Investigation of Occurrences of *tert*-butyl alcohol in Raton Basin Groundwater

COLORADO
Oil & Gas Conservation Commission
Department of Natural Resources

COGCC Special Project 2130

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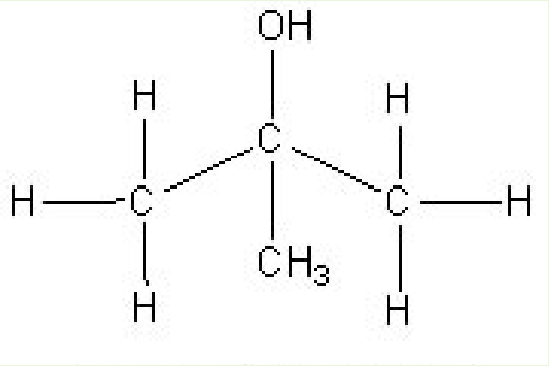
Environmental Protection Specialist
Colorado Oil and Gas Conservation Commission

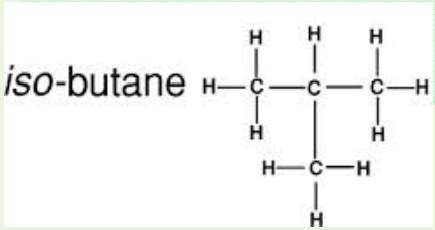
- TBA
- Raton Basin geology & coal bed methane
- EPA national study of hydraulic fracturing
  - Raton Basin retrospective case study
- COGCC special projects study sampling and COGCC database
- EPA data
- Pioneer Natural Resources data
- Compilation of data from all sources above and from literature
- Evaluation of potential sources, media and pathways
- Summary report
  - 4 geographic areas in which TBA was detected in groundwater
    - North Fork Ranch and Wet Canyon
    - Rancho la Garita & Arrowhead Ranchettes
    - Burro and Colorado Canyons
    - Gulnare
- Conclusions



$C_4H_{10}O$
2-methyl-2-propanol
CASRN 75-65-0

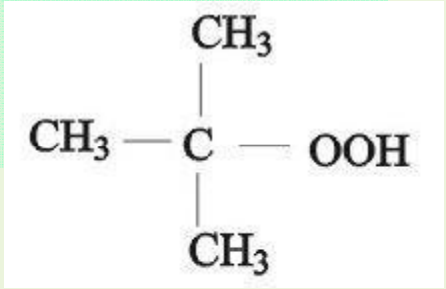
synonyms – *tert*-butyl alcohol, *tert*-butanol, TBA

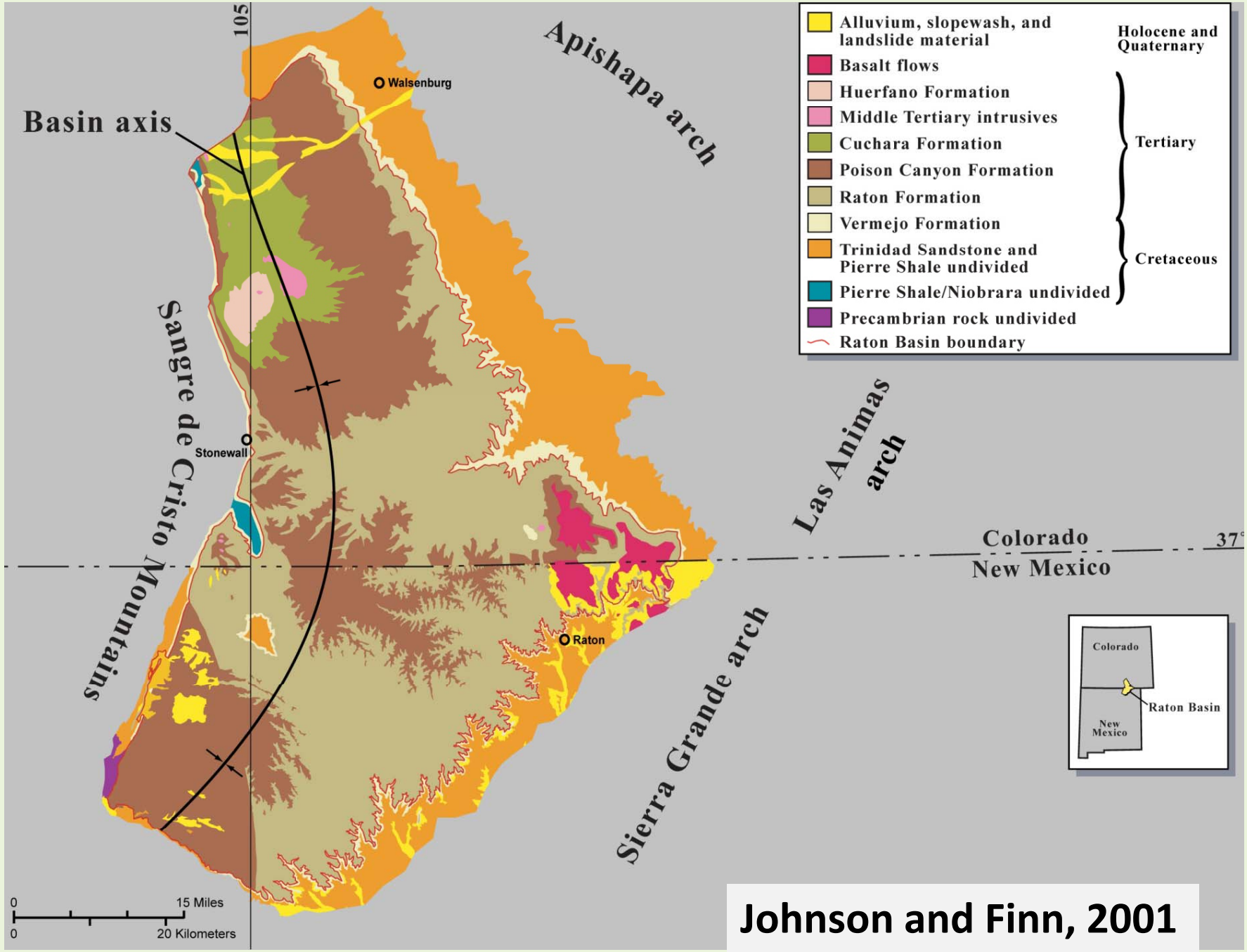
- **TBA Uses**
  - **industrial processes**
    - **– production of butylene elastomers used in rubber manufacturing**
  - **cosmetics and fragrances, detergents, shampoos**
  - **octane enhancer and/or oxygen source in gasoline**
  - **denaturant in ethanol**



C_4H_{11}
2-methylpropane

$C_4H_{10}O_2$
tert-butyl hydroperoxide

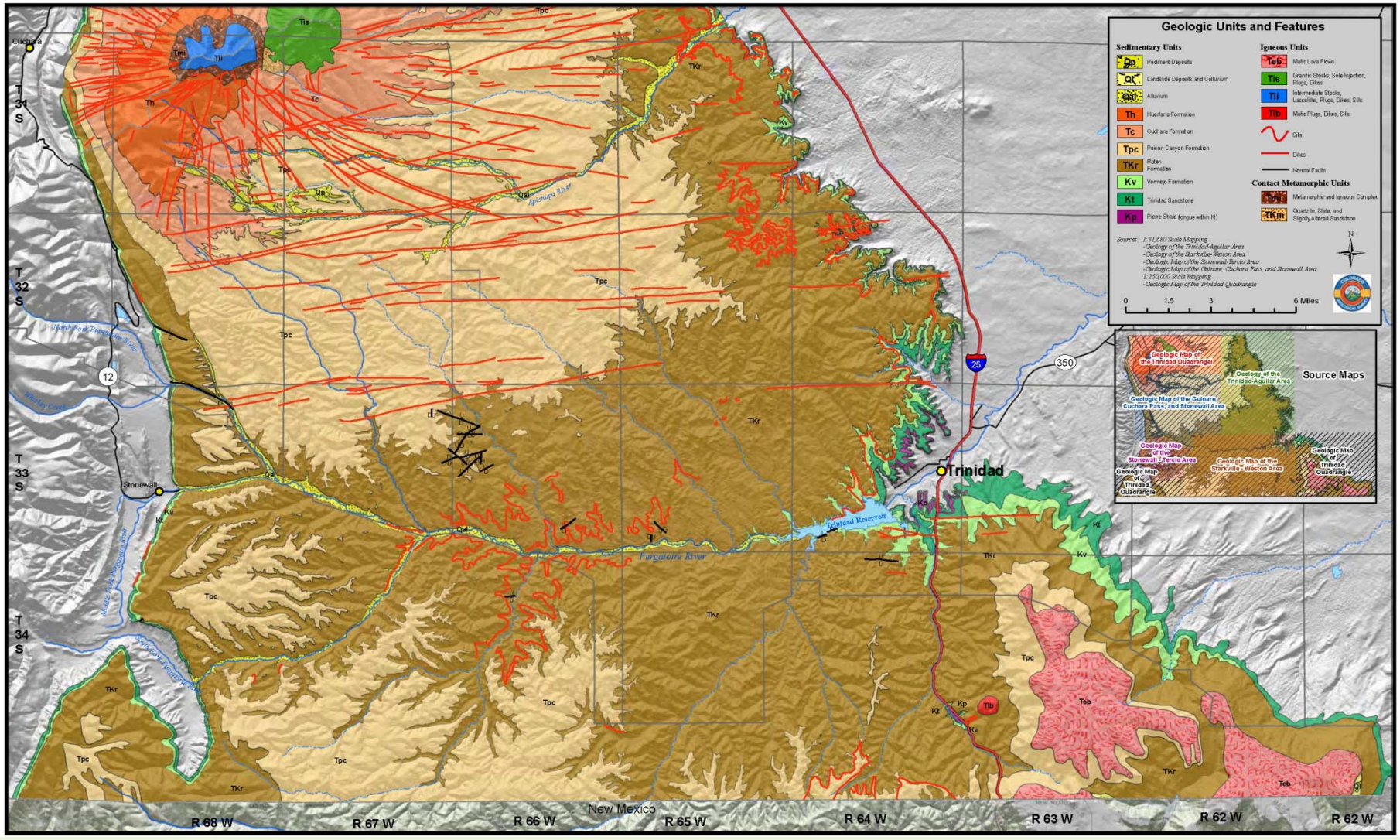



Alluvium, slopewash, and landslide material
Holocene and Quaternary
Basalt flows
Huerfano Formation
Middle Tertiary intrusives
Cuchara Formation
Poison Canyon Formation
Raton Formation
Vermejo Formation
Tertiary
Trinidad Sandstone and Pierre Shale undivided
Cretaceous
Pierre Shale/Niobrara undivided
Precambrian rock undivided
Raton Basin boundary
Basin axis
Apishapa arch
Walsenburg
Stonewall
Raton
Sangre de Cristo Mountains
Las Animas arch
Sierra Grande arch
Colorado
New Mexico
37°
105
0
15 Miles
0
20 Kilometers
Colorado
Raton Basin
New Mexico
Johnson and Finn, 2001

