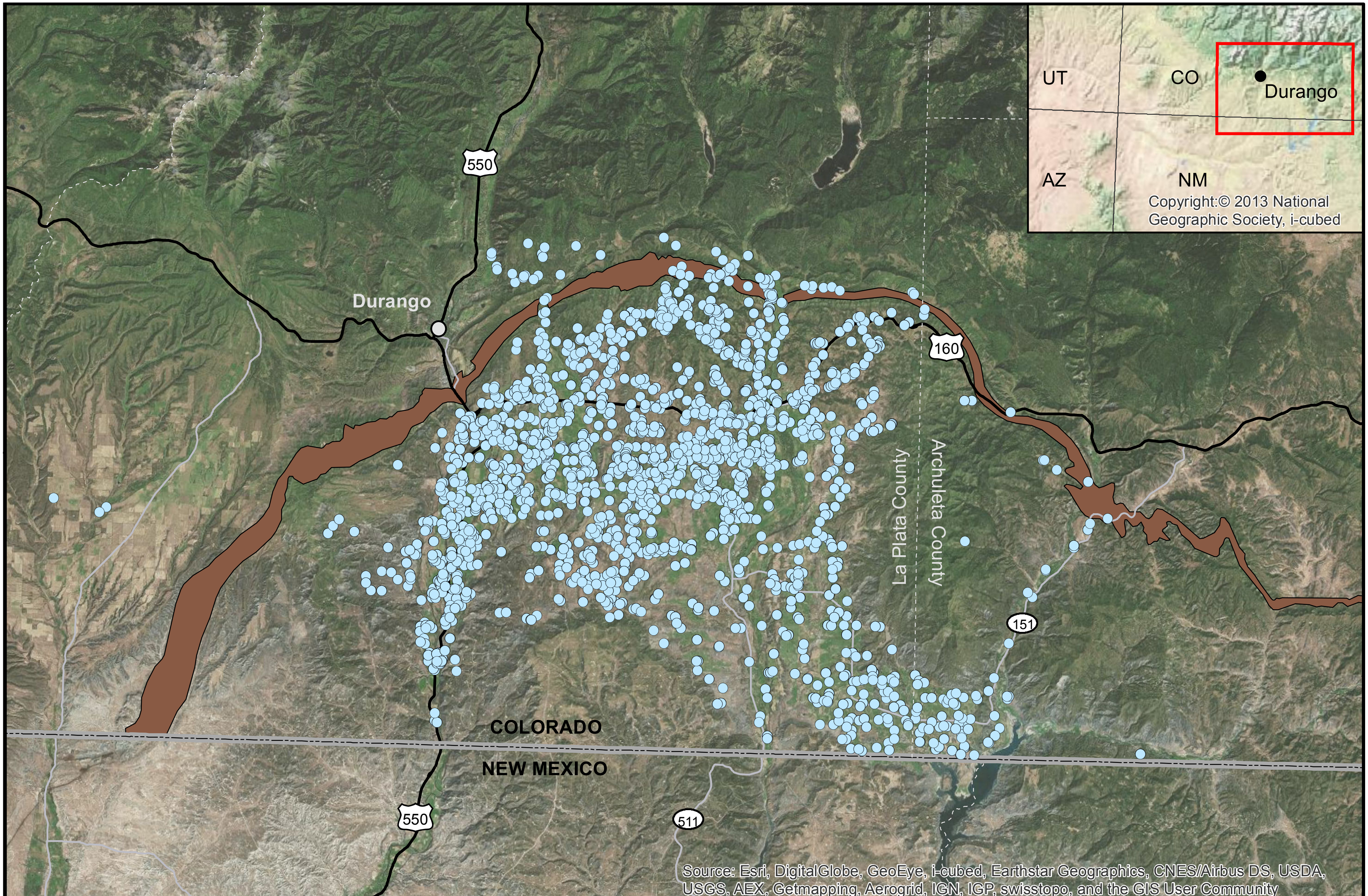
FacilityID	ResultID	SampleID	Sample Date	Analyte	Result (ppm)
702990	71275214	530312	10/10/2012	Methane, Field[1]	4.91
702990	71911473	535212	10/2/2013	Methane, Field	5.36
702990	72014828	538668	5/15/2014	Methane	4.5
706191	71933590	535962	11/18/2013	Methane	3.4
706191	72090153	541130	12/15/2014	Methane	11
706192	71888939	533864	11/21/2011	Methane, Field	3.39
706197	72019196	538833	6/19/2014	Methane, Field	10.23
706209	71275232	530315	10/10/2012	Methane, Field	7.44
706209	71908694	535214	10/2/2013	Methane, Field	3.41
706210	71911472	535227	10/2/2013	Methane, Field	2.5
706211	71275226	530314	10/10/2012	Methane, Field	8.6
706211	71911306	535229	10/2/2013	Methane, Field	6.91
706211	72014952	538676	7/15/2014	Methane	14
706261	71698012	468980	1/11/2011	Methane	21.1
706261	71427592	530510	6/12/2012	Methane, Field	11.03
706291	71702548	533143	2/5/2013	Methane, Field	3.97
706392	71993261	537898	9/9/2013	Methane, Field	4.19
706394	71992991	537884	9/9/2013	Methane, Field	2.98
706510	72015654	538702	1/23/2014	Methane, Field	9.27
706602	71600474	533034	1/9/2013	Methane, Field	2.45
706706	72040920	539636	9/26/2014	Methane	4.3
706718	72091888	541199	1/12/2012	Methane, Field	9.27
707071	71367186	532073	9/20/2011	Methane, Field	3.25
707112	71367206	532059	9/27/2011	Methane, Field	7.84
707140	72093164	541257	1/17/2012	Methane, Field	2.46
750067 [2]	71695667	529946	6/11/2012	Methane, Field	13.9
752822 [2]	71990127	537699	5/20/2014	Methane	4.2
752823 [2]	71913638	534852	8/6/2013	Methane	2.82
752826 [2]	71906166	534846	8/5/2013	Methane	4.51
752826	71990055	537693	5/22/2014	Methane	14
752865 [2]	71913641	534854	9/9/2013	Methane	25.4
752865	71990079	537695	5/22/2014	Methane	24

