FACTORS AFFECTING FORENSIC ANALYSIS AND INTERPRETATION OF IMPACTS FROM STRAY GAS HYDROCARBONS - PRESSURE, MIXING, OXIDATION, DILUTION

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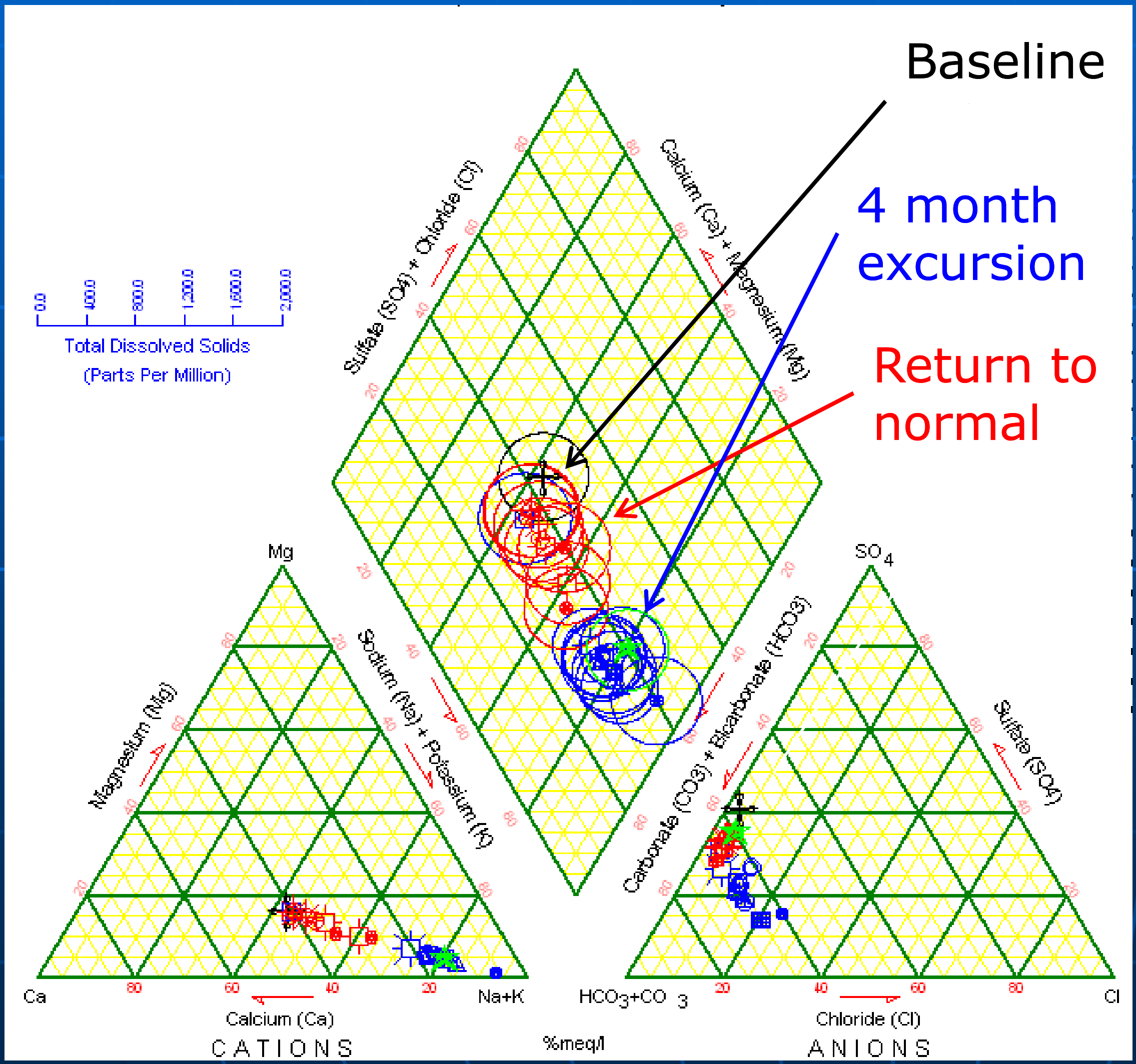
FORENSIC ANALYSIS

- Provide defensible data
  - What and where is the gas well point source?
  - When is impact attenuating?
- Characterize potential point sources and discharge
  - Sample casing head gas and production gas
  - Sample free and dissolved gas in groundwater
- Compare source to discharge
  - Gas ratios
  - Stable isotopes
- Address factors affecting composition and concentration
  - Fractionation – migration/solubility
  - Mixing (stripping biogenic methane)
  - Oxidation
  - Dilution

PRESSURE

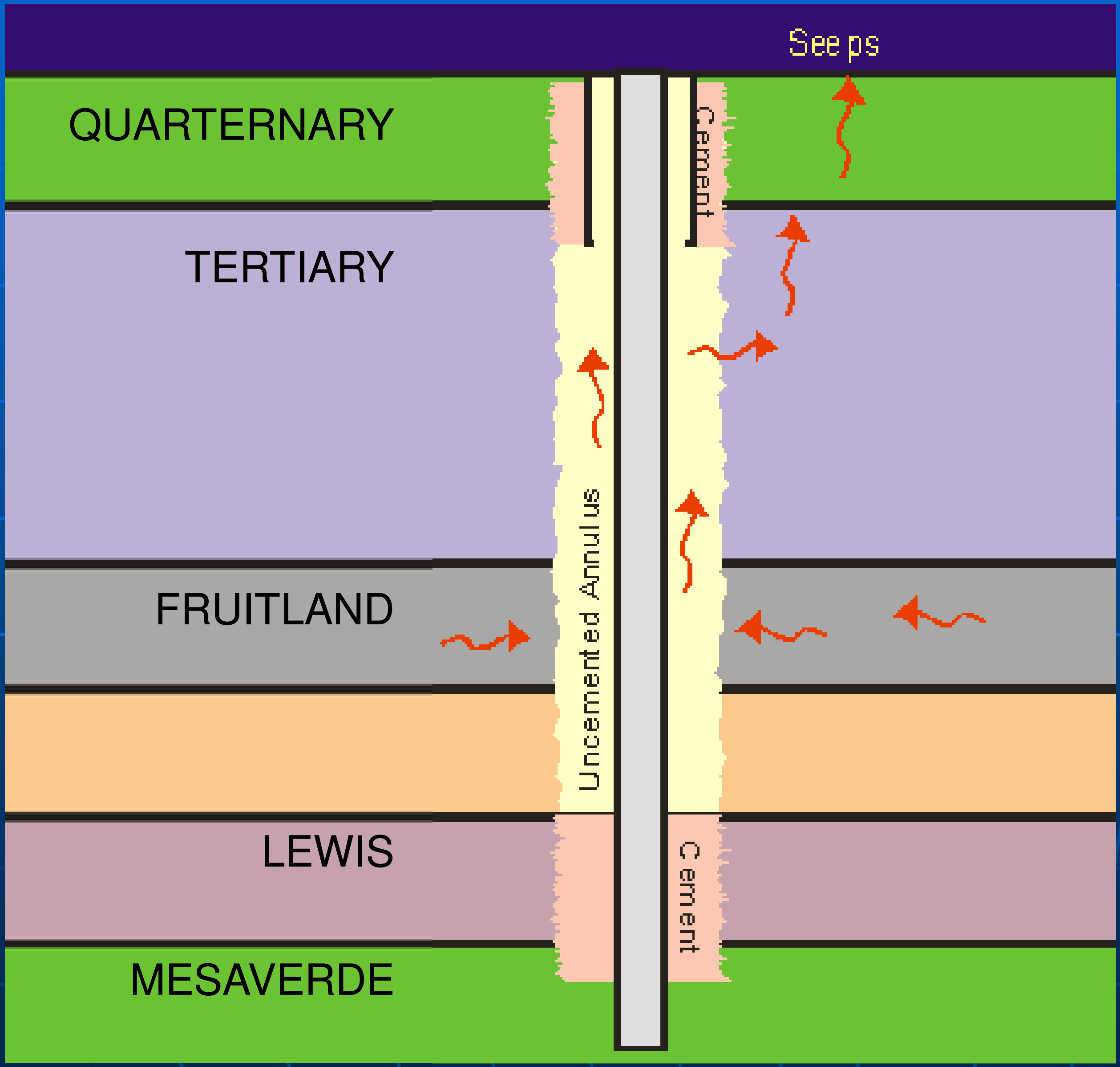
- Upper 1000-1500 feet of crust highly permeable
  - Vertical stress < horizontal stress
- Well bore annulus integrity is key to stray gas sources
  - Accidental blow outs
  - Improperly abandoned wells (historic practices)
  - Failed cement jobs
- Buoyant gas finds shortest path to the surface
  - Stream valleys
  - Water wells
  - Breakthrough limits further migration

EXTREME PRESSURE NOT REQUIRED TO MOBILIZE FLUIDS AT SHALLOW DEPTHS

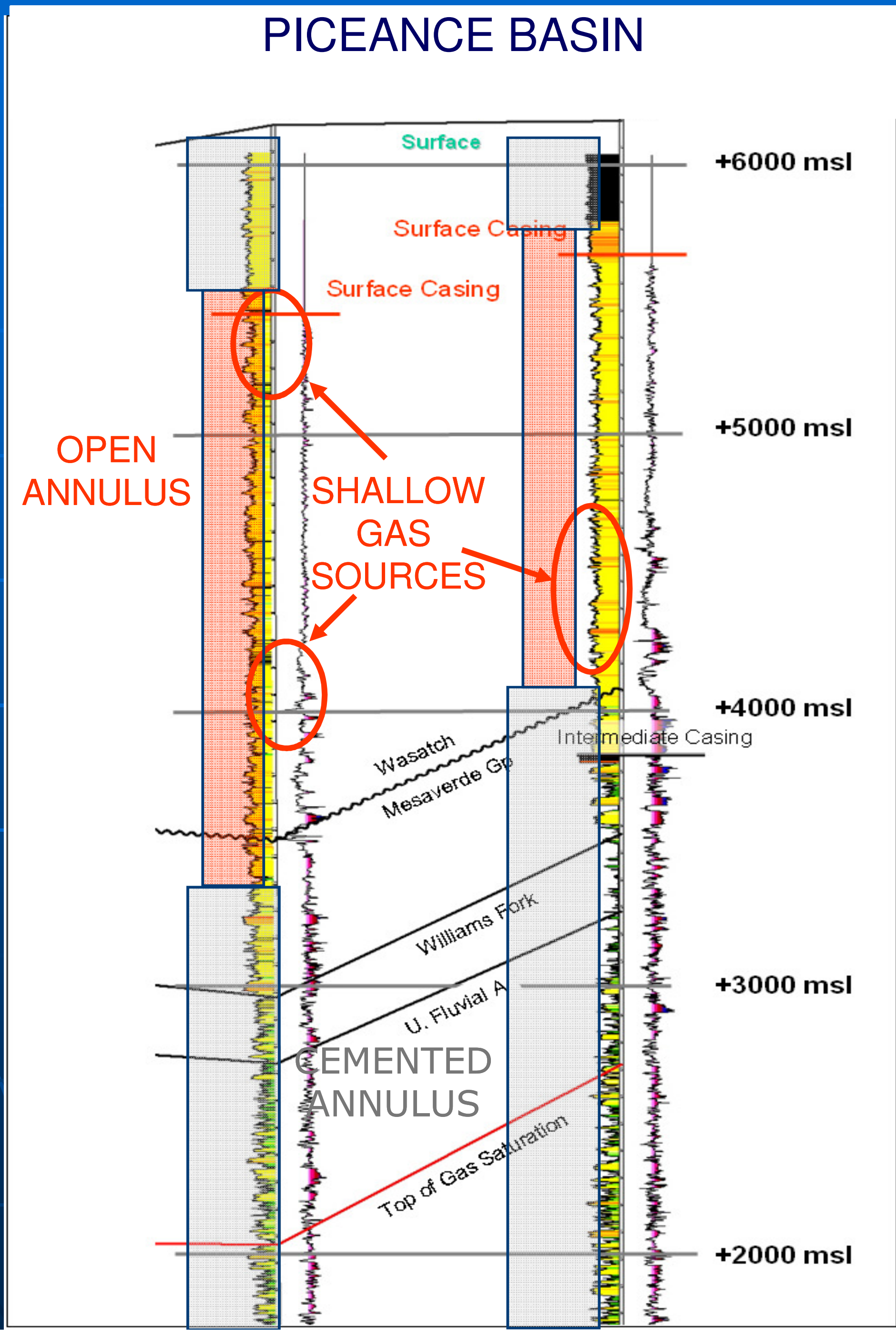


- E.G. RATON BASIN
  - Aquifer fluids mobilized 1/3 mile away while pressuring bit with air at 800’