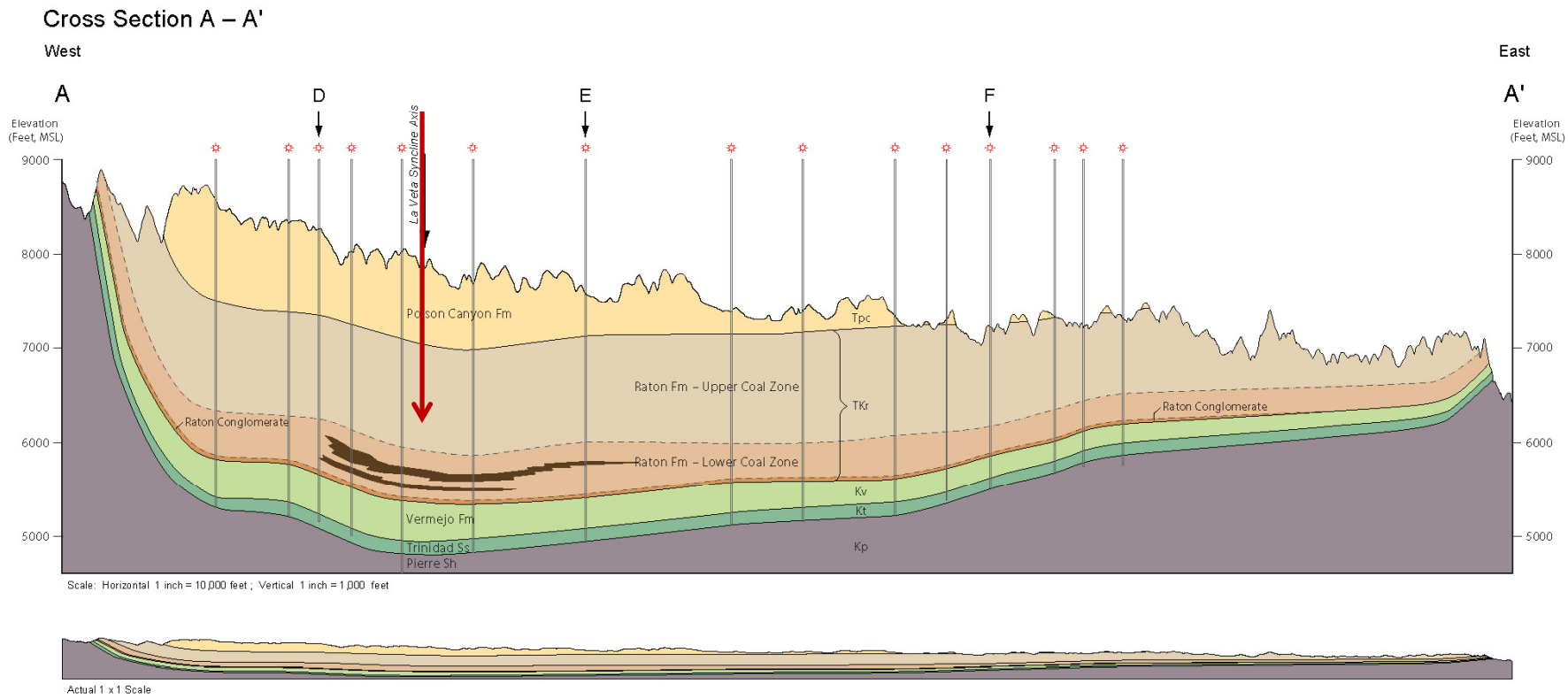
Formation	Thickness (feet)	Lithology
Poison Canyon Formation	0-2500	arkosic conglomerates and sandstones, siltstones and shale
Raton Formation	0-2000	sandtone, siltstone, shale and coal with conglomerate near base
Vermejo Formation	0-380	silty and coaly shale, carbonaceous siltstone, sandstone beds and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