Notes

1. Field methane results were excluded from Time-Concentration plots and Mann-Kendall analysis.

2. Well had no methane or field methane results in 2011 Updated Trend and Data Analysis.

FIGURES



LOCATIONS OF METHANE RESULTS
San Juan Basin Water
Quality Analysis Project
San Juan Basin, CO

LEGEND

- Fruitland Outcrop
- Methane Samples (2,064 wells)

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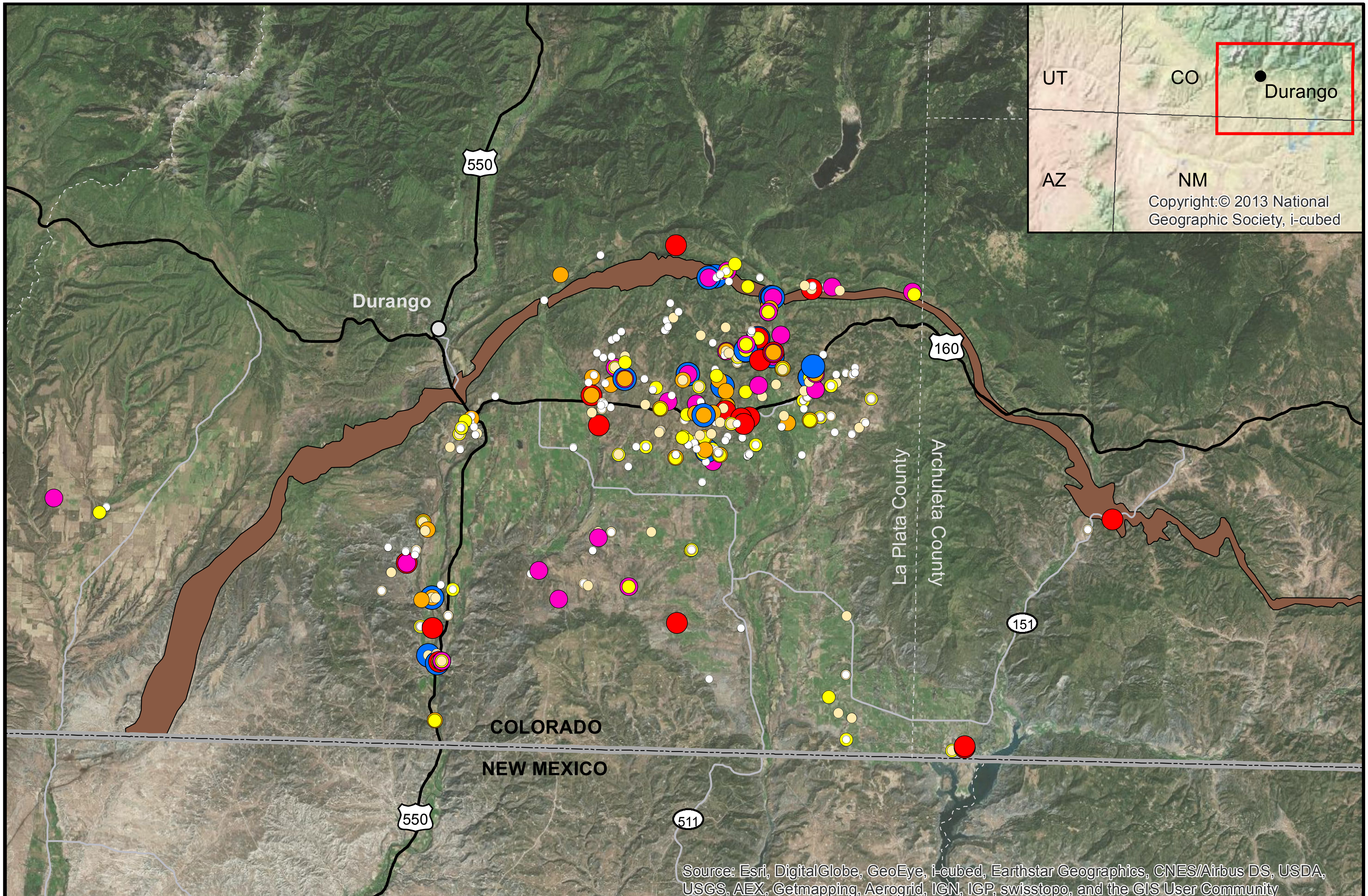
FIGURE
1

Project No. 32820023



LOCATIONS OF METHANE RESULTS ≥ 2 ppm
San Juan Basin Water
Quality Analysis Project
San Juan Basin, CO