LOW PRESSURE CBG INVADING SHALLOW AQUIFERS THROUGH OPEN ANNULUS



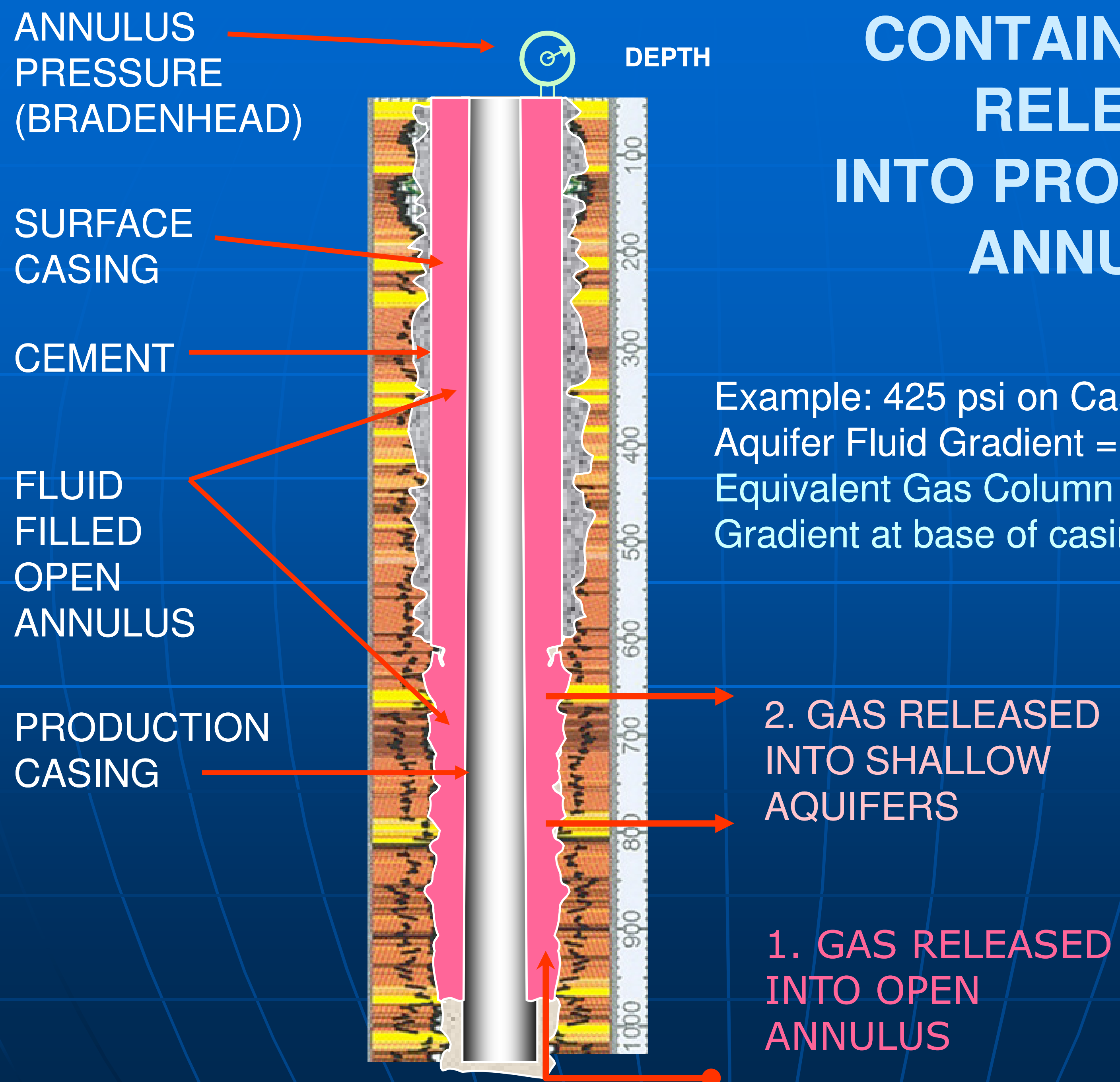
- SAN JUAN BASIN
  - Open annulus: historic production practices



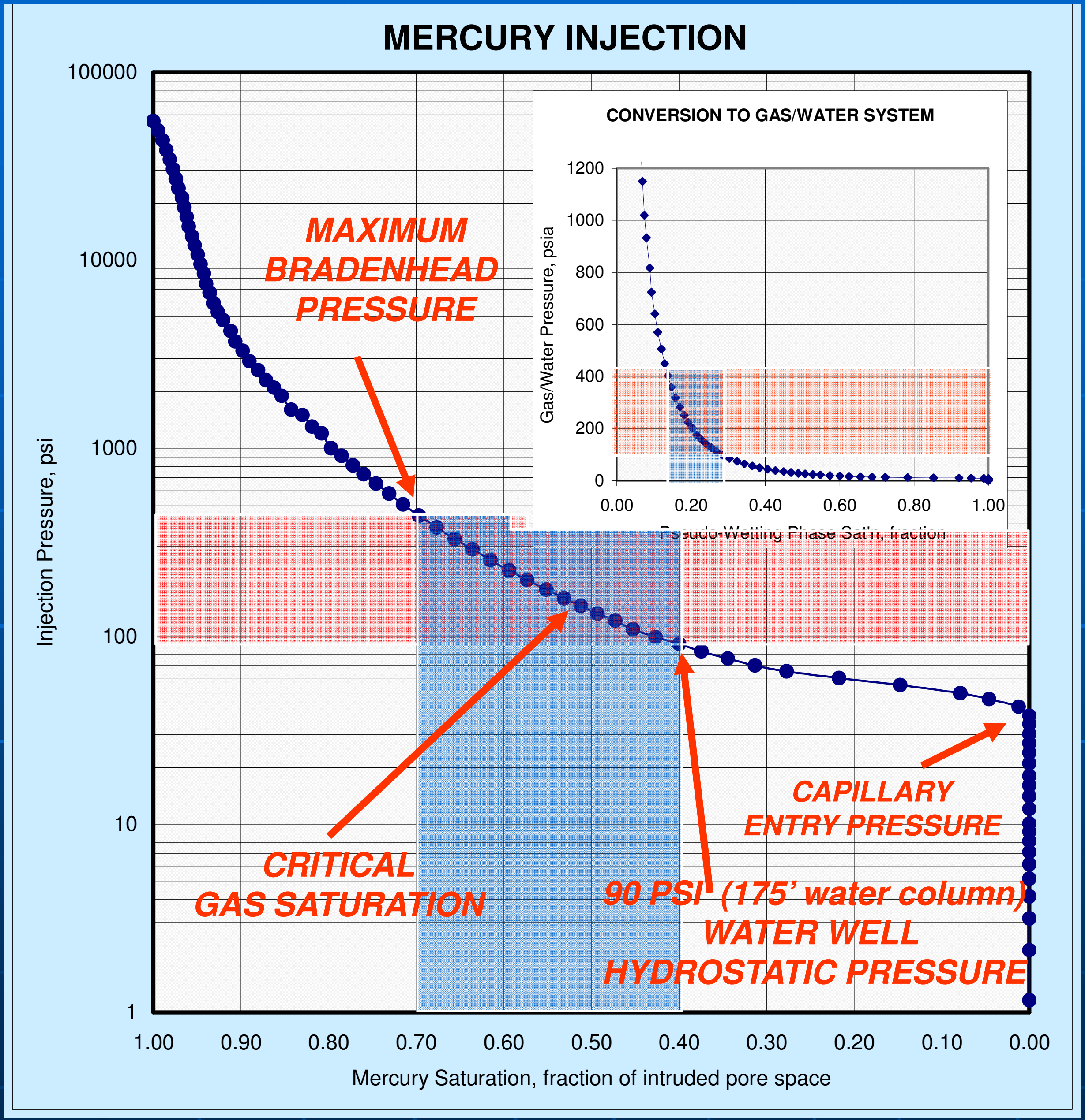
BOUYANCY PRESSURE ALLOWS GAS MIGRATION FROM ANNULUS

CONTAINED GAS RELEASE INTO PRODUCTION ANNULUS

Example: 425 psi on Casing head
Aquifer Fluid Gradient = .438 psi/ft
Equivalent Gas Column = 970’ **OR**
Gradient at base of casing: 0.69 psi/ft



SHALLOW FRACTURES & SAND MATRIX GAS INVASION INTO SANDS



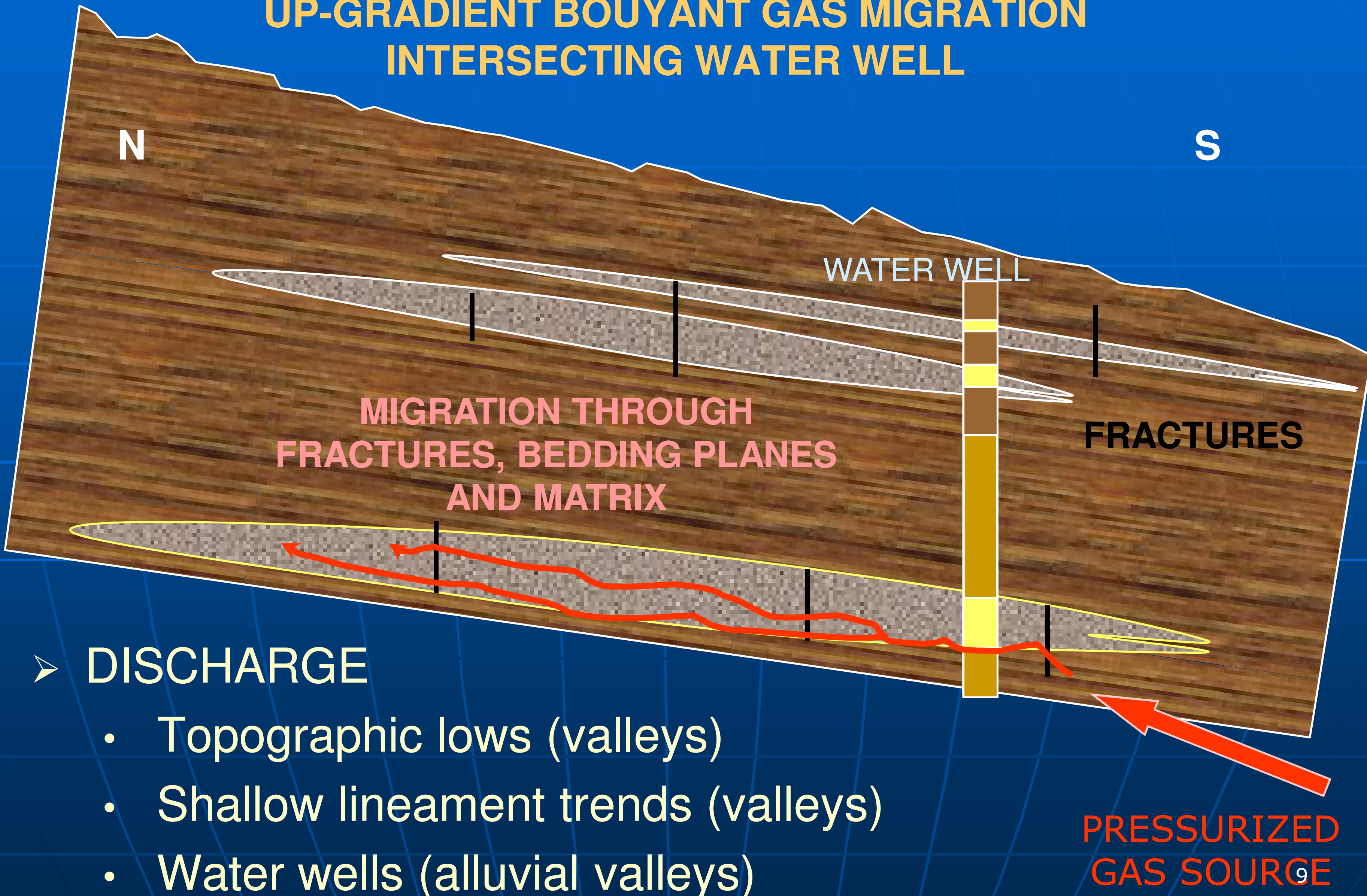
GAS FLOW DEPENDENT ON DRAINAGE PROPERTIES

POROSITY: 15%
PERMEABILITY: 5.38 md

LOWEST CAPILLARY ENTRY PRESSURES THROUGH SHALLOW BEDDING PLANE AND HORIZONTAL FRACTURES

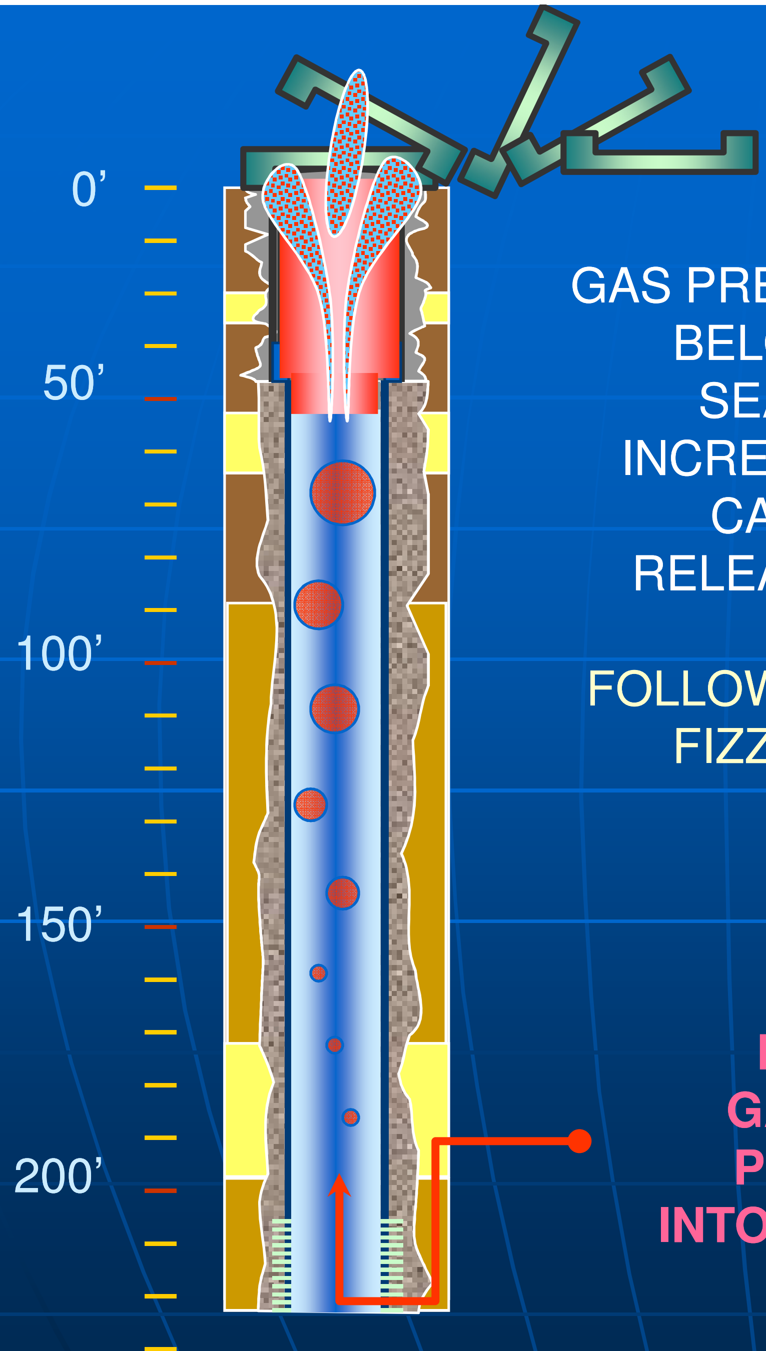
FREE GAS MOVEMENT IN GROUNDWATER

UP-GRADIENT BOUYANT GAS MIGRATION INTERSECTING WATER WELL



- DISCHARGE
  - Topographic lows (valleys)
  - Shallow lineament trends (valleys)
  - Water wells (alluvial valleys)