Topper *et al.*, 2011

Composite Geologic Map of the Raton Basin In Colorado

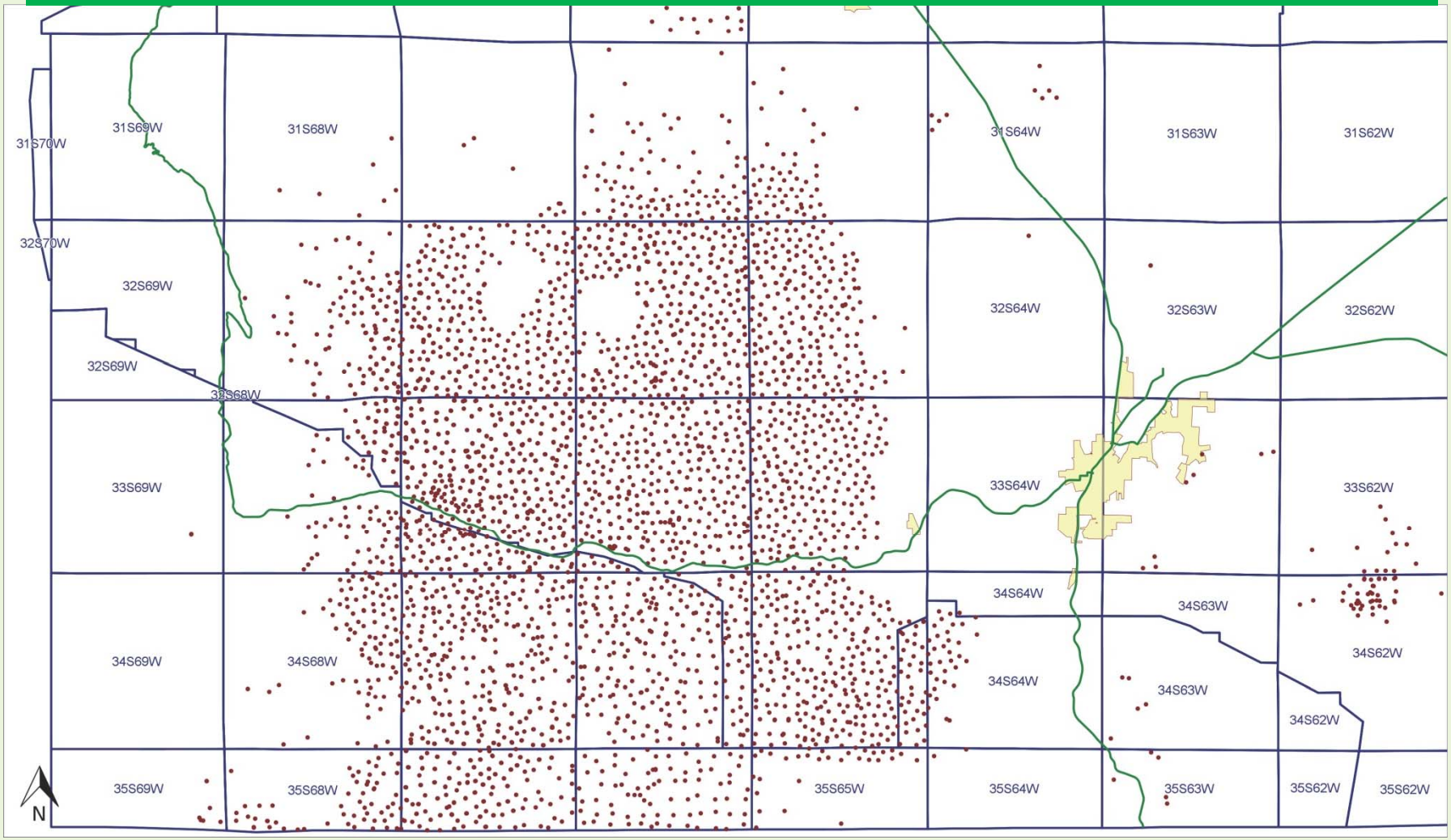


Topper *et al.*, 2011



Topper *et al.*, 2011

Las Animas County Oil and Gas Wells



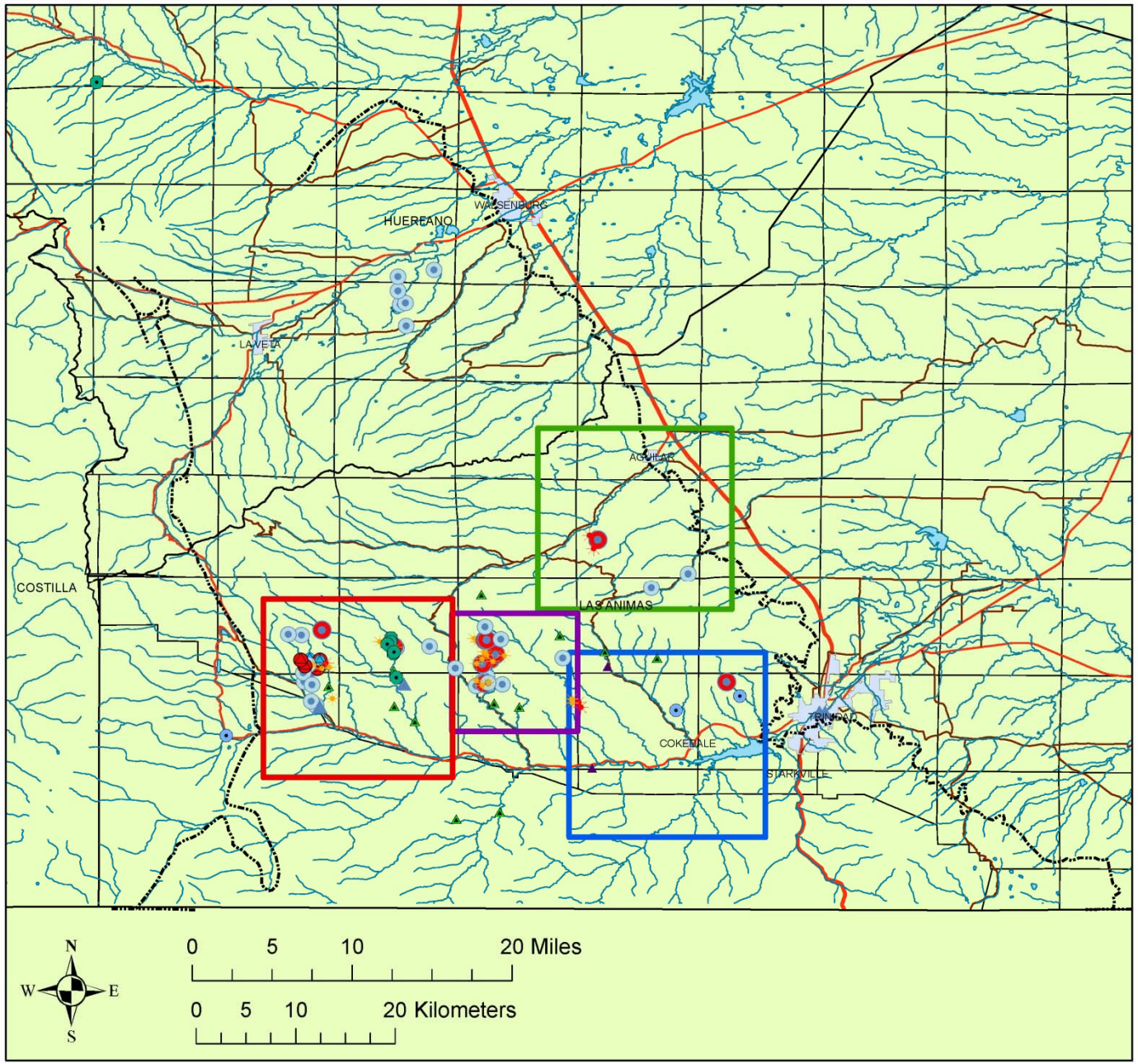
in 2014 ≈3050 active wells,
≈86BCF gas produced,
≈55 million bbls produced H_2O

EPA's Study of Hydraulic Fracturing for Oil and Gas and Its Potential Impact on Drinking Water Resources

QAPP for Hydraulic Fracturing Retrospective Case Study, Raton Basin, CO (GWERD)

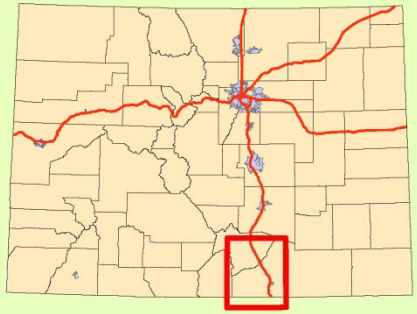
This QAPP describes the technical details and associated quality assurance and quality control procedures for the Las Animas and Huerfano Counties, Colorado, Raton Basin case study.

Map 1 TBA Sample Locations Raton Basin



TBA Sample Locations

- CBM well, TBA Detection
- CBM well, ND
- Discharge, ND
- monitoring well TBA Detection
- monitoring well, ND
- surface water, ND
- surface water, ND(<2)
- water well, TBA Detection
- water well, ND <2
- water well, ND
- water well, ND(<50)
- Map 2 - N.F.R. and Wet Canyon
- Map 3 - Rancho La Garita
- Map 4 - Reilly & Burro Canyons
- Map 5 - Gulnare
- LasAnimasMRoads
- Highway
- Interstate
- Extent of Vermejo Coals



Summary of Types of Facility/Matrices Sampled

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%**

Investigation

- Source(s)
- Media
- Pathways
- Need to use all data available to evaluate
  - Major ion and trace element geochemistry
  - Gas composition and isotope composition
  - Water isotope composition
  - Organic compounds present including aromatics, isobutane and methane
  - Microbial populations present
  - Well construction and products used

Possible Sources

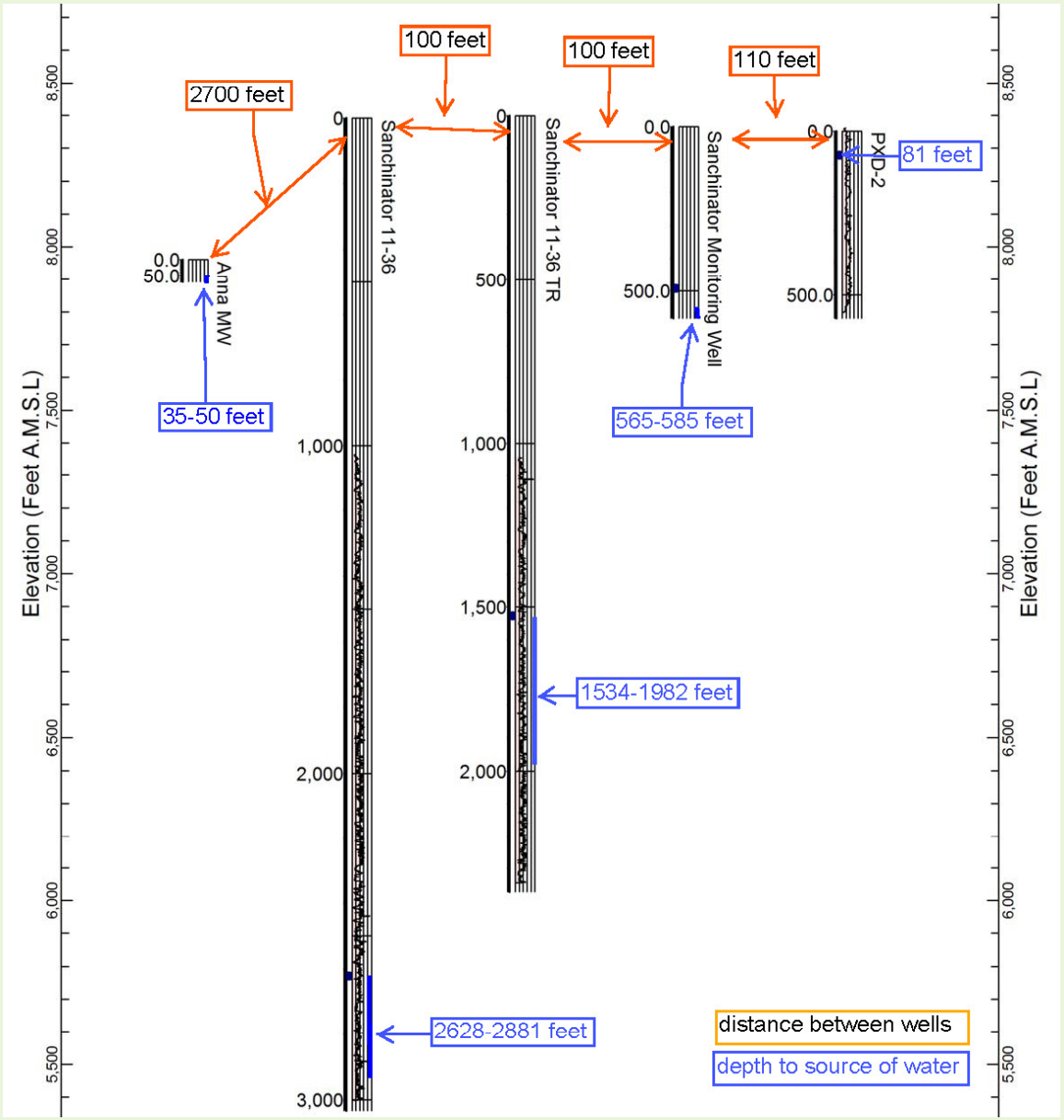
1 Direct	Household product containing TBA disposal to septic systems with infiltration to groundwater
2 Indirect	Spills of gasoline - containing MTBE and isobutane with subsequent microbial degradation
3 Indirect	Spills of gasoline – containing isobutane with subsequent microbial degradation
4 Indirect	**Seeps or releases of natural gas – containing isobutane with subsequent microbial degradation**
5 Indirect	**Use of 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**