N

0 1 2 3 4 5 Miles

LEGEND

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

Fruitland Outcrop

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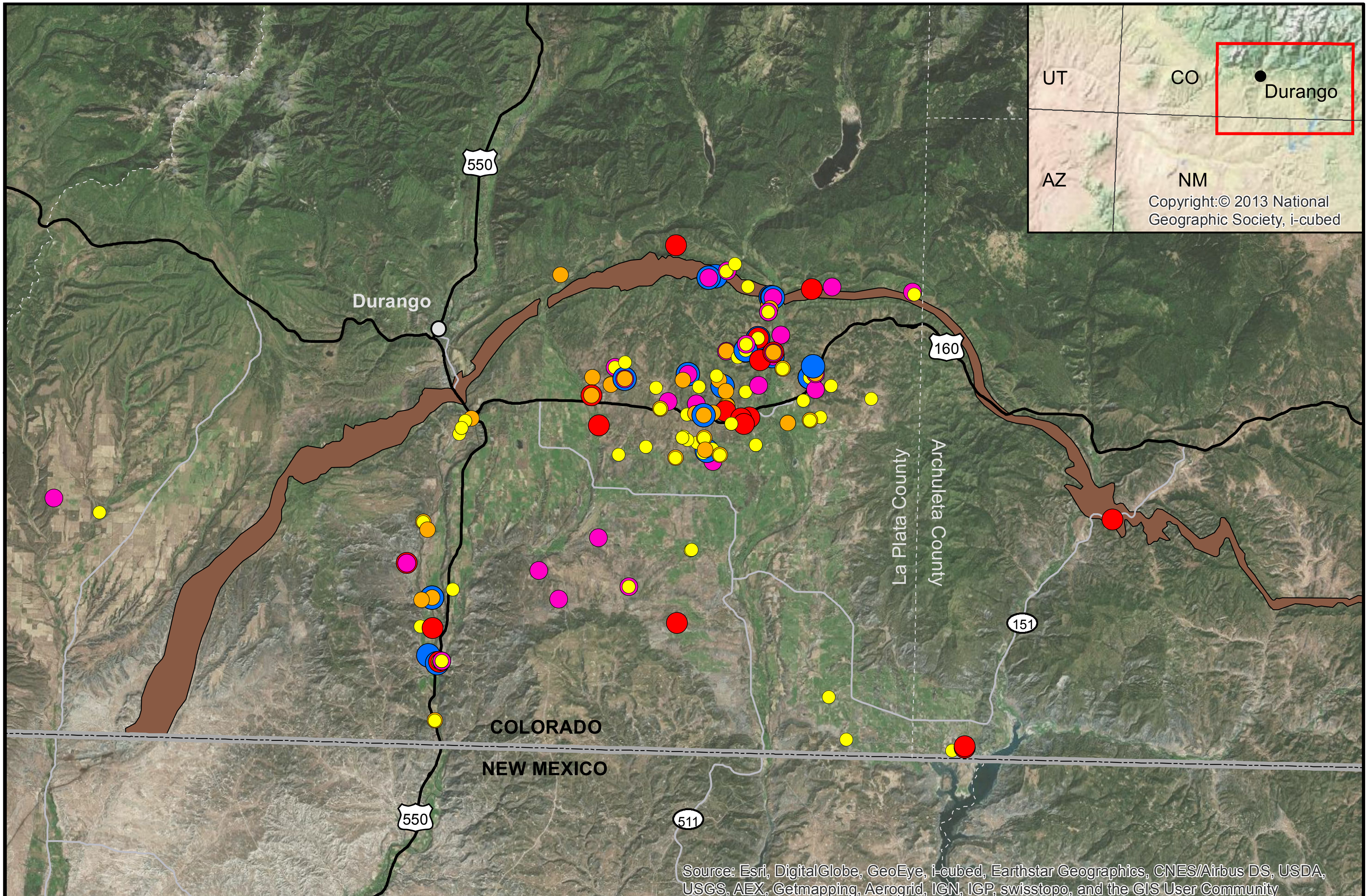
FIGURE
2

Project No. 32820023



LOCATIONS OF METHANE RESULTS ≥ 10 ppm
San Juan Basin Water
Quality Analysis Project
San Juan Basin, CO

LEGEND

Methane Concentration (ppm)