PRESSURE IS REQUIRED TO DISPLACE WATER IN A WELL



GAS PRESSURE
BELOW
SEAL
INCREASES
CAP
RELEASED

FOLLOWED BY
FIZZING

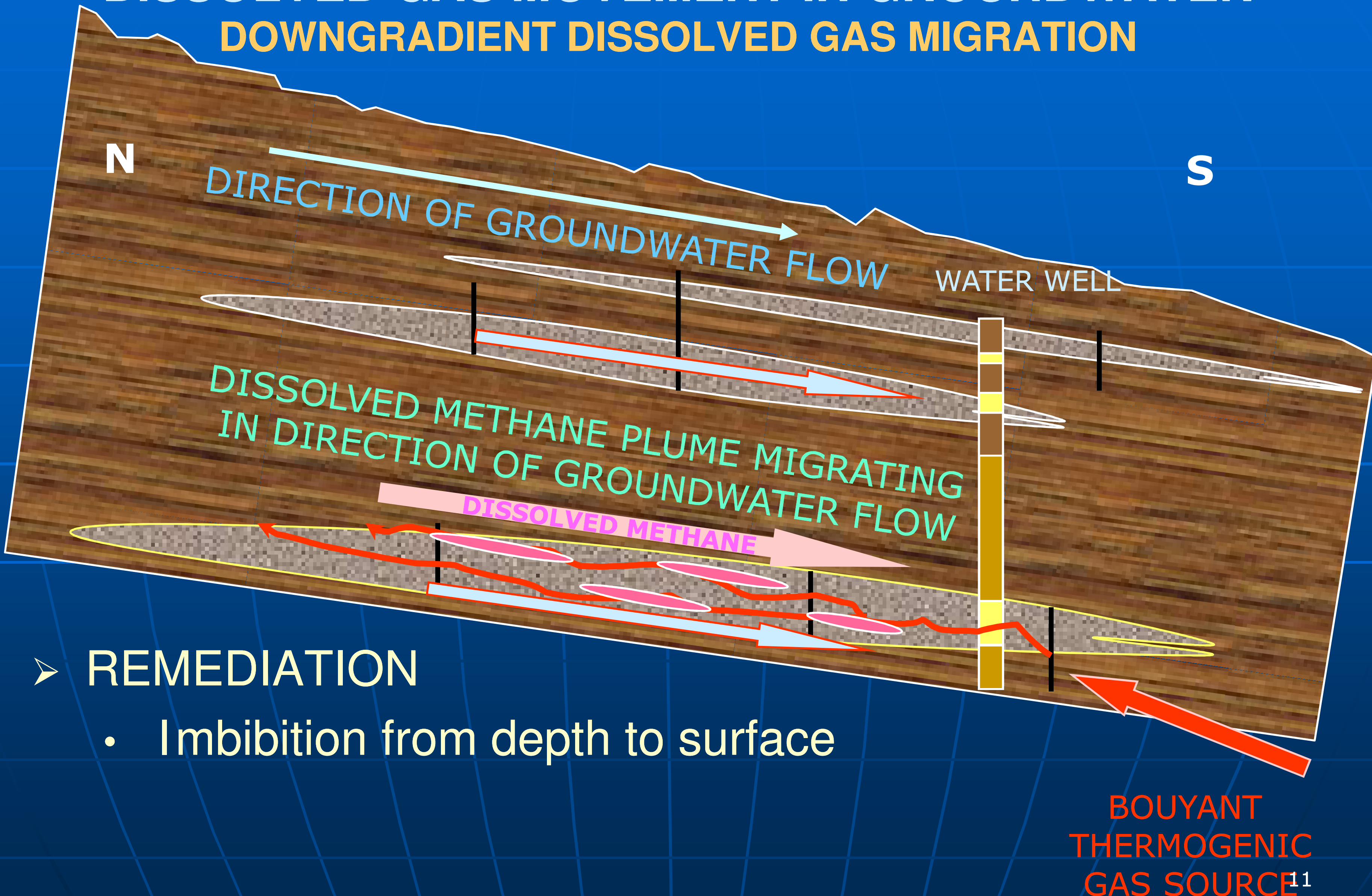
WATER PRESSURE
AT BASE OF
175' WATER COLUMN

75.15 psi
+
11.9 psi ATMOSPHERIC @ 5800'
= 87 PSI minimum pressure

**MINIMUM
GAS ENTRY
PRESSURE
INTO WELL BORE
>87 psi**

DISSOLVED GAS MOVEMENT IN GROUNDWATER

DOWNGRADIENT DISSOLVED GAS MIGRATION

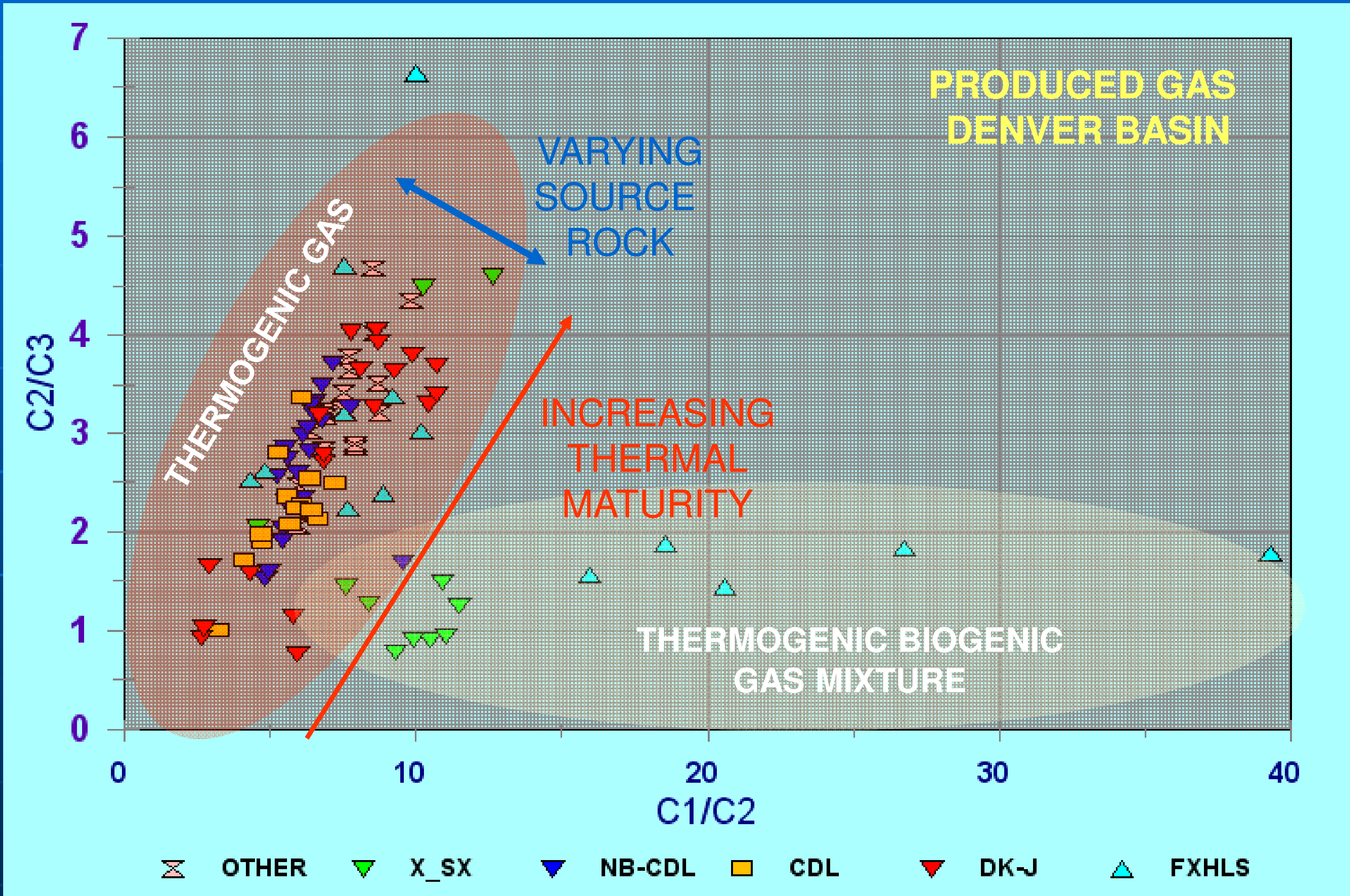


- REMEDIATION
  - Imbibition from depth to surface

WHEN ARE GAS SOURCE SIGNATURES UNIQUE?

- Production gases always vary from well to well
  - Source rock type
  - Source rock maturity
  - Migration and migration fractionation
  - Reservoir compartmentation (mixed @ 100,000 yrs)
- Source to discharge composition constant when:
  - No migration fractionation
  - No mixing with other sources
    - Biogenic
    - Thermogenic (historic releases)