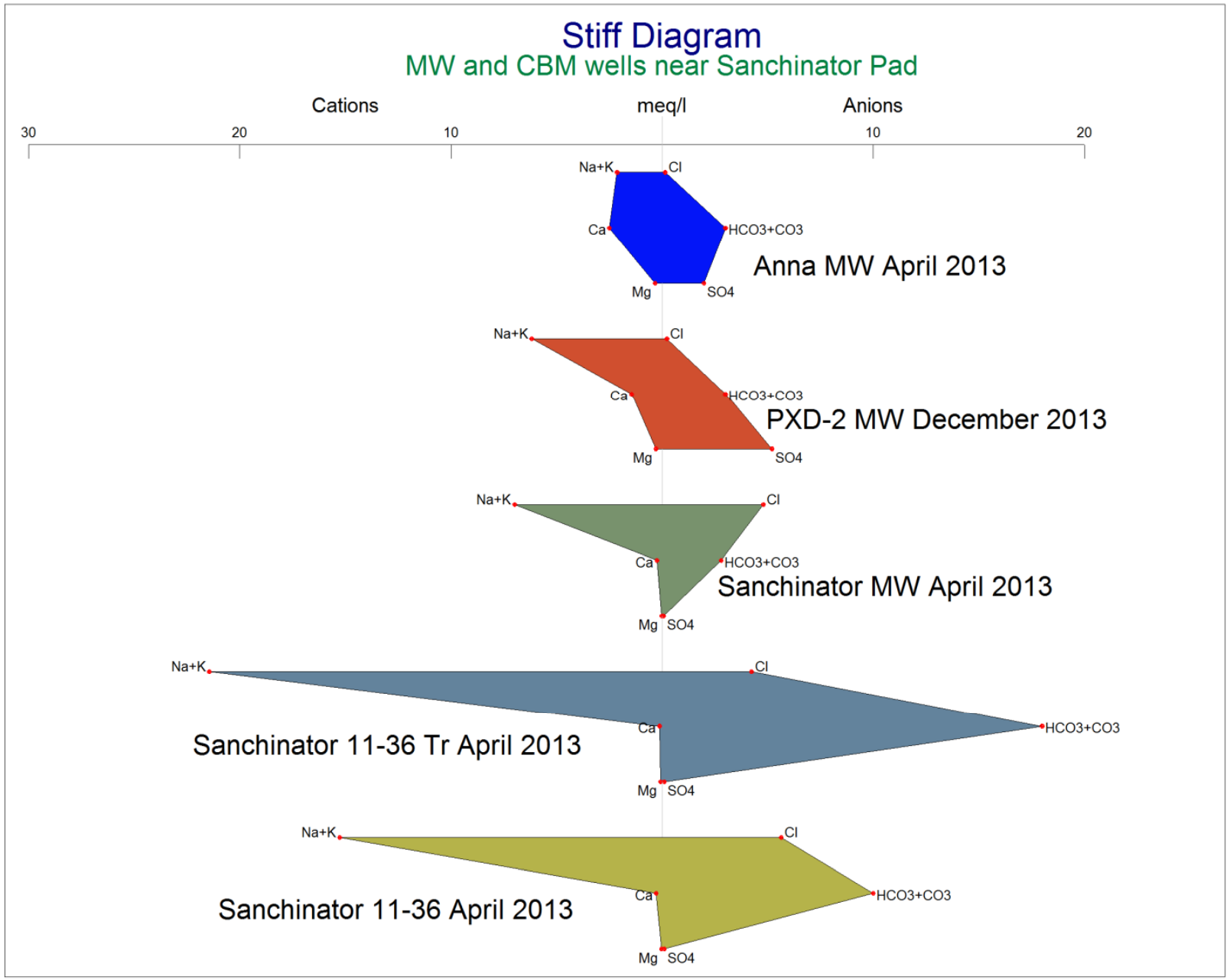
Media for migration

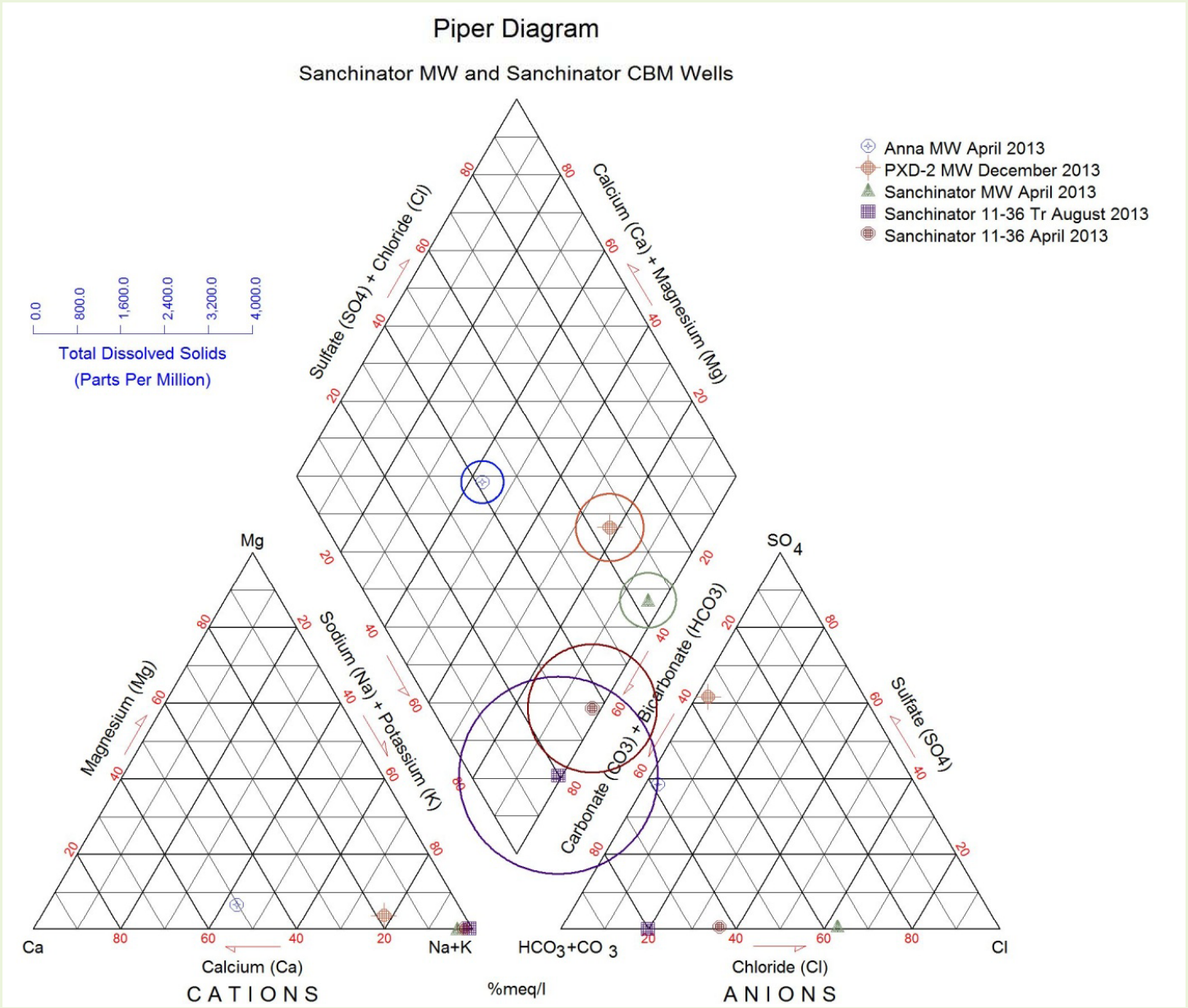
- **Some sources listed imply what media**
  - **Groundwater**
    - *e.g.*, possible sources 1, 2, 3 and 8
  - **Groundwater produced from CBM operations**
    - *e.g.*, possible sources 5, 8, 9 and 10
  - **In situ**
    - *e.g.*, possible sources 6 and 7
  - **Natural gas**
    - *e.g.*, possible source 4

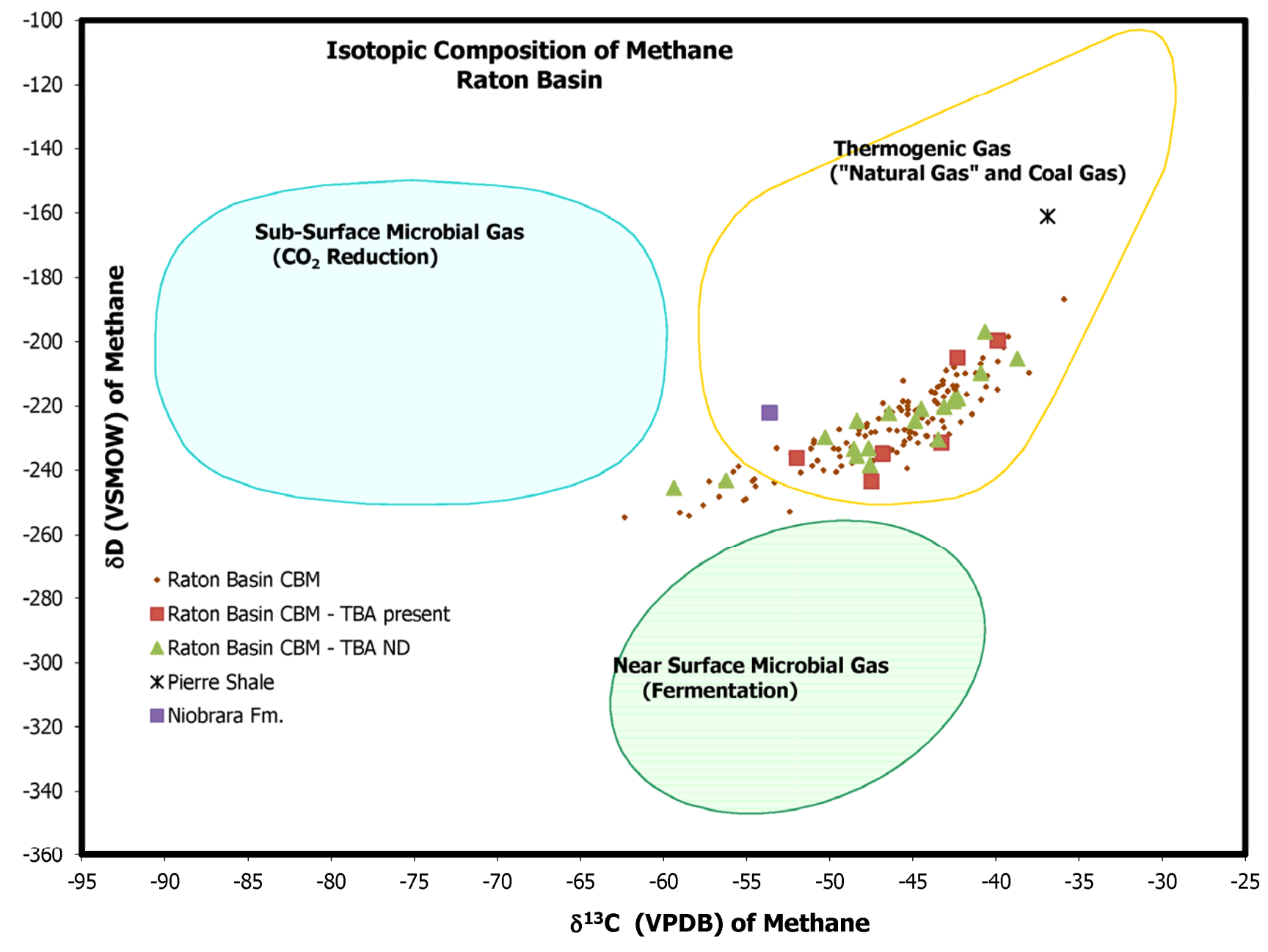
Summary of Major Ion Composition of Groundwater from the Basin