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

Fruitland Outcrop

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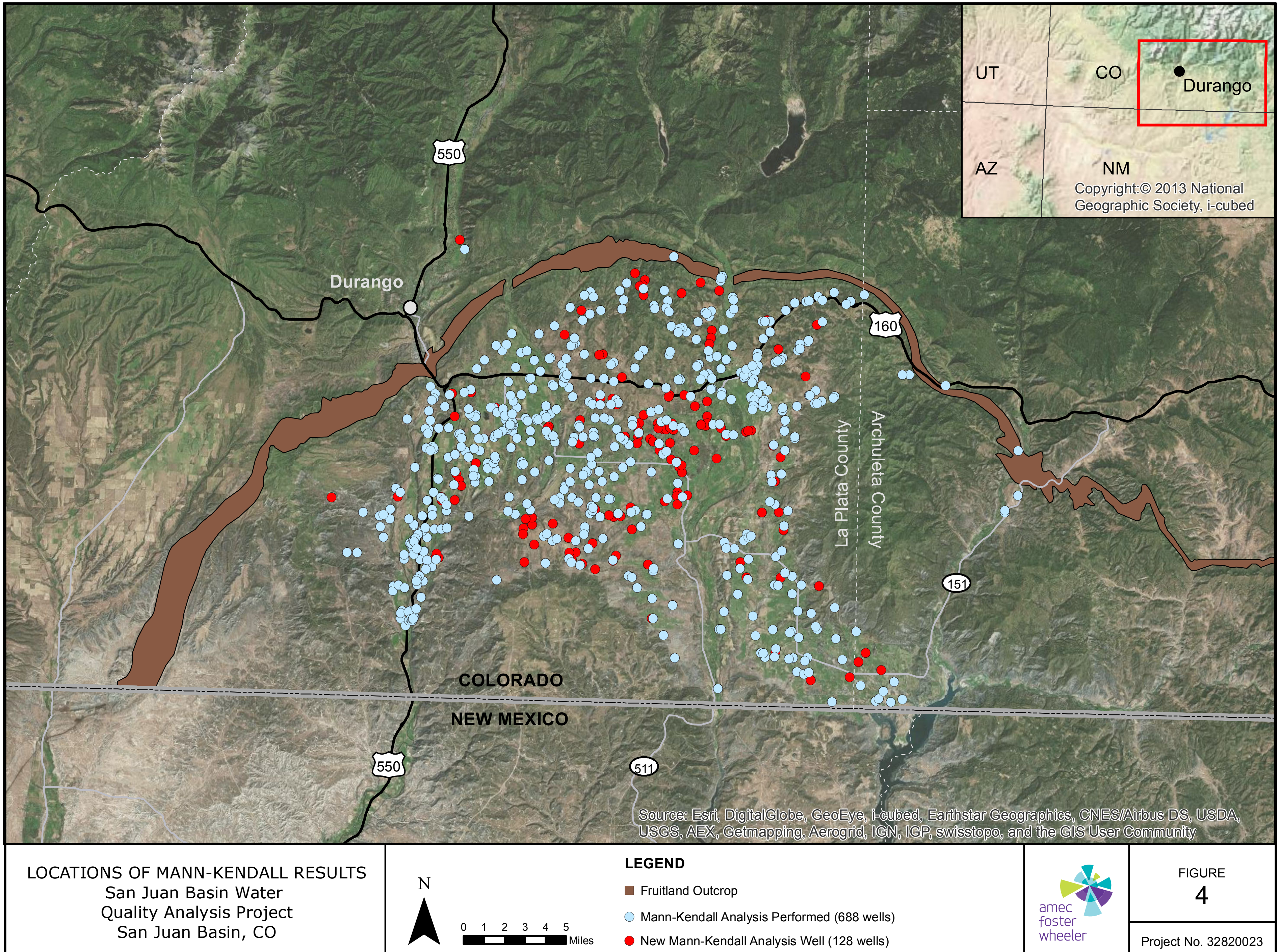
FIGURE
3

Project No. 32820023



LOCATIONS OF MANN-KENDALL RESULTS
San Juan Basin Water
Quality Analysis Project
San Juan Basin, CO

LEGEND

- Fruitland Outcrop
- Mann-Kendall Analysis Performed (688 wells)
- New Mann-Kendall Analysis Well (128 wells)