GAS RATIOS ARE UNIQUE



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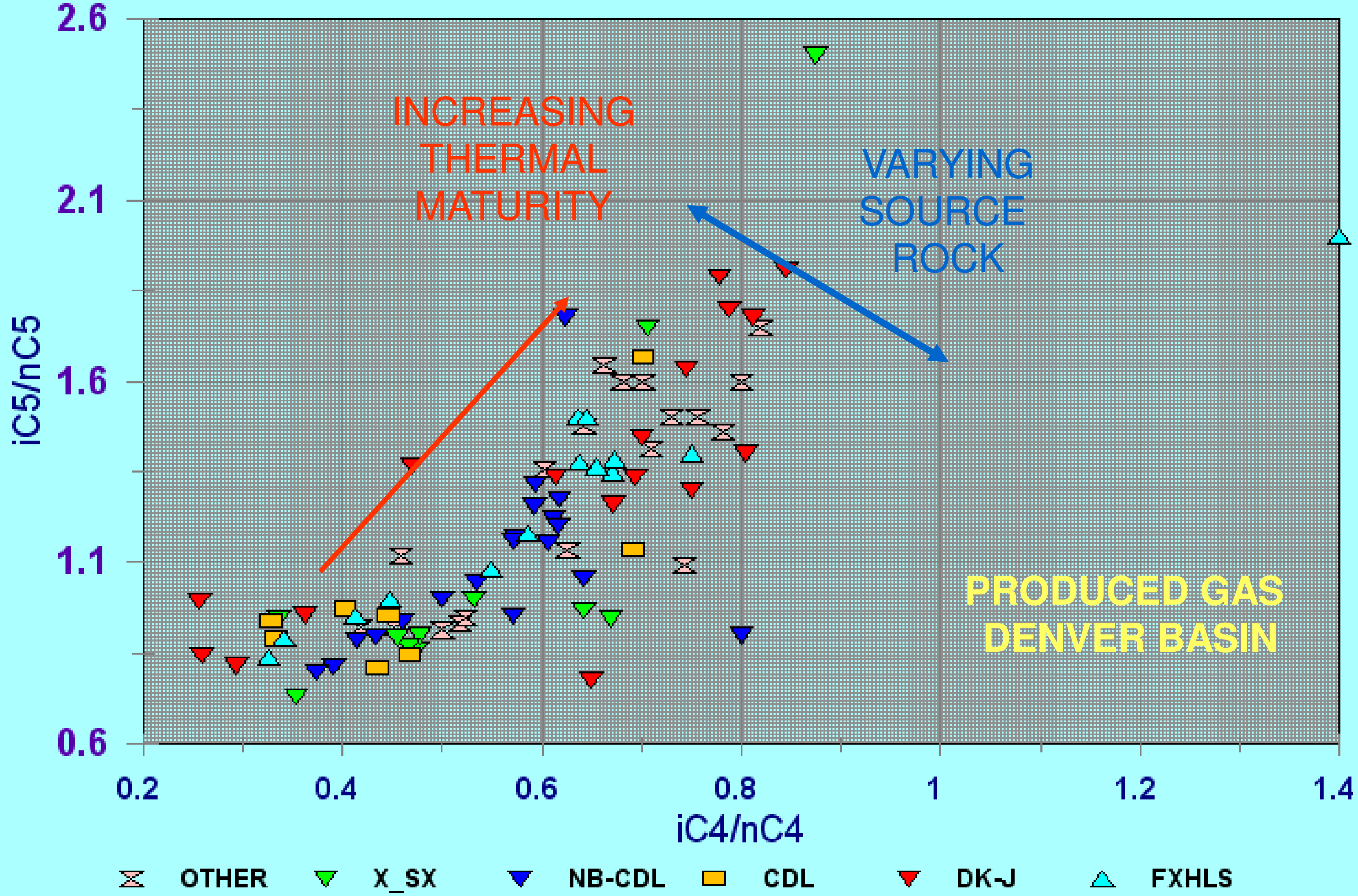
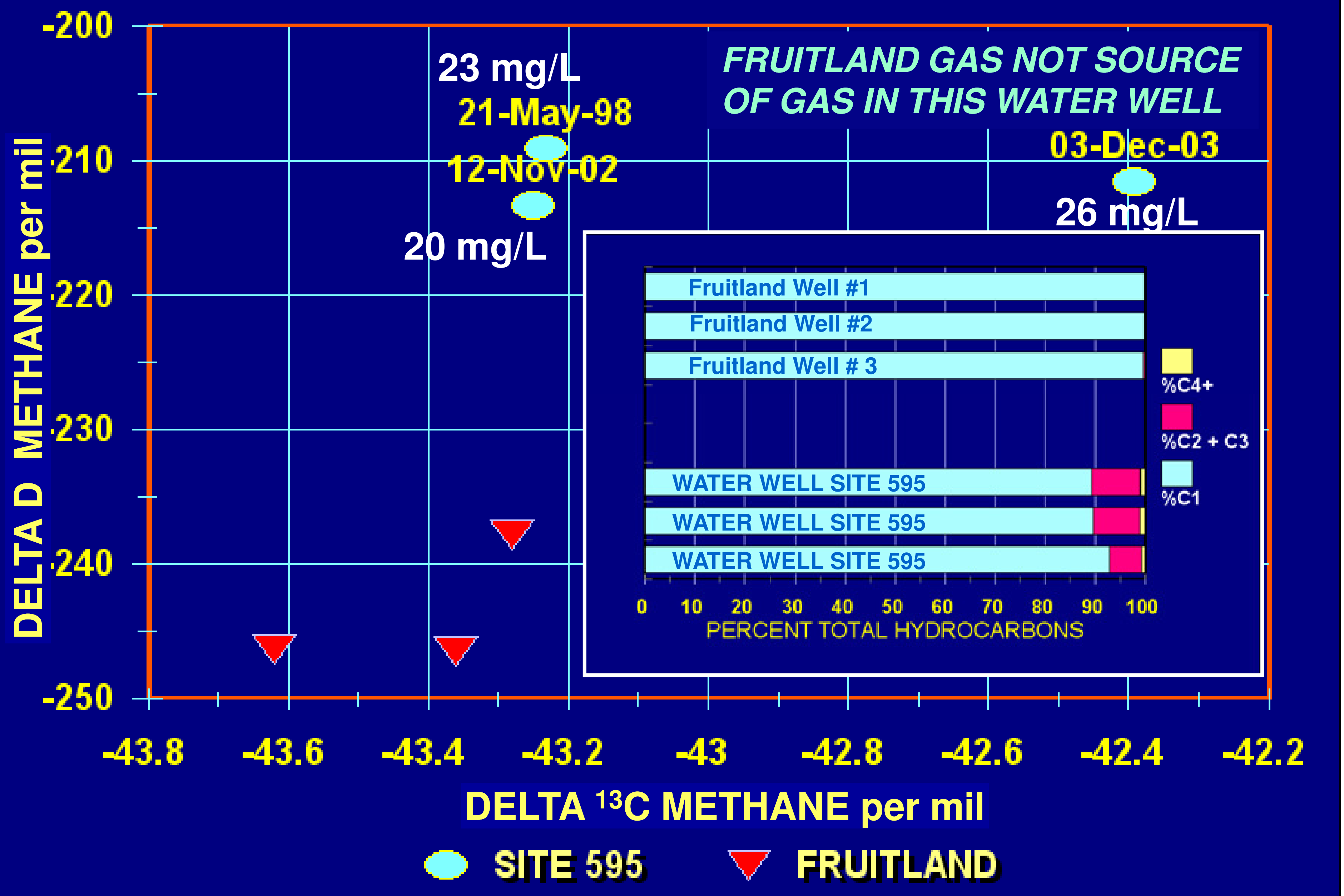
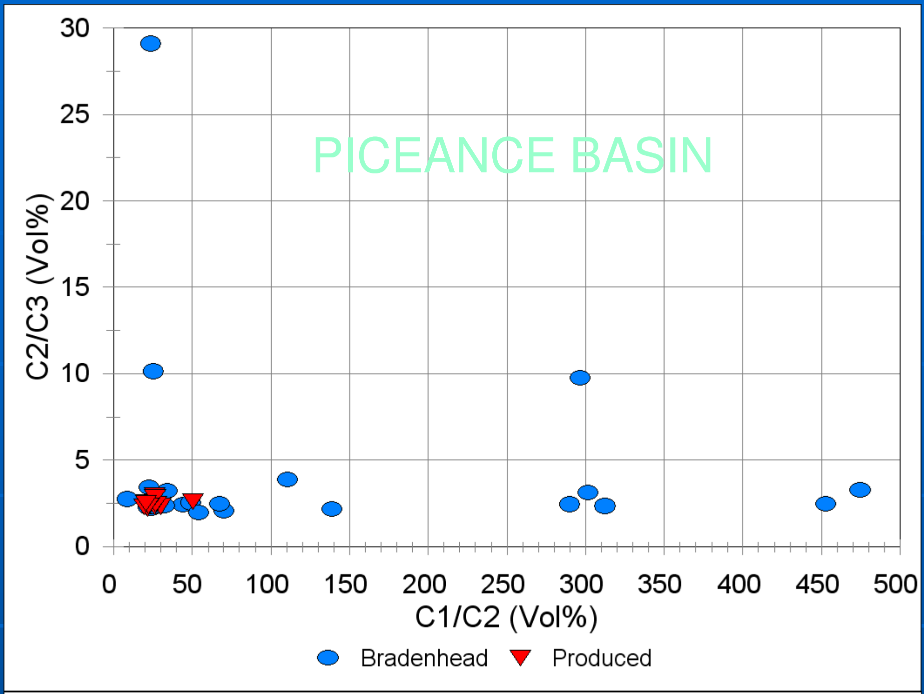
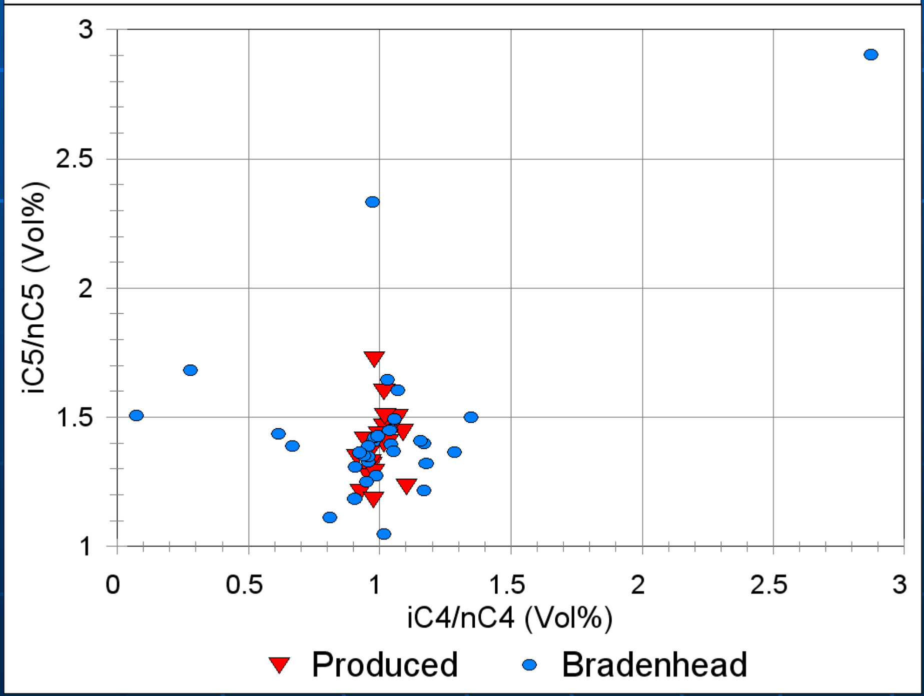