		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

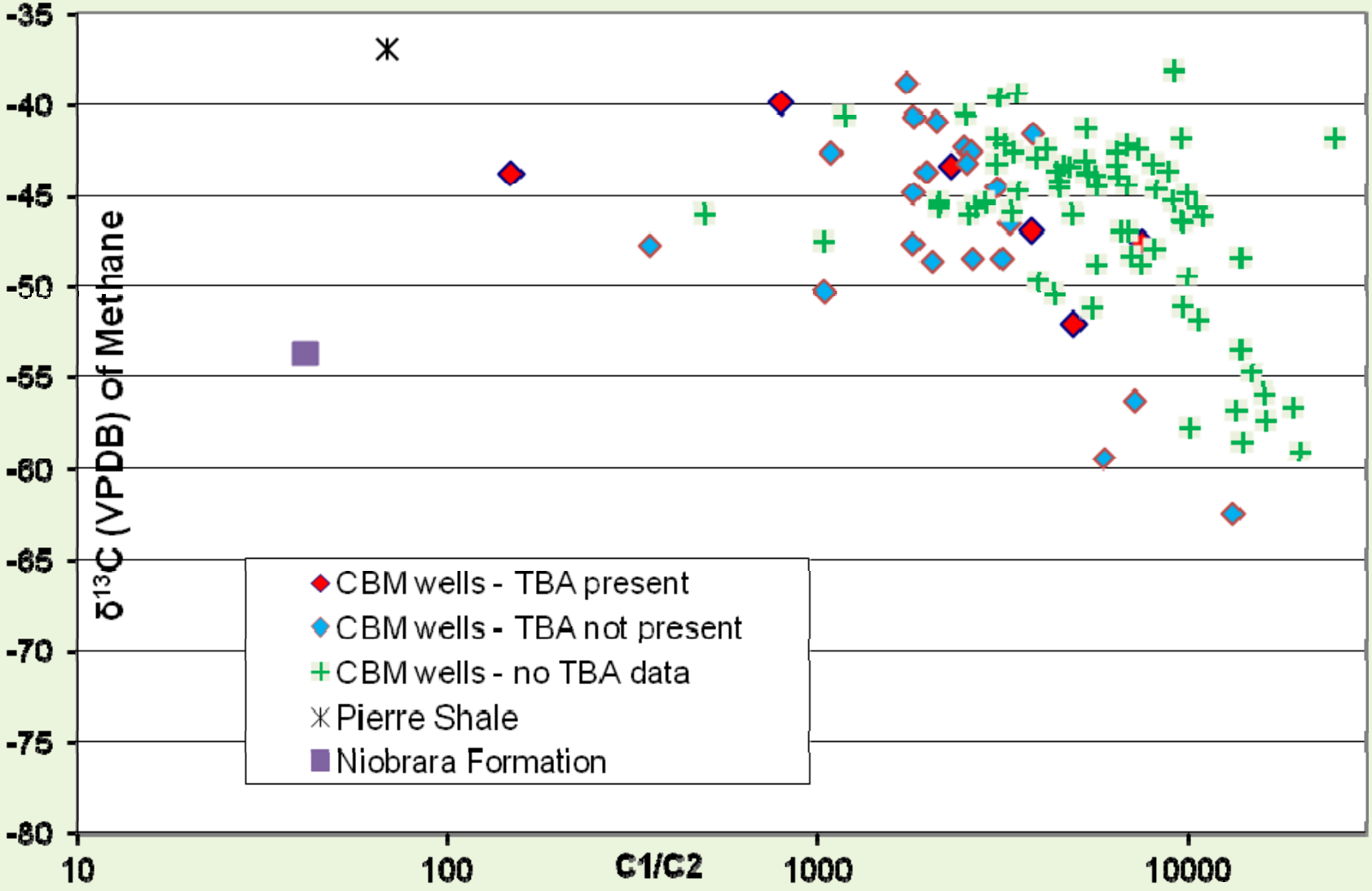

100 feet
100 feet
110 feet
2700 feet
0
0
0.0
0.0
Sanchinator 11-36
Sanchinator 11-36 TR
Sanchinator Monitoring Well
PXID-2
81 feet
0.0
50.0
Anna MW
35-50 feet
500
500.0
500.0
565-585 feet
1,000
1,000
1,500
1534-1982 feet
2,000
2,000
2628-2881 feet
3,000
Elevation (Feet A.M.S.L)
8,500
8,000
7,500
7,000
6,500
6,000
5,500
distance between wells
depth to source of water

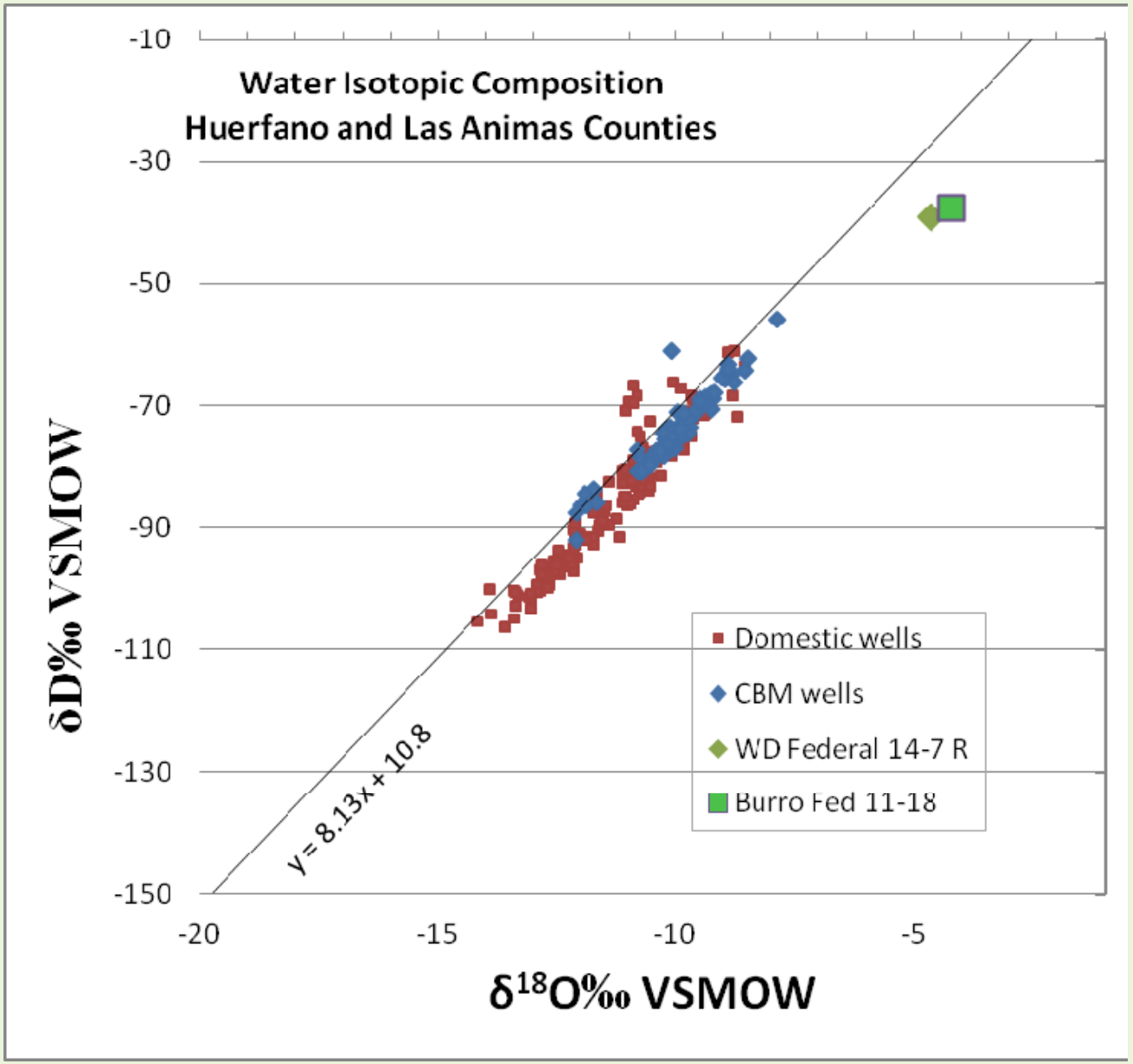

Stiff Diagram
MW and CBM wells near Sanchinator Pad
Cations
meq/l
Anions
30
20
10
10
20
Na+K
Cl
Ca
HCO3+CO3
Mg
SO4
Anna MW April 2013
PXD-2 MW December 2013
Sanchinator MW April 2013
Sanchinator 11-36 Tr April 2013
Sanchinator 11-36 April 2013


Piper Diagram
Sanchinator MW and Sanchinator CBM Wells
Anna MW April 2013
PXD-2 MW December 2013
Sanchinator MW April 2013
Sanchinator 11-36 Tr August 2013
Sanchinator 11-36 April 2013
0.0
800.0
1,600.0
2,400.0
3,200.0
4,000.0
Total Dissolved Solids
(Parts Per Million)
Sulfate (SO4) + Chloride (Cl)
Calcium (Ca) + Magnesium (Mg)
Mg
Magnesium (Mg)
Sodium (Na) + Potassium (K)
Ca
Na+K
Calcium (Ca)
CATIONS
SO4
Sulfate (SO4)
Carbonate (CO3) + Bicarbonate (HCO3)
HCO3+CO 3
Cl
Chloride (Cl)
ANIONS
%meq/l