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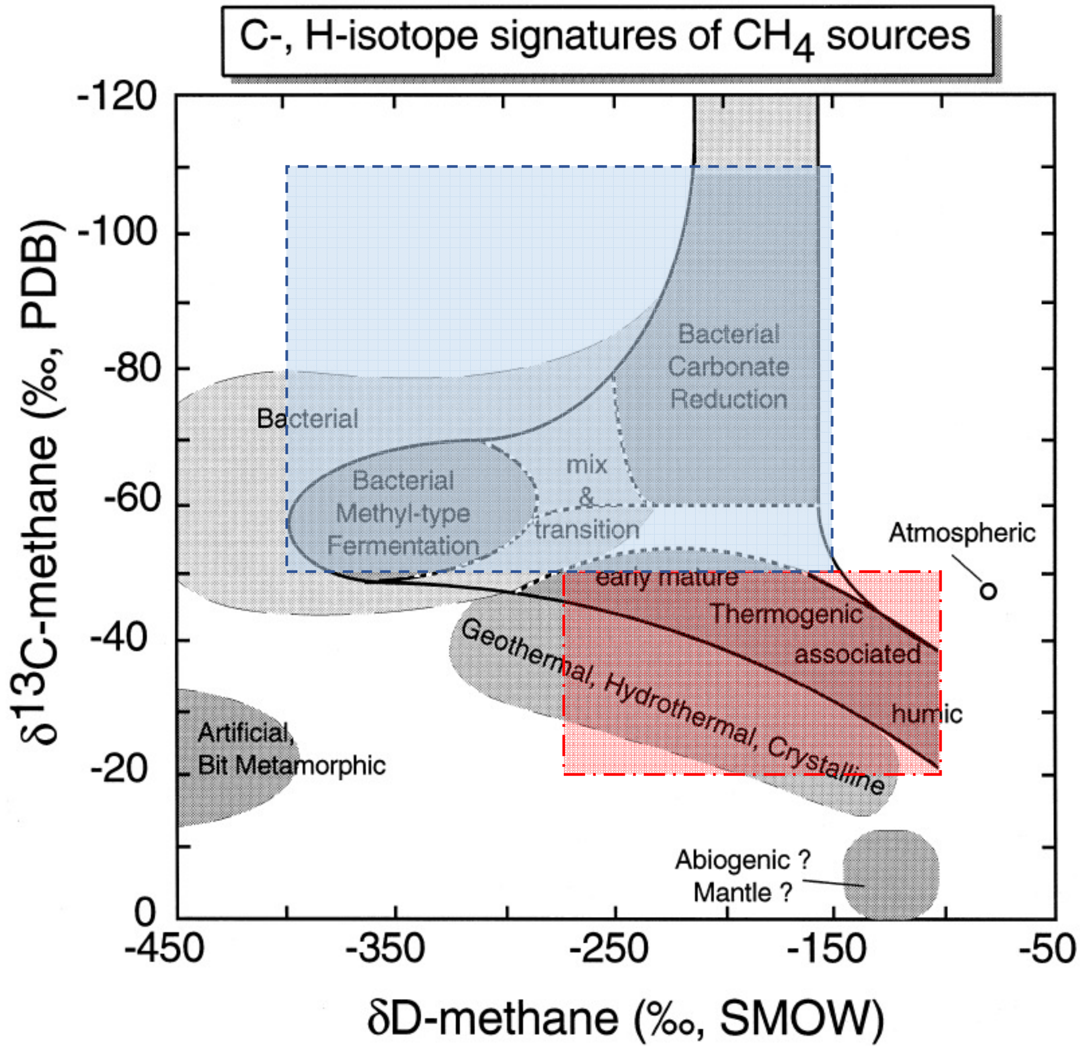
FIGURE
4