SOMETIMES PRESENCE OR ABSENCE SUFFICIENT TO ELIMINATE POTENTIAL SOURCES

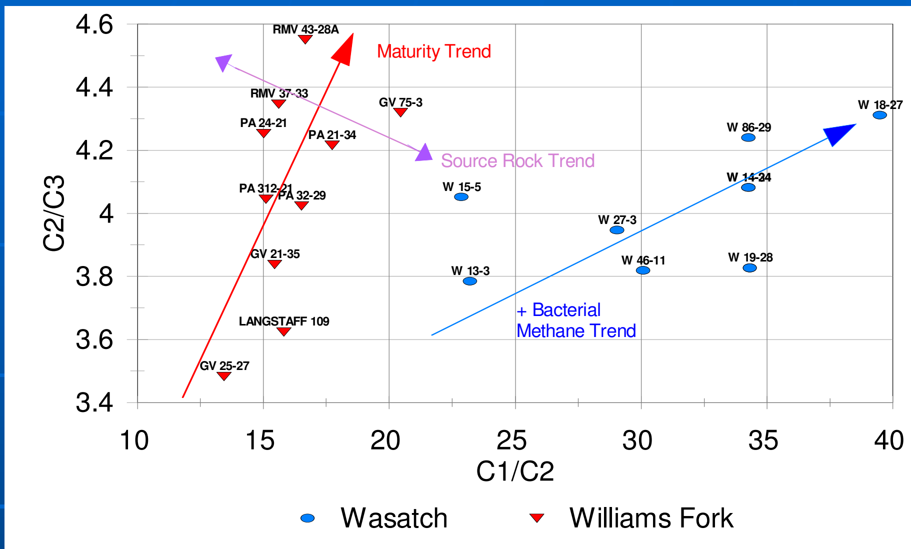


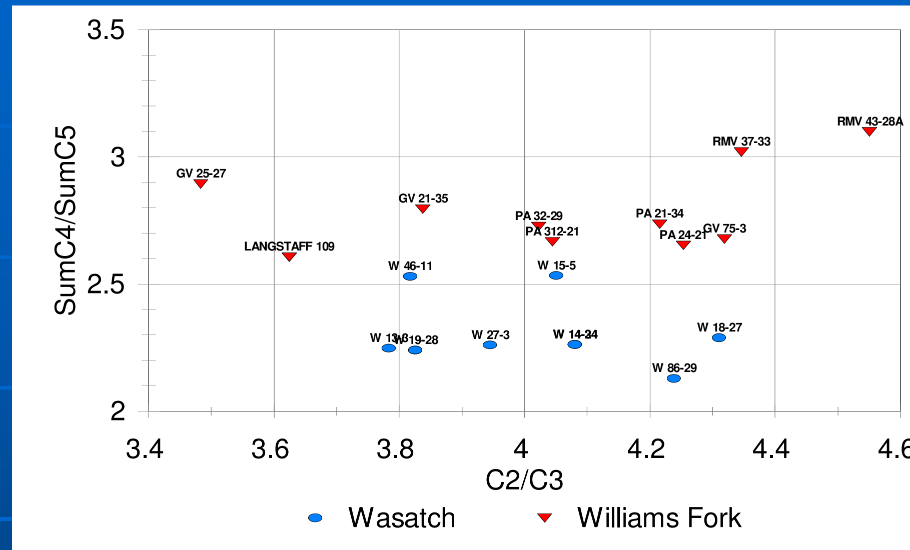


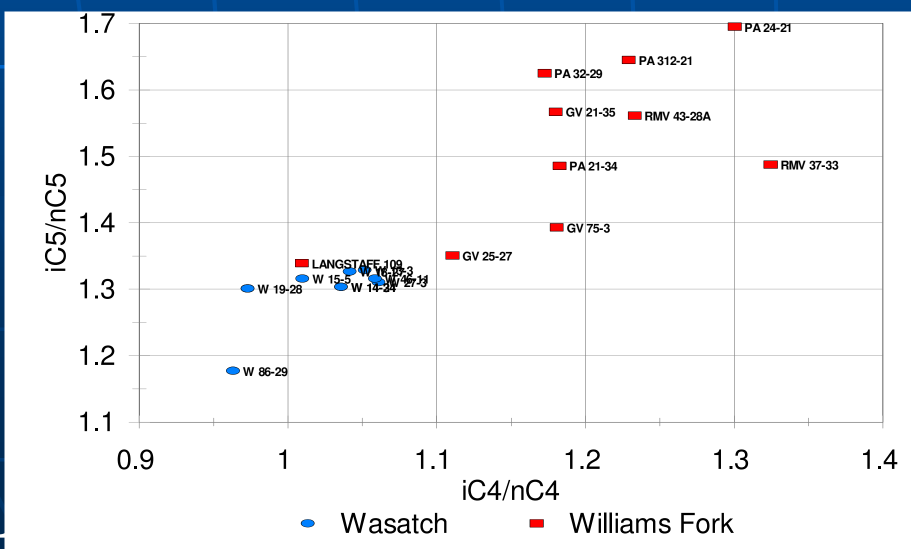


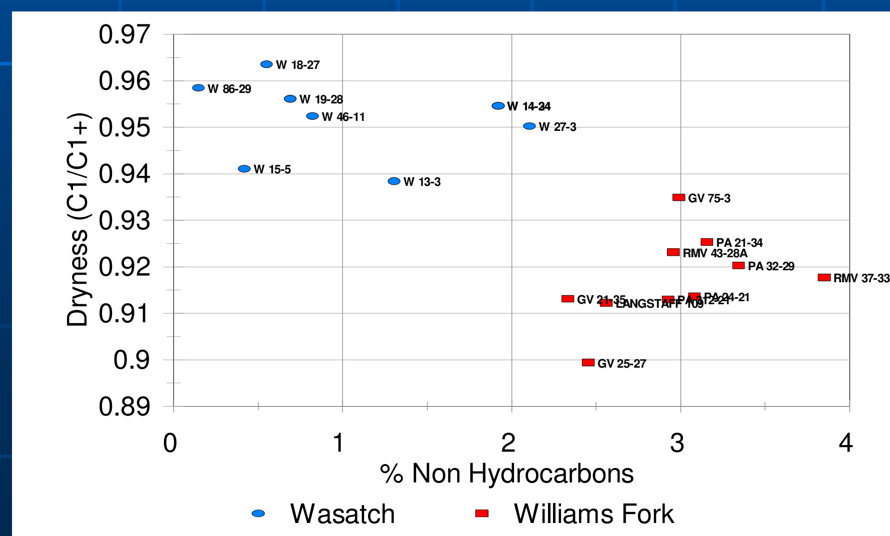
CASING HEAD AND PRODUCTION GAS COMPOSITION NOT NECESSARILY THE SAME

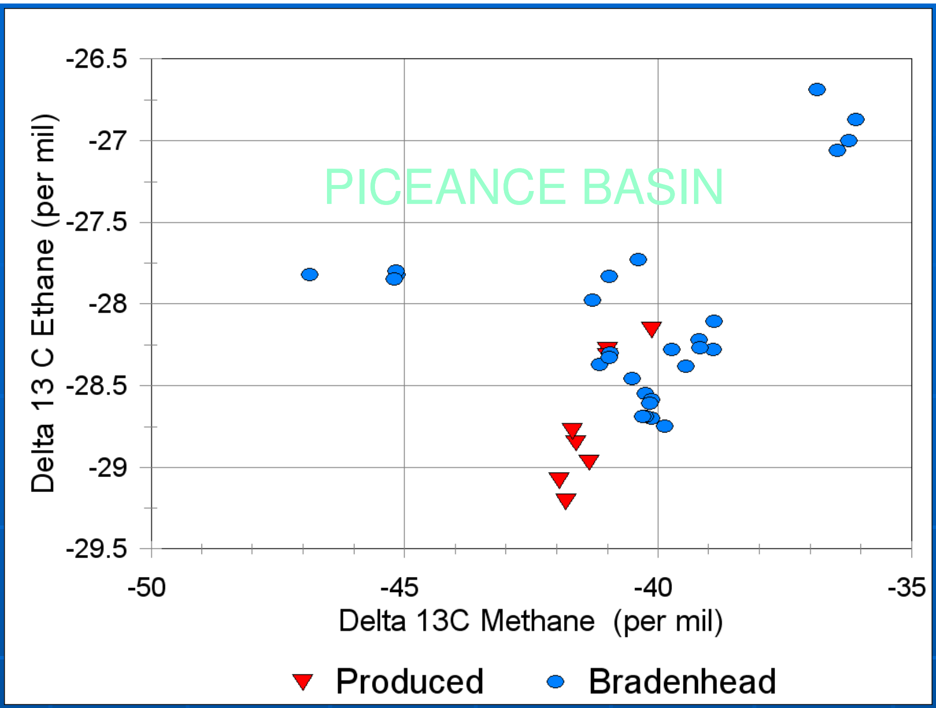
SHALLOW COMMERCIAL GAS SANDS IN RULISON FIELD DIFFER FROM UNDERLYING WILLIAMS FORK

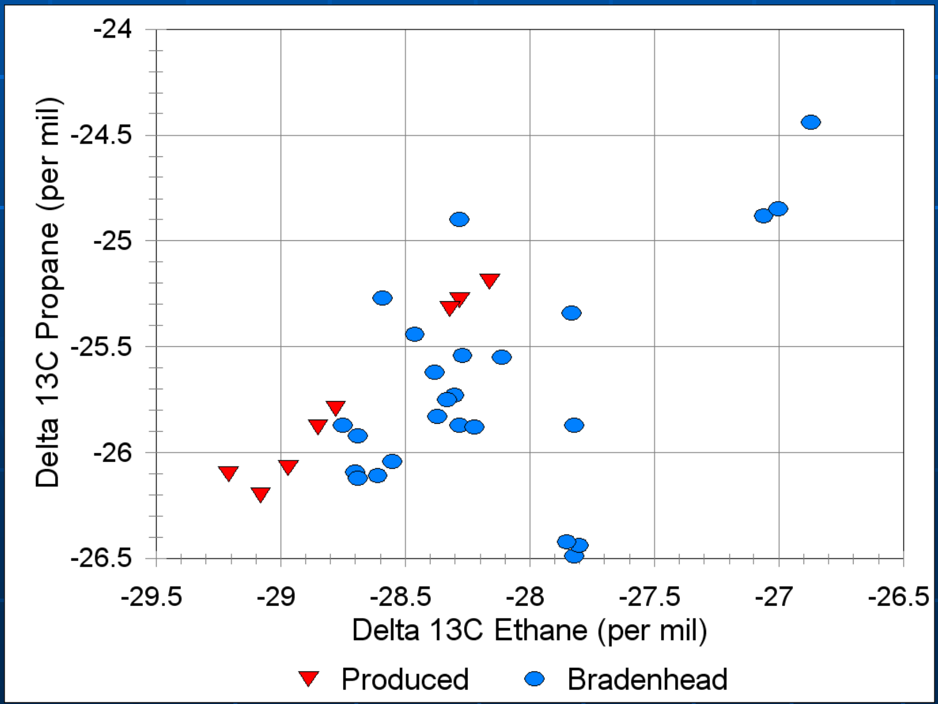












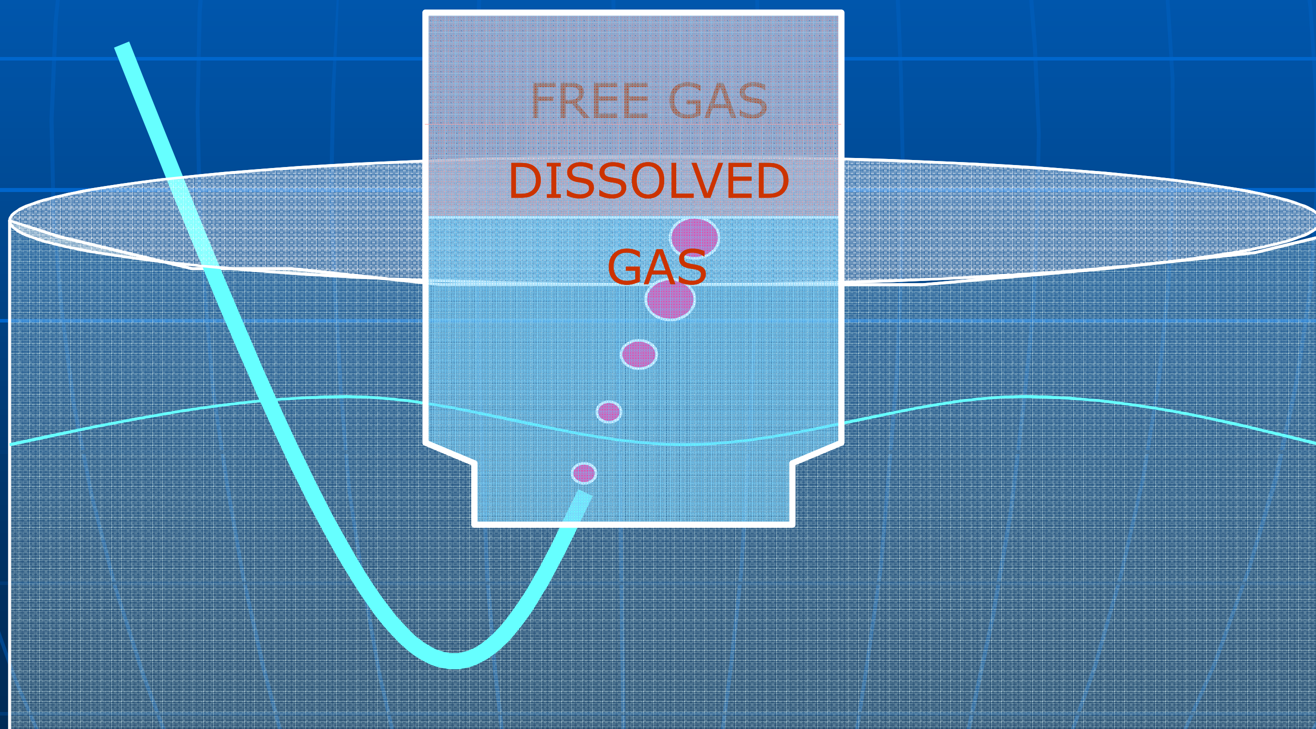
CASING HEAD AND PRODUCTION GAS STABLE ISOTOPIC COMPOSITION NOT NECESSARILY THE SAME

IMPLICATIONS?