Isotopic Composition of Methane
Raton Basin
Thermogenic Gas
("Natural Gas" and Coal Gas)
Sub-Surface Microbial Gas
(CO_2 Reduction)
Near Surface Microbial Gas
(Fermentation)
Raton Basin CBM
Raton Basin CBM - TBA present
Raton Basin CBM - TBA ND
Pierre Shale
Niobrara Fm.
δD (VSMOW) of Methane
δ13C (VPDB) of Methane
-100
-120
-140
-160
-180
-200
-220
-240
-260
-280
-300
-320
-340
-360
-95
-90
-85
-80
-75
-70
-65
-60
-55
-50
-45
-40
-35
-30
-25

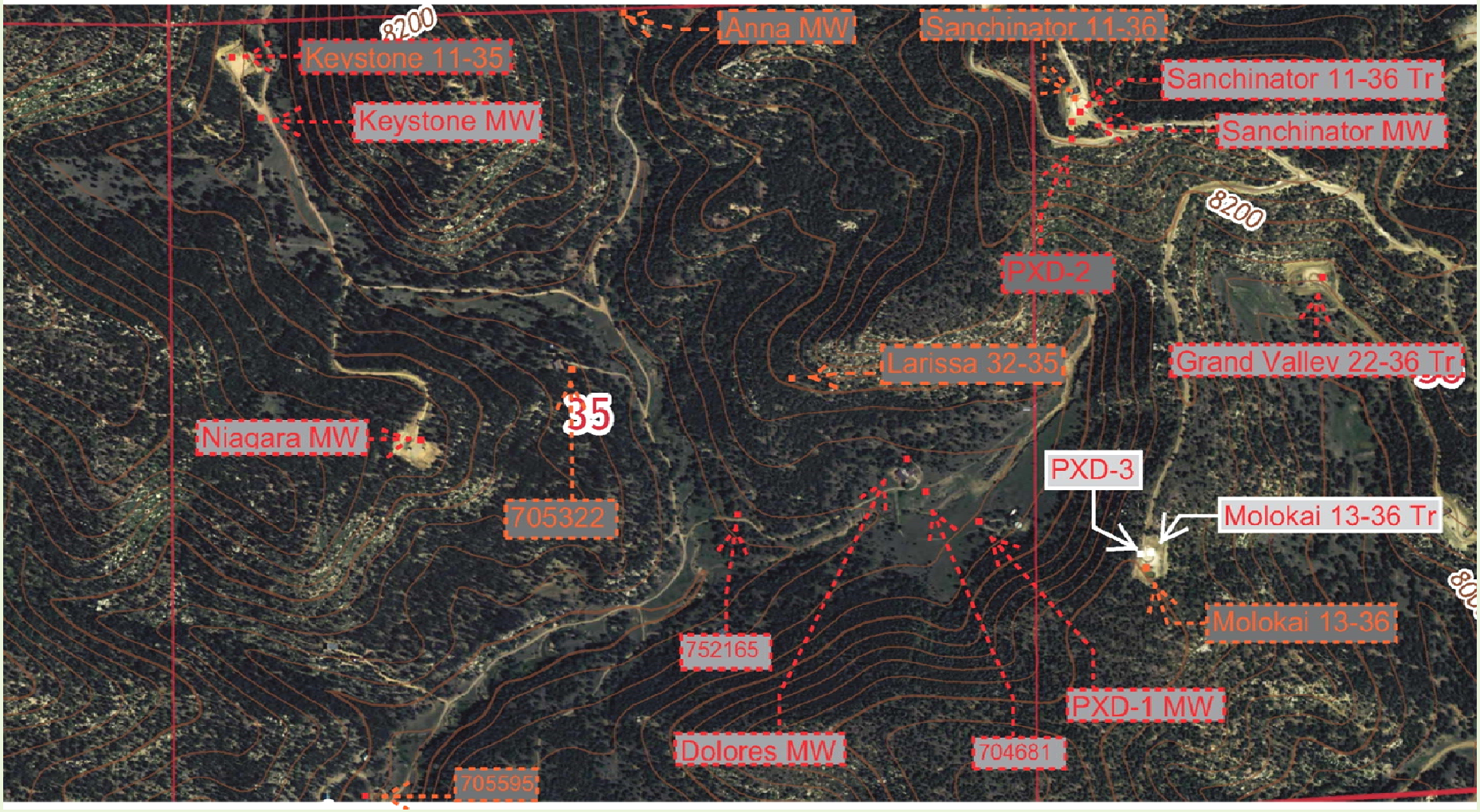
Carbon Isotopic Composition of methane versus methane/ethane Ratio



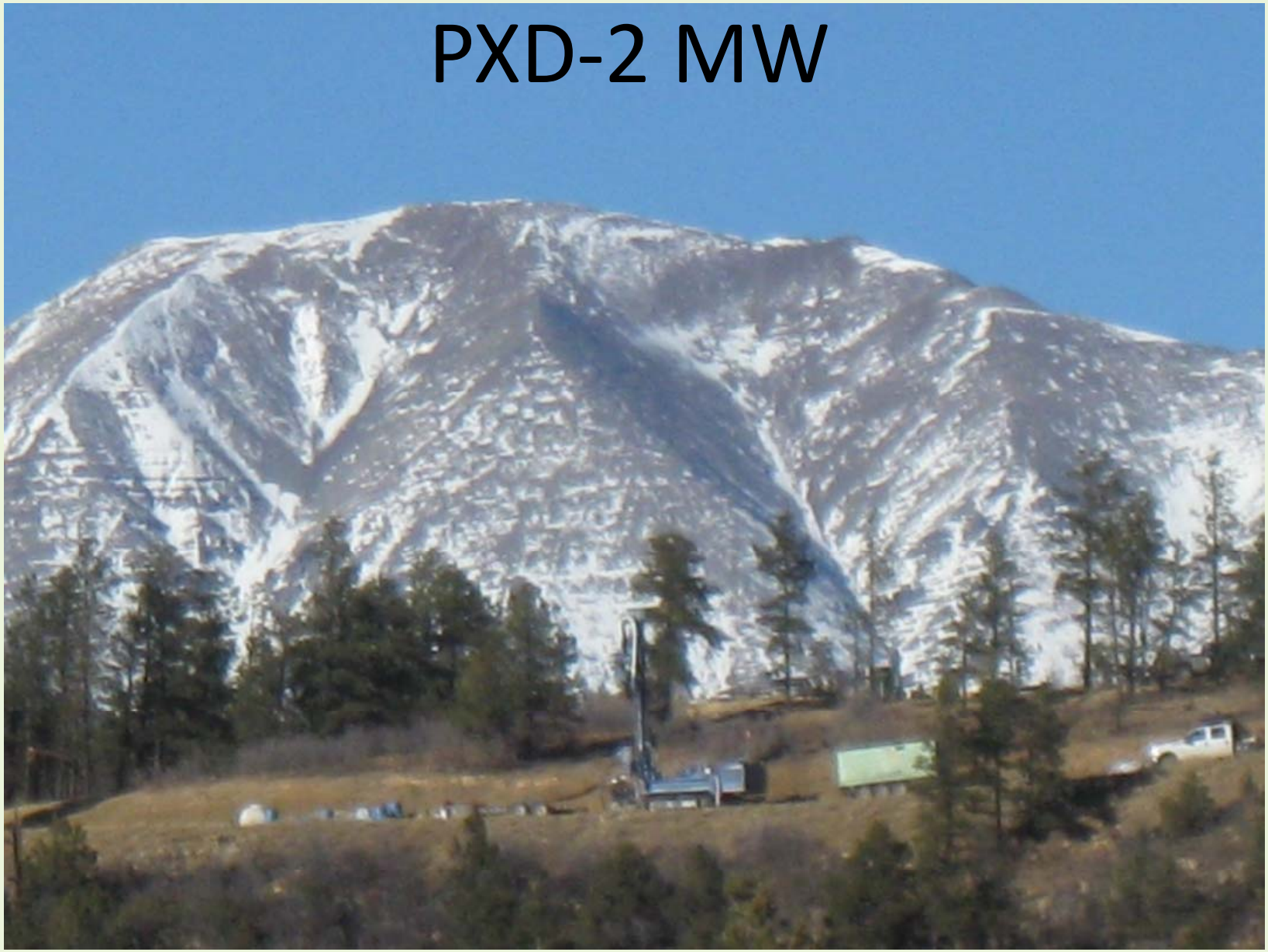

Water Isotopic Composition
Huerfano and Las Animas Counties
δD‰ VSMOW
δ18O‰ VSMOW
-10
-30
-50
-70
-90
-110
-130
-150
-20
-15
-10
-5
y = 8.13x + 10.8
Domestic wells
CBM wells
WD Federal 14-7 R
Burro Fed 11-18