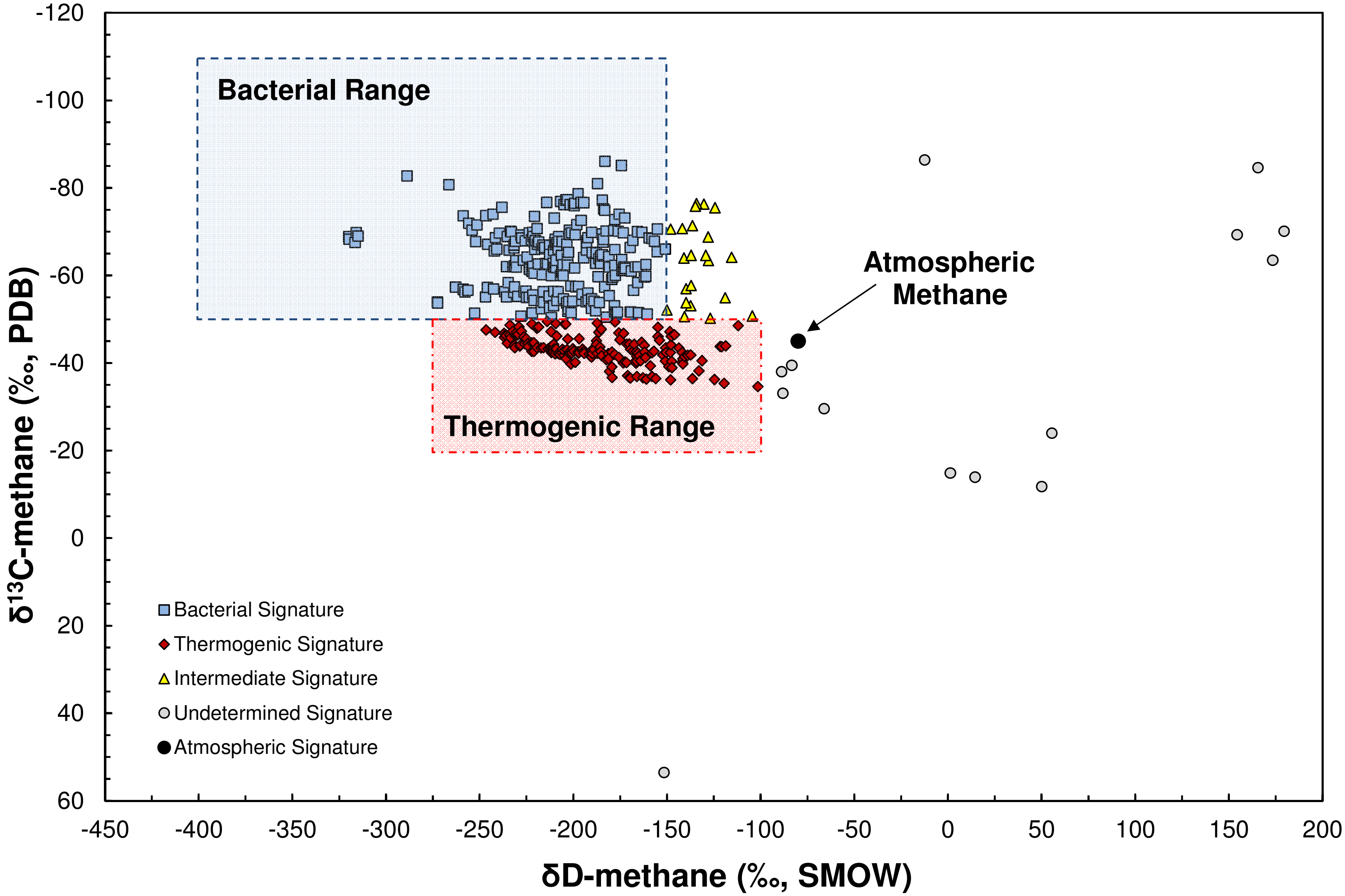
Project No. 32820023



From Whiticar, M.J. (1999)

C-, H- ISOTOPE SIGNATURES OF METHANE SOURCES
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