WATER/MONITOR WELL SAMPLES FOR COLLECTING NATURAL GAS ARE OF TWO TYPES

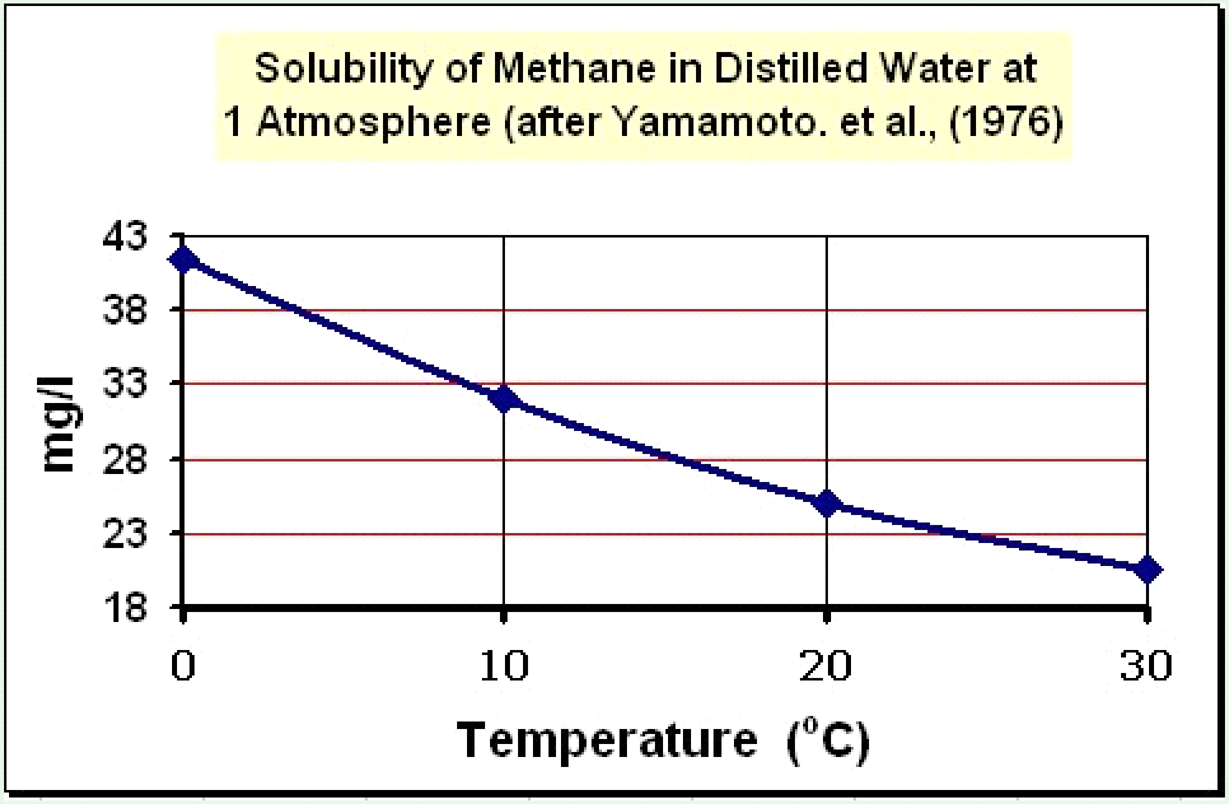
FREE GAS COLLECTED

DISSOLVED GAS

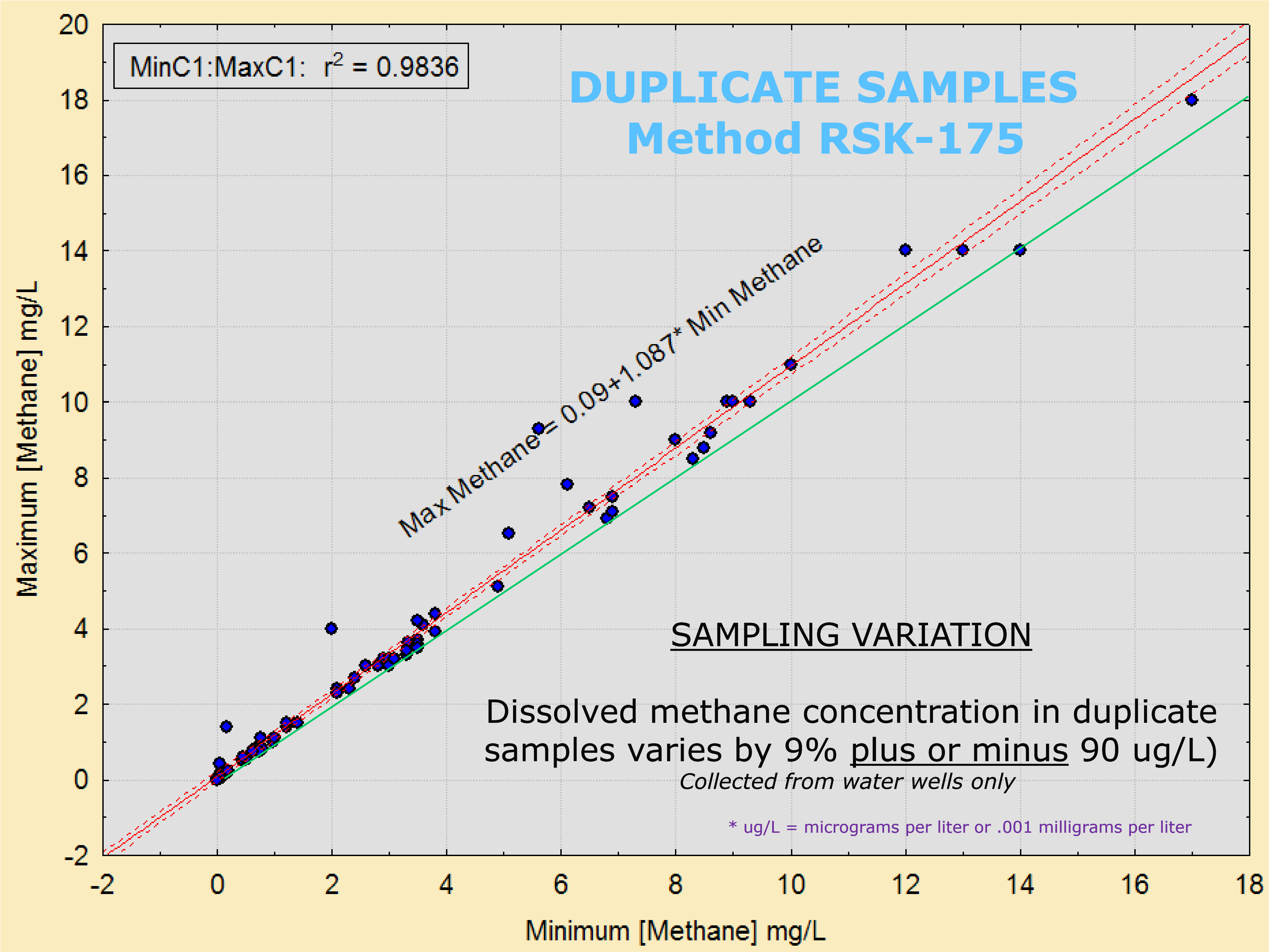


ADDRESSING DISSOLVED GAS CONCENTRATION

METHANE SOLUBILITY IS LOW

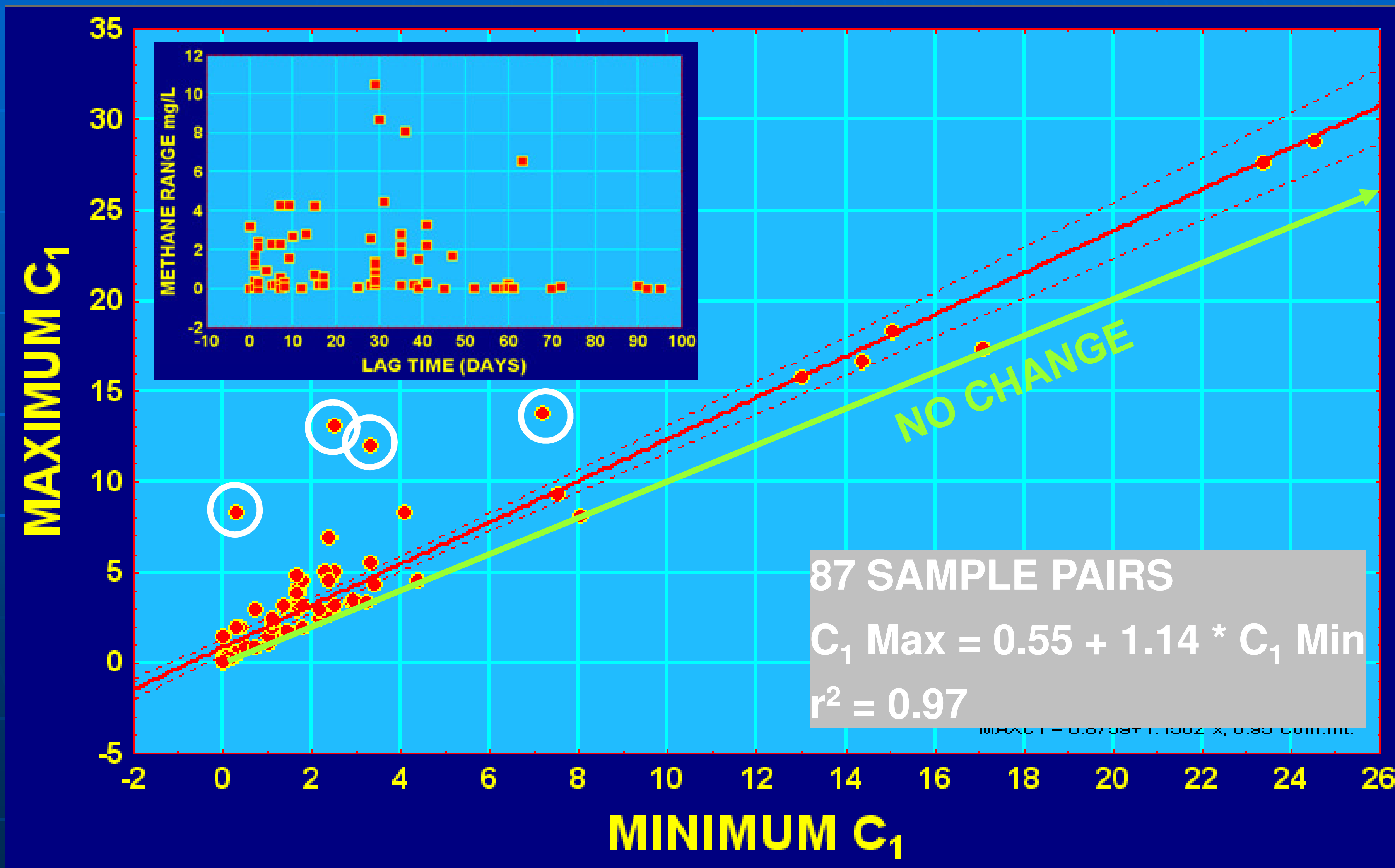


Reference: *Yamamoto, S Alcauskas, J B and Crozier, T E (1976). Solubility of methane in distilled water and seawater. Journal of Chemical and Engineering Data, 21, (1), 78-80.*



DUPLICATE SAMPLES
Method RSK-175
MinC1:MaxC1: r2 = 0.9836
Max Methane = 0.09+1.087* Min Methane
SAMPLING VARIATION
Dissolved methane concentration in duplicate samples varies by 9% plus or minus 90 ug/L)
Collected from water wells only
* ug/L = micrograms per liter or .001 milligrams per liter
Maximum [Methane] mg/L
Minimum [Methane] mg/L
-2
0
2
4
6
8
10
12
14
16
18
20

SHORT TERM VARIABILTY ADDRESSED USING MULTIPLE SAMPLES FROM SINGLE SITES



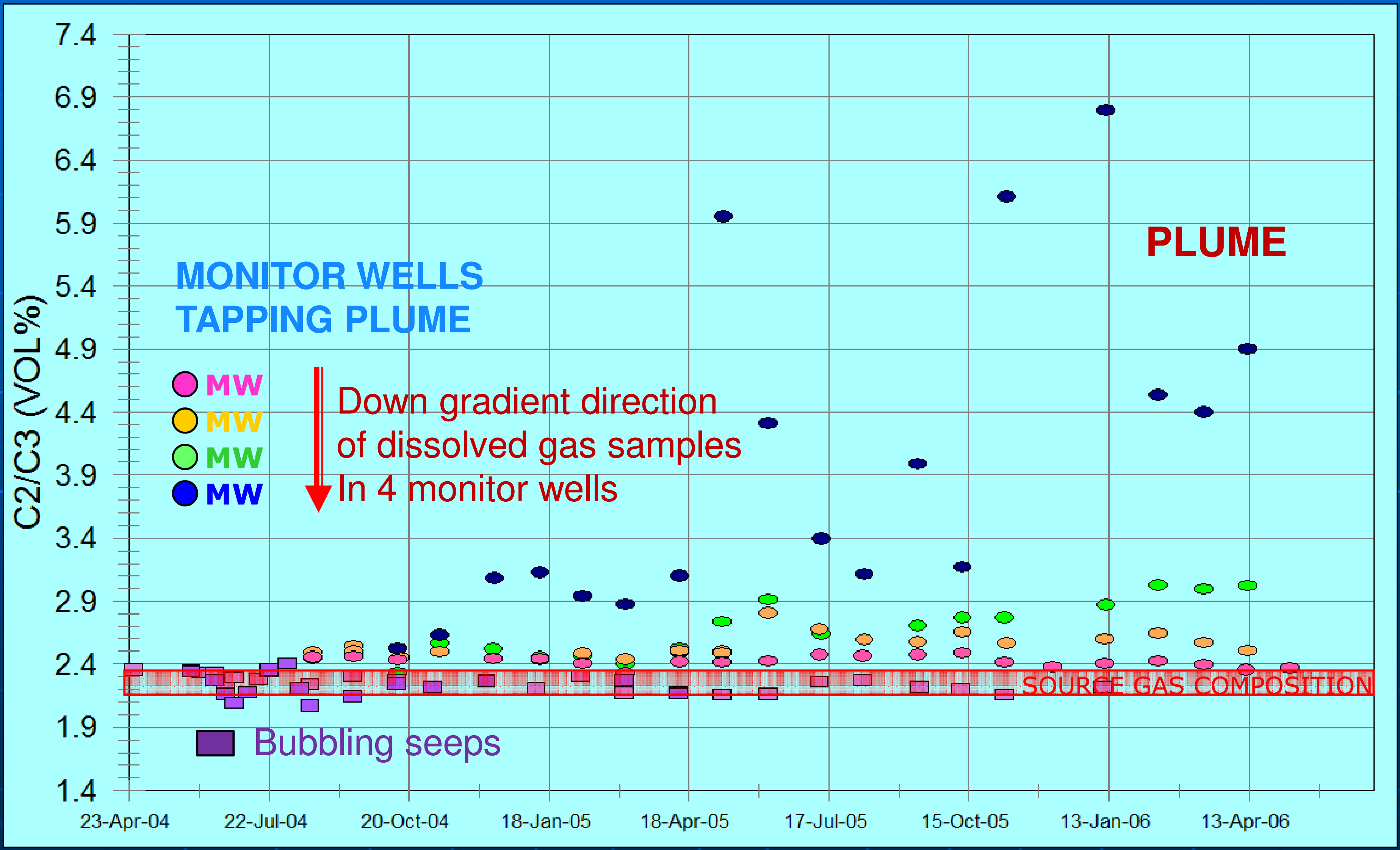
DISSOLVED GAS COMPOSITION AND HENRY'S LAW

- Dissolved gas phase composition obeys Henry's Law under equilibrium solution & exsolution
  - Partial pressure controls relative solubility of source gas in dissolved phase
  - Gas exsolved in equilibrium with a headspace will reflect relative concentration of free phase source gas
  - Therefore gas ratios are useful for identifying source gases in samples with dissolved gas
- Free gas phase
  - Discharge of free gas driven by pressure gradient maintains chemical and isotopic composition of source gas
- Stable isotopes not affected by solution/exsolution