Pathways

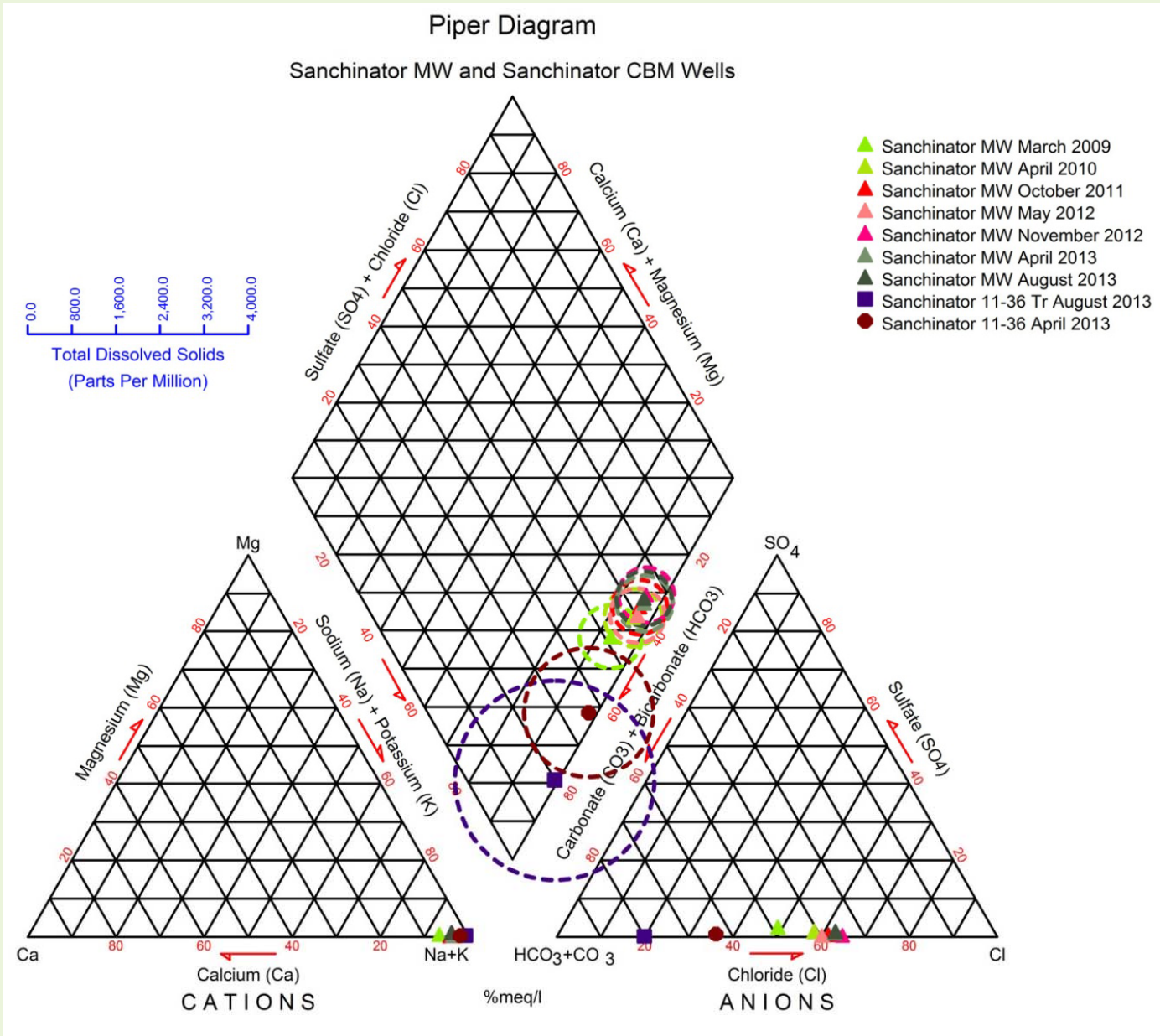
- **Some sources define what pathways possible and what time frame**
  - In situ (short time frame)
  - Surface flow (spills or releases) with infiltration to shallow groundwater (short-medium time frame)
  - Infiltration and migration in groundwater over hundreds or thousands of feet (medium-long time frame)


8200
Anna MW
Sanchinator 11-36
Keystone 11-35
Sanchinator 11-36 Tr
Keystone MW
Sanchinator MW
8200
PXD-2
Larissa 32-35
Grand Valley 22-36 Tr
35
Niagara MW
PXD-3
705322
Molokai 13-36 Tr
Molokai 13-36
752165
PXD-1 MW
Dolores MW
704681
705595

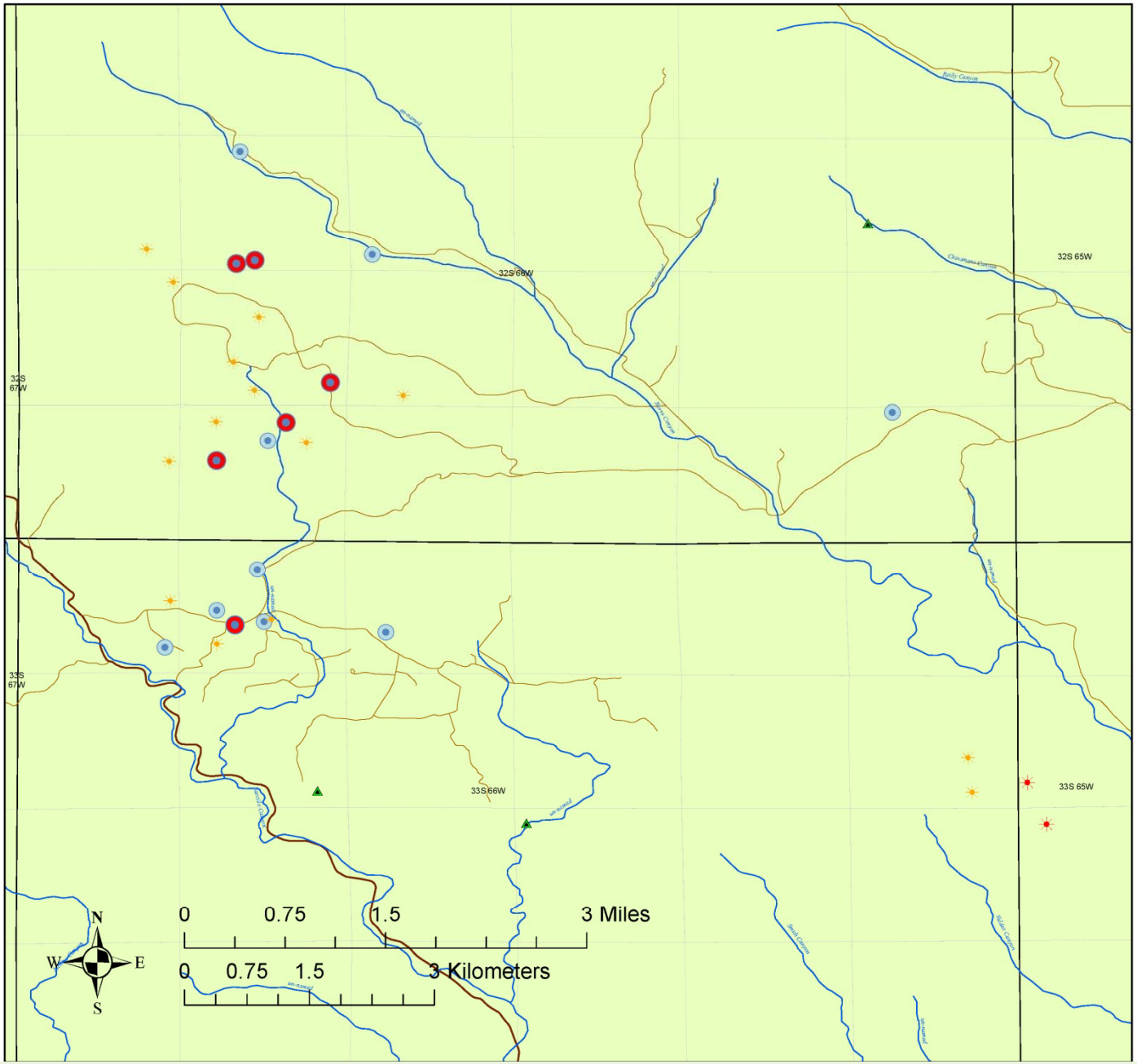
PXD-2 MW



- PXD-2 and PXD-3 MW drilling did not indicate the presence of groundwater in potential pathways between CBM locations and nearby water and domestic wells with TBA present

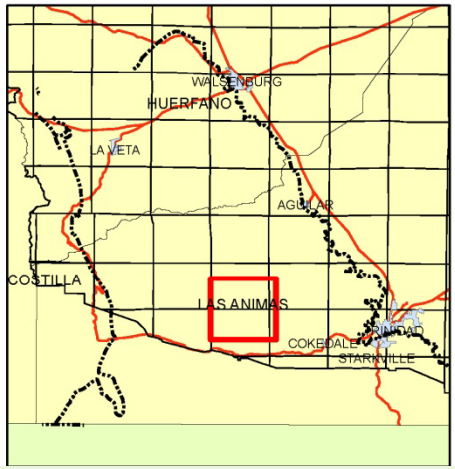

Piper Diagram
Sanchinator MW and Sanchinator CBM Wells
Sanchinator MW March 2009
Sanchinator MW April 2010
Sanchinator MW October 2011
Sanchinator MW May 2012
Sanchinator MW November 2012
Sanchinator MW April 2013
Sanchinator MW August 2013
Sanchinator 11-36 Tr August 2013
Sanchinator 11-36 April 2013
0.0
800.0
1,600.0
2,400.0
3,200.0
4,000.0
Total Dissolved Solids
(Parts Per Million)
Sulfate (SO4) + Chloride (Cl)
Calcium (Ca) + Magnesium (Mg)
Mg
Magnesium (Mg)
Sodium (Na) + Potassium (K)
Ca
Na+K
Calcium (Ca)
CATIONS
SO4
Carbonate (CO3) + Bicarbonate (HCO3)
Sulfate (SO4)
HCO3+CO 3
Cl
Chloride (Cl)
ANIONS
%meq/l