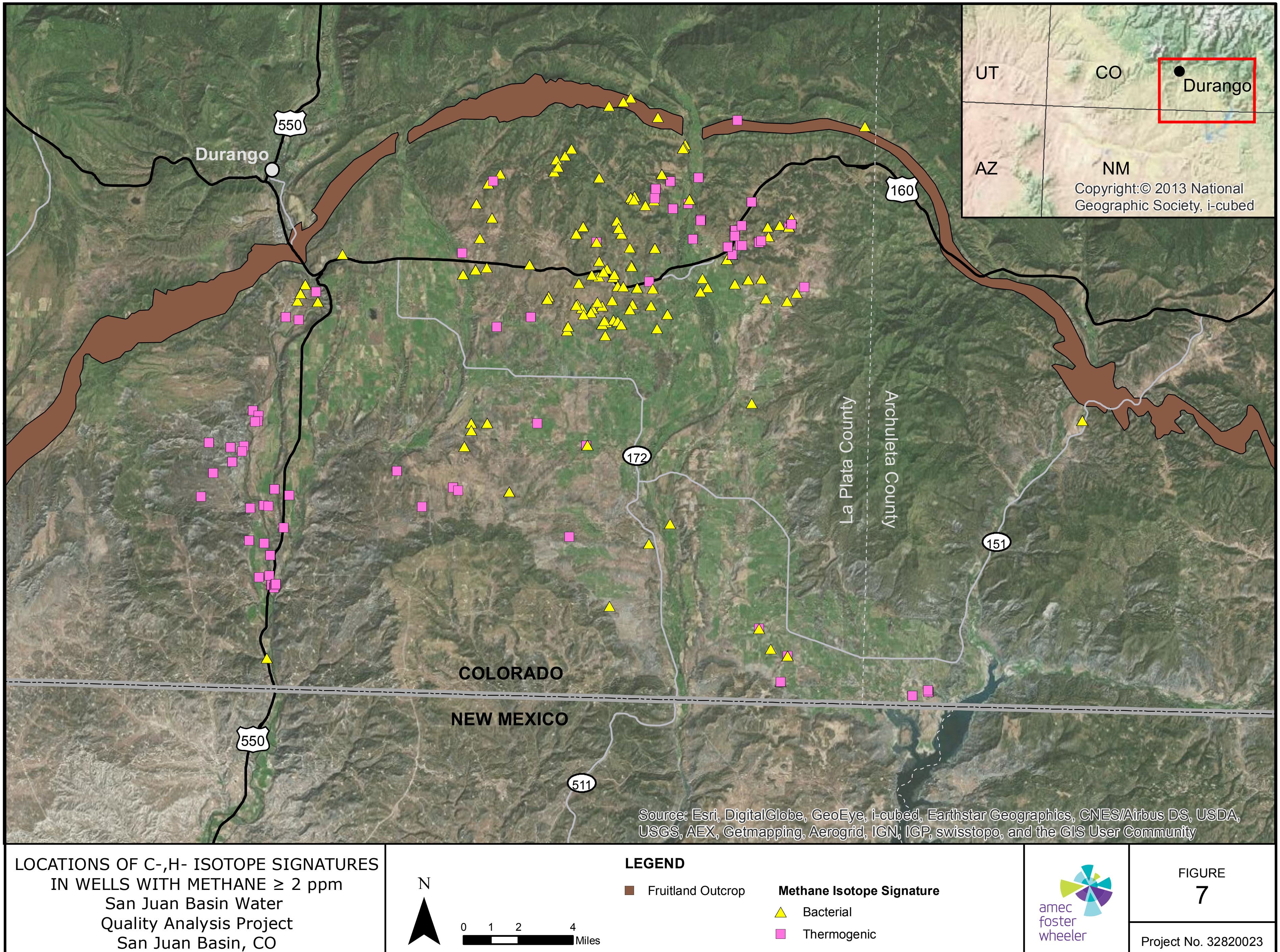
Project No.	32820023
Figure	**5**



C, H - ISOTOPE SIGNATURES IN WELLS WITH METHANE ≥ 2 PPM
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

Project No. 32820023

Figure 6



LOCATIONS OF C-,H- ISOTOPE SIGNATURES IN WELLS WITH METHANE ≥ 2 ppm
San Juan Basin Water Quality Analysis Project
San Juan Basin, CO

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FIGURE 7

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APPENDICES

(Digital copy provided on CD)

Appendix A, Non-Detect Results with No Detection Limit

Appendix B, Time-Concentration Plots

Appendix C, Mann-Kendall Results