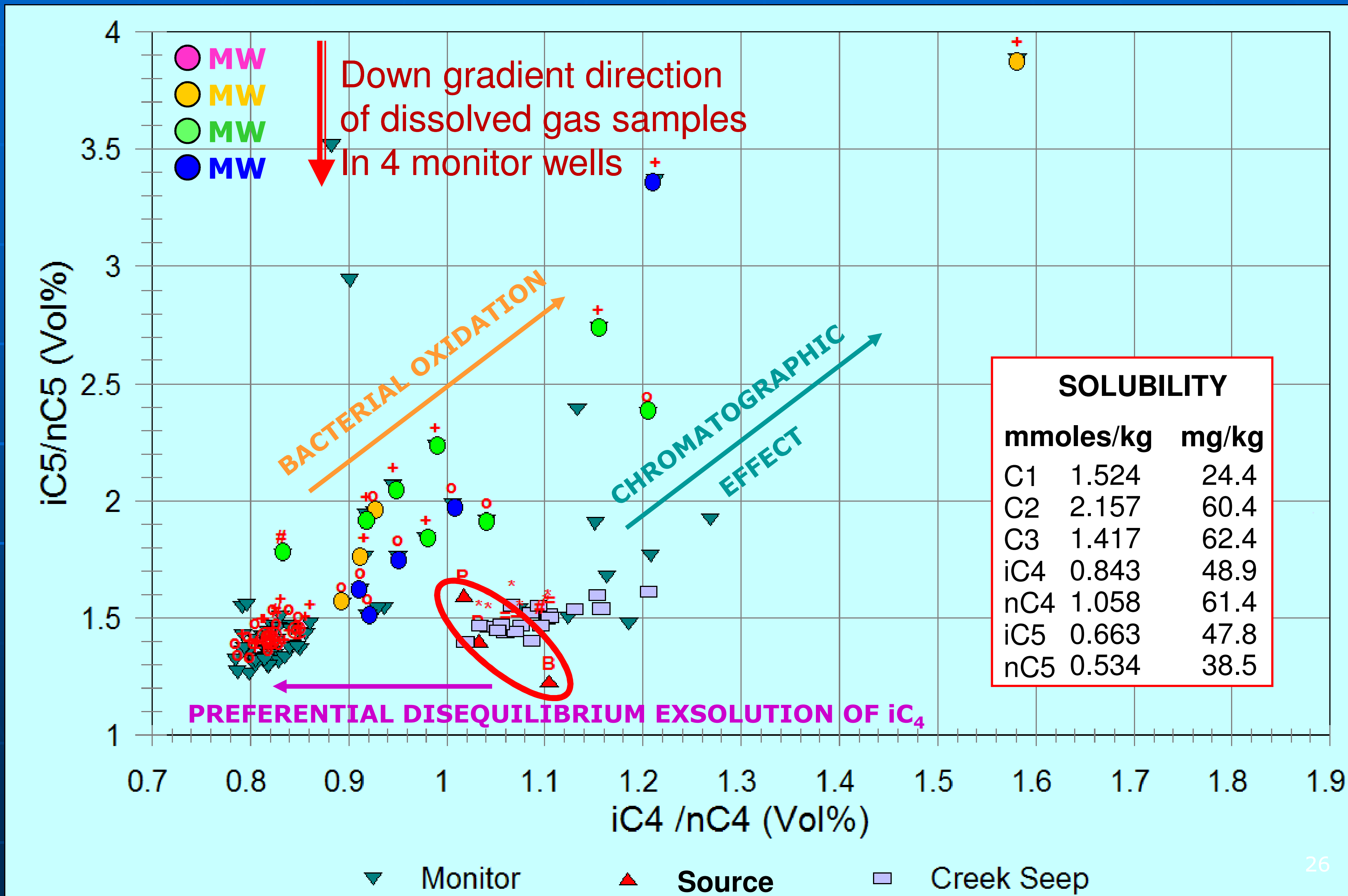
USEFUL RATIOS FOR CROSS PLOTS

- $[C_1/\Sigma C_1+]$ or $[C_1/C_2]$ or $[C_1/C_2+C_3]$ or $[C_2+/\Sigma C_1+]$
  - Susceptible to biogenic methane mixing
- C_2/C_3 or $C_2/\Sigma C_2+$
- $C_3/\Sigma C_3+$
- ΣC_4 isomers/ ΣC_5 isomers
- Isomer ratios
  - iC_4/nC_4
  - iC_5/nC_5

EXAMPLE GAS RATIO IN FREE GAS PHASE VS. DISSOLVED PHASE: SPATIAL/TEMPORAL CHANGES



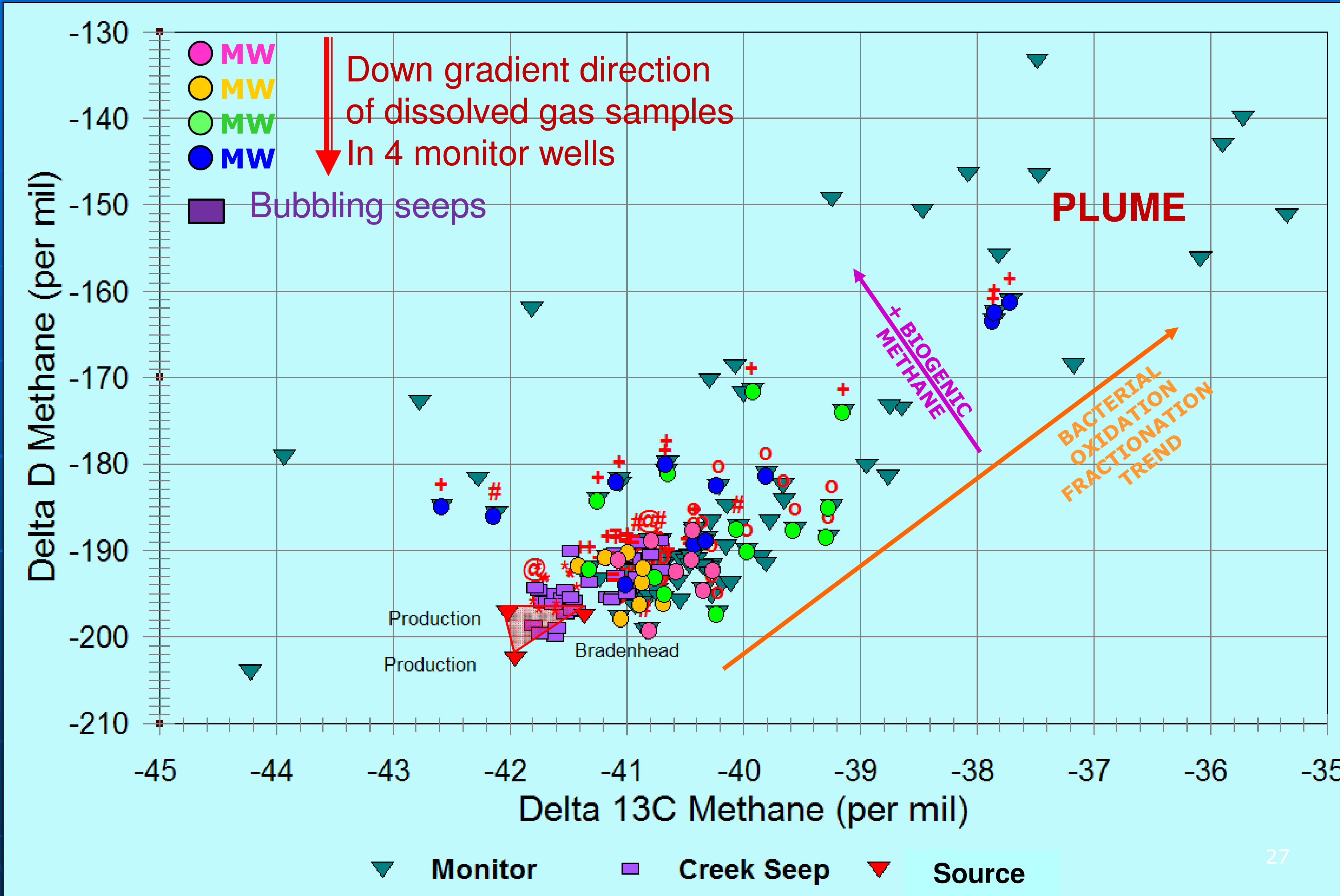
FREE GAS PHASE vs. DISSOLVED GAS PHASE COMPOSITION : BUTANE ISOMERS OFFSET



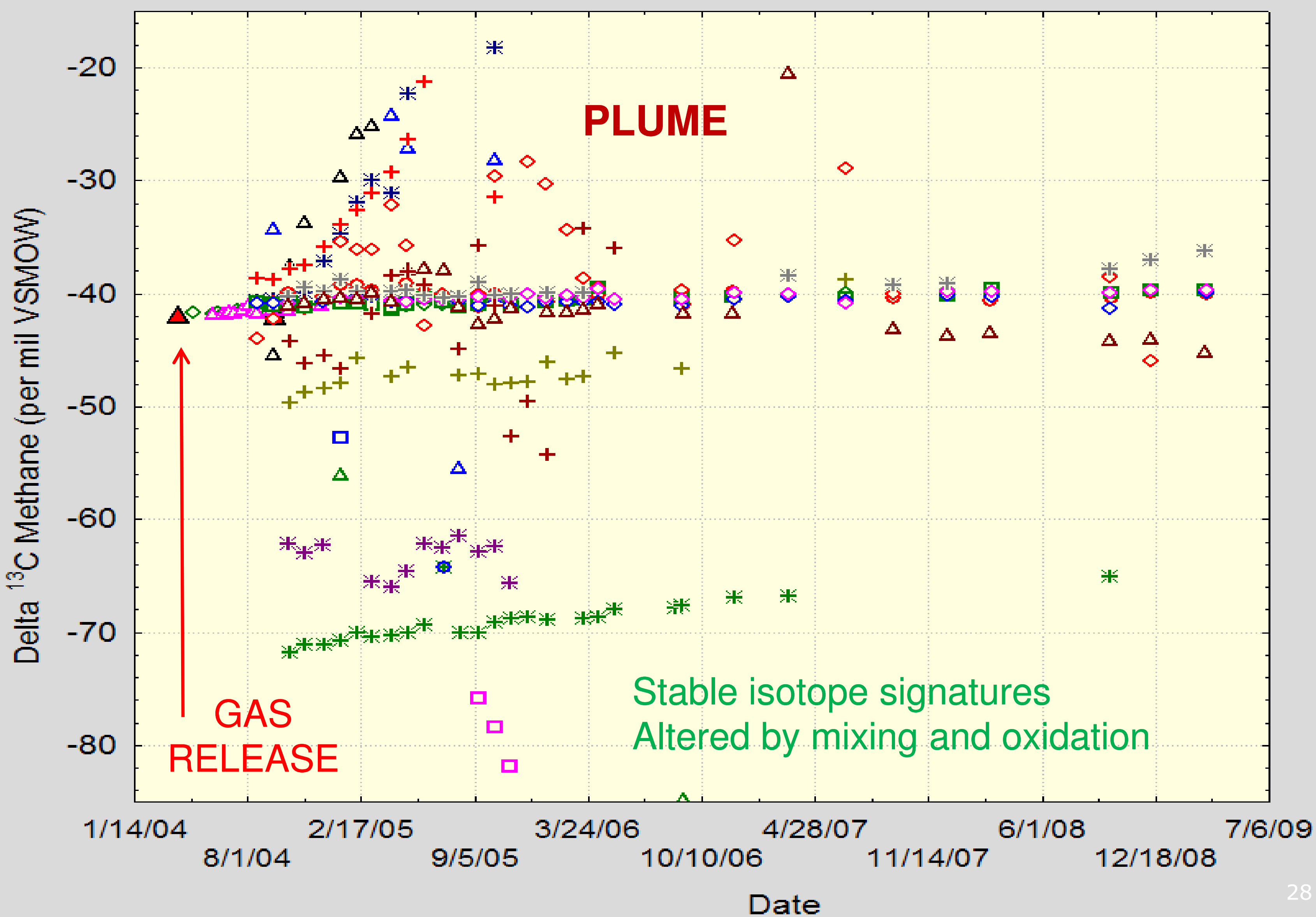
SOLUBILITY

	mmoles/kg	mg/kg
C1	1.524	24.4
C2	2.157	60.4
C3	1.417	62.4
iC4	0.843	48.9
nC4	1.058	61.4
iC5	0.663	47.8
nC5	0.534	38.5