Map 3 TBA Sample Locations Rancho La Garita and Arrowhead Ranchettes



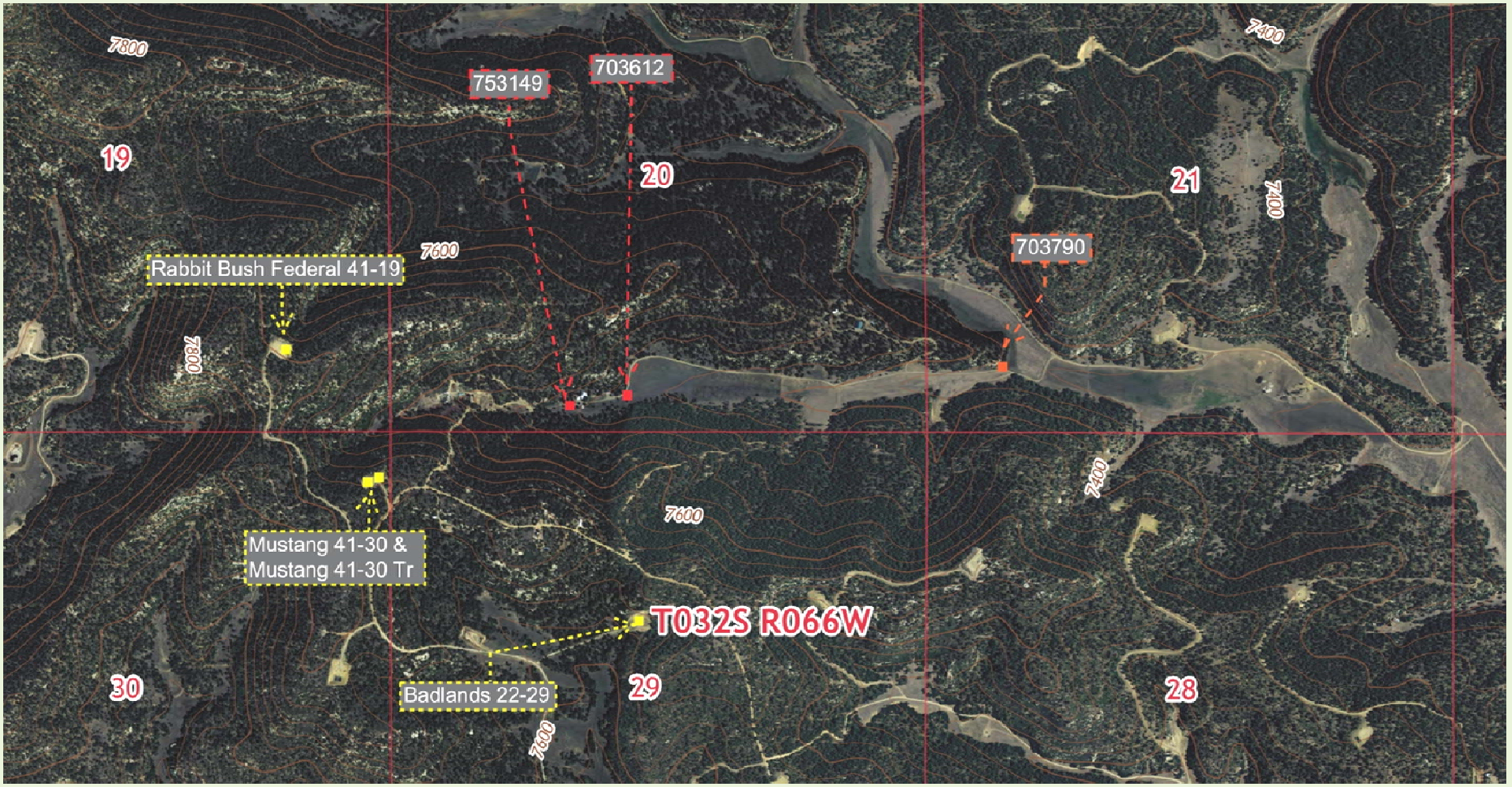
TBA Sample Locations

- CBM well, TBA Detection
- CBM well, ND
- Discharge, ND
- monitoring well TBA Detection
- monitoring well, ND
- surface water, ND
- surface water, ND(<2)
- water well, TBA Detection
- water well, ND <2
- water well, ND
- water well, ND(<50)
- forestrds
- Rivers
- Major Roads
- Local Roads
- Highway
- Rail Road
- Lakes
- Township
- Sections



2 wells with TBA

- More than 2300 feet from nearest CBM
- One well sampled in 1981 for major ions
  - Major ion chemistry same in 2014 as in 1981
- Major ion chemistry of 2nd well not similar to original well
  - Separate groundwater source but only 600 feet other well
- CBM wells nearby sampled – TBA not detected
- Groundwater flow estimated to take greater than 40 years from nearest CBM well
- Groundwater from both wells have aromatic organics and unusually wet gas composition


753149
703612
703790
Rabbit Bush Federal 41-19
Mustang 41-30 &
Mustang 41-30 Tr
Badlands 22-29
T032S R066W
19
20
21
30
29
28
7800
7600
7400

Summary

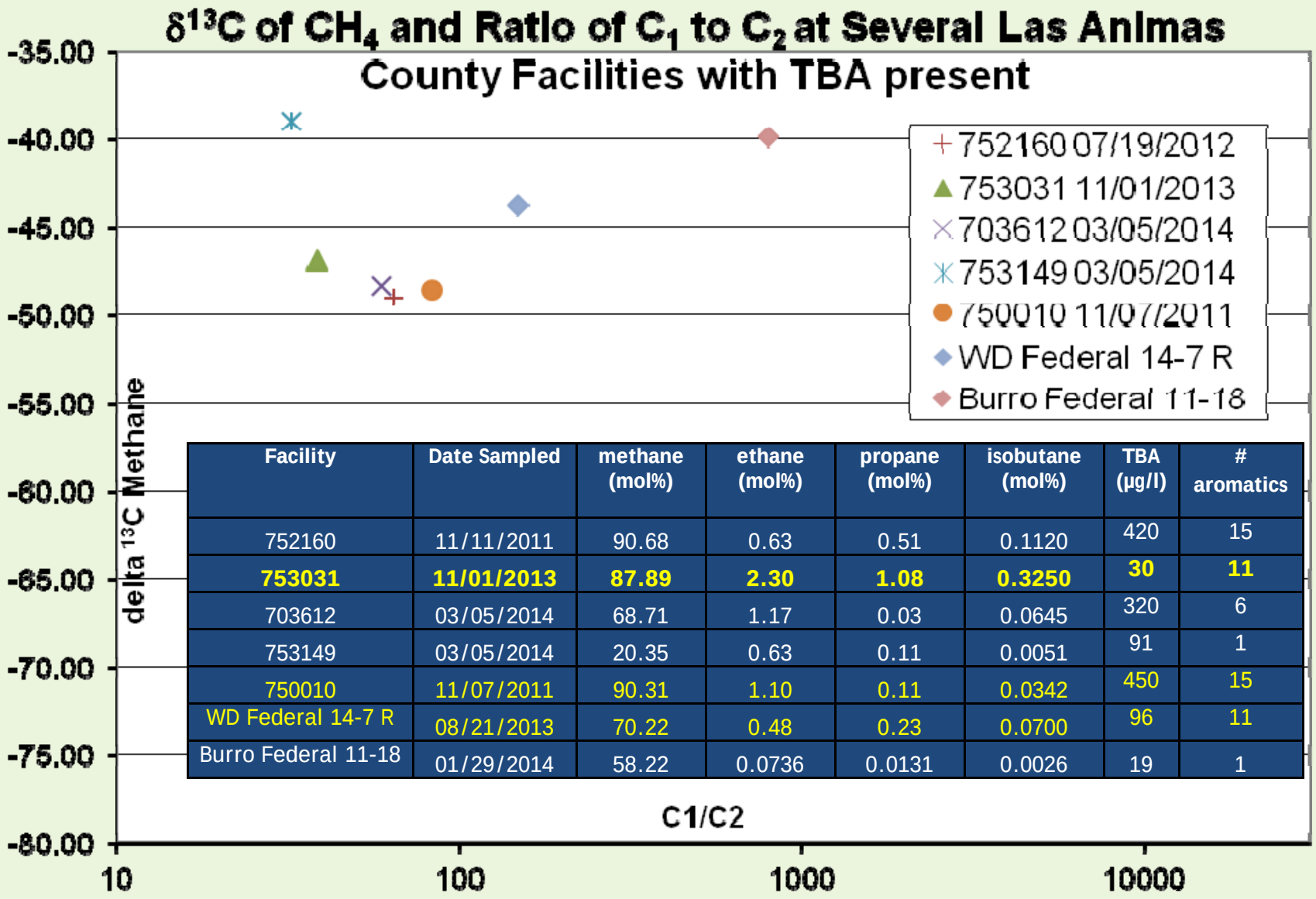
- Products used in drilling and completing CBM wells do not indicate presence of TBA as ingredient and do not indicate presence of possible precursor (*tert*-butyl hydroperoxide)
- TBA not detected in frac flowback samples
- TBA detected in approximately same % of produced water samples as from domestic water wells sampled

Summary (continued)

- One CBM well with TBA detected has produced water volumes greater than 100 times the frac volume and no chemical products used downhole since the completion
- This CBM well has unusual gas composition for Raton Basin CBM with lowest methane to ethane ratio of any we have data for
- Isobutane concentration in WD Federal sample is significantly greater than in most CBM samples from the Basin

Summary (continued)

- presence of isobutane not conclusive evidence of production of TBA by microbial degradation of isobutane
- must have methanotrophs and then still need certain methanotrophs



Facility	Date Sampled	methane (mol%)	ethane (mol%)	propane (mol%)	isobutane (mol%)	TBA (µg/l)	# aromatics
752160	11/11/2011	90.68	0.63	0.51	0.1120	420	15
753031	**11/01/2013**	**87.89**	**2.30**	**1.08**	**0.3250**	**30**	**11**
703612	03/05/2014	68.71	1.17	0.03	0.0645	320	6
753149	03/05/2014	20.35	0.63	0.11	0.0051	91	1
750010	11/07/2011	90.31	1.10	0.11	0.0342	450	15
WD Federal 14-7 R	08/21/2013	70.22	0.48	0.23	0.0700	96	11
Burro Federal 11-18	01/29/2014	58.22	0.0736	0.0131	0.0026	19	1

	WD Federal 14-7R (2013)	WD Federal 14-7R (2014)	753031	750010
	cells/ml	cells/ml	cells/ml	cells/ml
methanogens	2.73×10^{4}	1.99×10^{6}	49.5	44
methane oxidizing bacteria	2.98×10^{7}	7.42×10^{3}	2.85×10^{5}	9.61×10^{6}
soluble methane monooxygenase producers	not analyzed	7.12×10^{3}	4.38×10^{3}	not analyzed

Conclusions

- No sources of TBA identified from chemicals and products used in CBM drilling or completions
- Produced water from ≈20% of CBM has TBA
- At present, no link can be found between oil and gas exploration and production activities and TBA in groundwater accessed by domestic water wells, but the exact source of TBA in some Las Animas county groundwater cannot be identified, either.

Acknowledgements

Landowners
CDPHE
EPA
Pioneer Natural Resources and Norwest