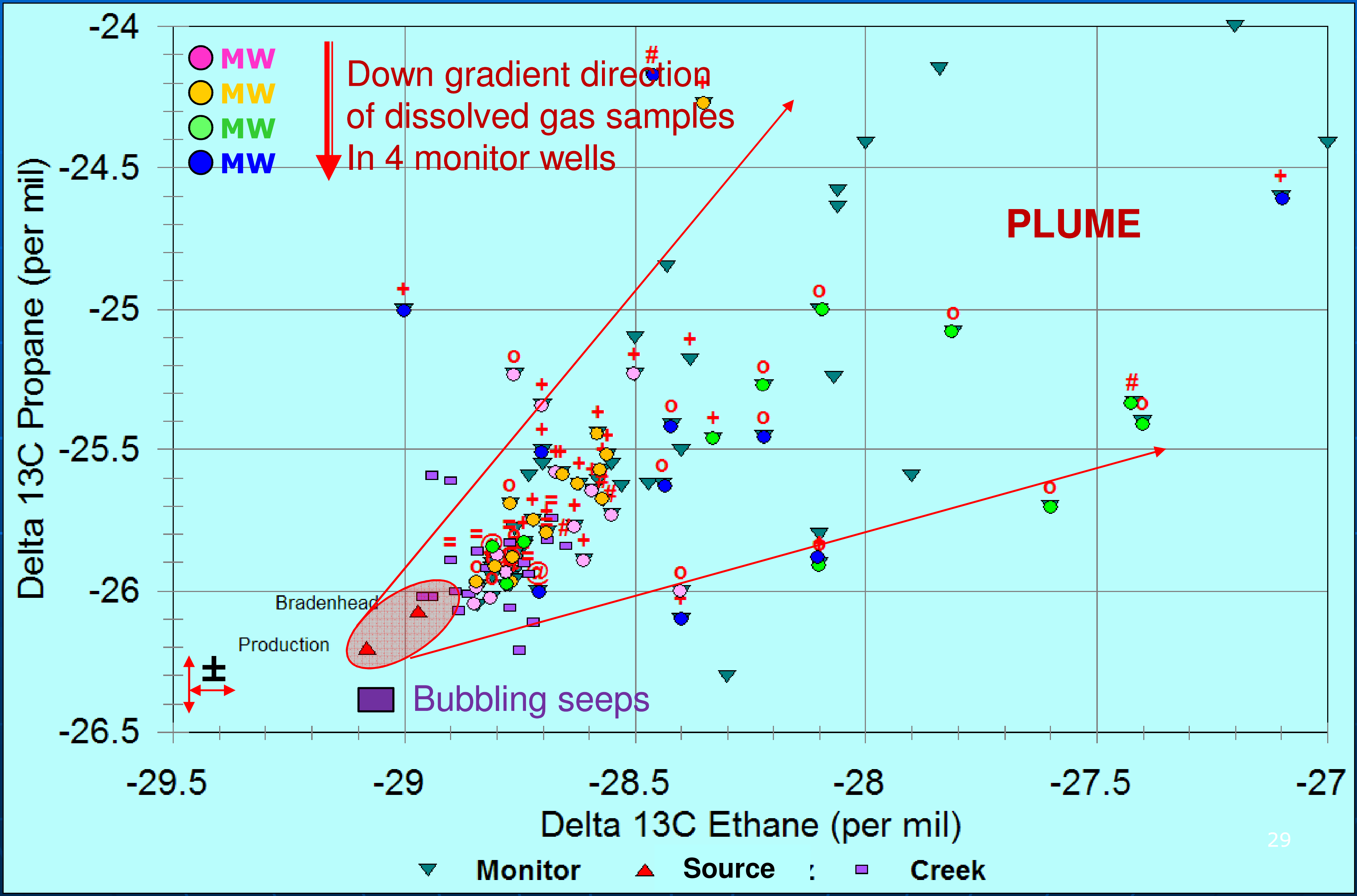
STABLE ISOTOPES NOT FRACTIONATED



STABLE ISOTOPE VARIABILITY

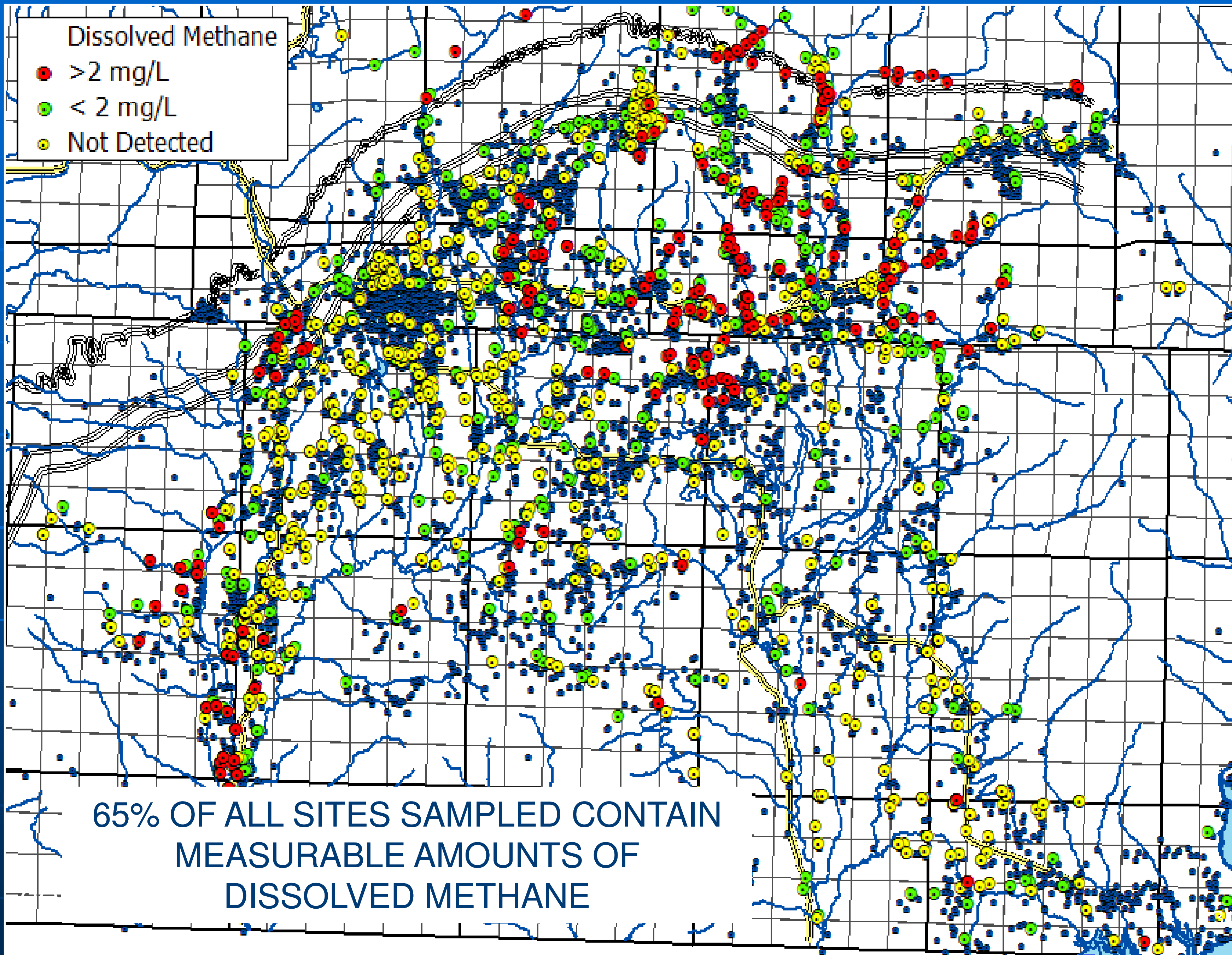


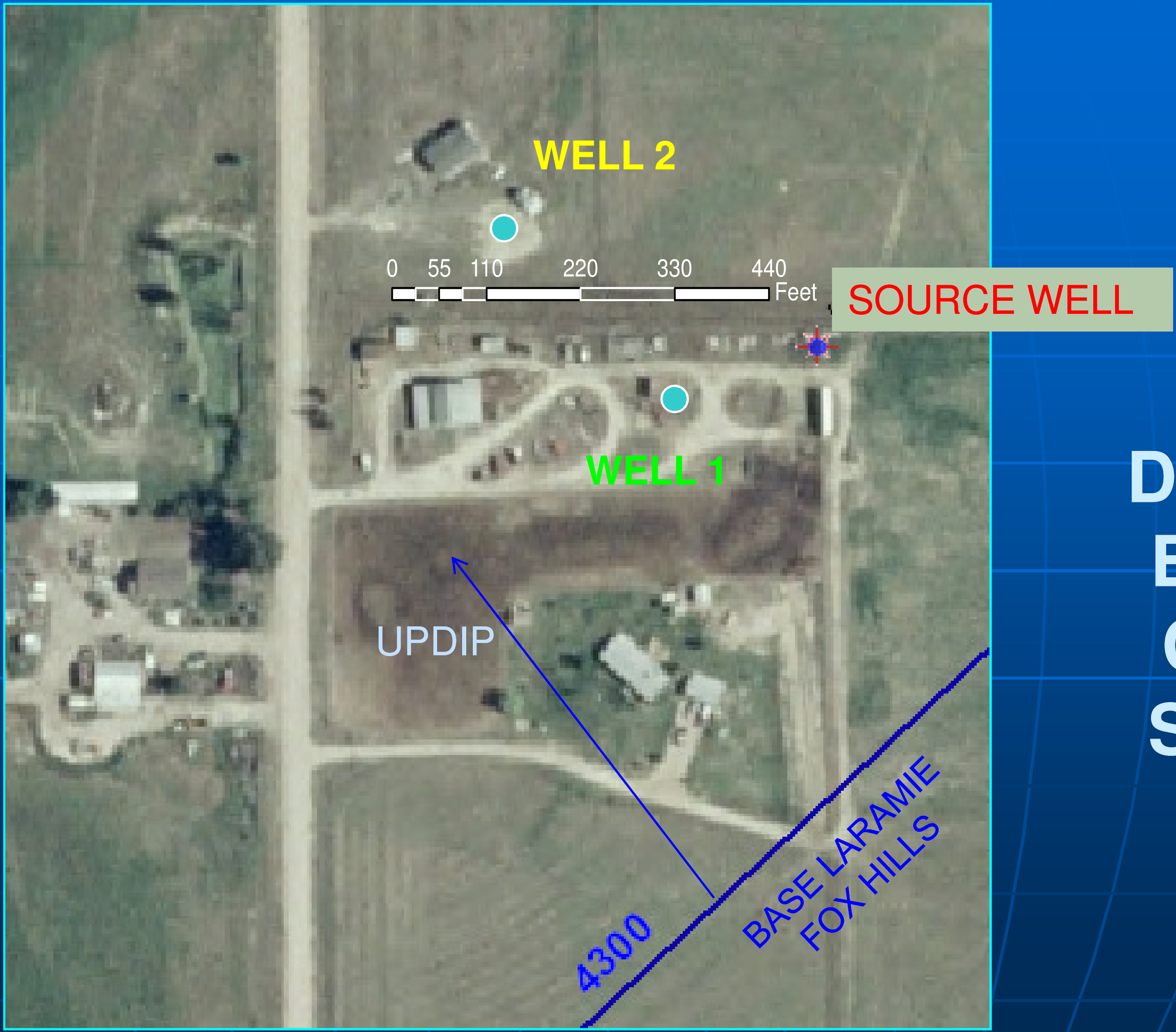
STABLE ISOTOPE SCATTER INCREASES WITH TIME AND LOCATION DOWN GRADIENT



MIXED GAS SOURCES

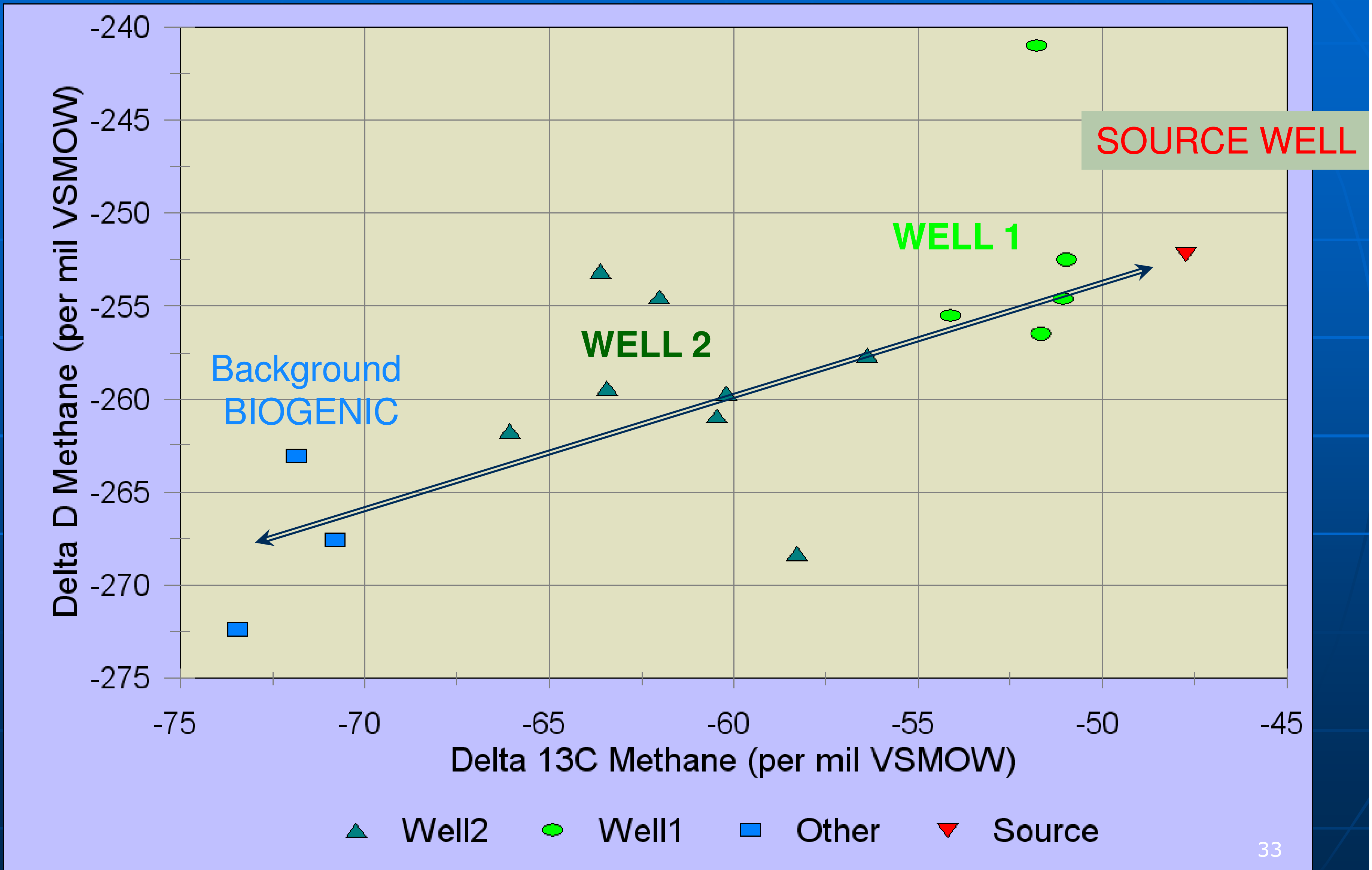
- Biogenic methane ubiquitous in bedrock aquifers
  - >50 water wells with detectable dissolved methane
  - CO_2 reduction dominant reaction pathway
- Mixing affects gas ratios using methane
  - $[C_1/ \Sigma C_1+]$ or $[C_1/C_2]$ or $[C_1/C_2+C_3]$ or $[C_2+/ \Sigma C_1+]$
- Mixing affects stable isotope ratios
  - $\delta^{13}C$, D Methane more negative
  - $\delta^{13}C$, D Ethane more negative


Dissolved Methane
>2 mg/L
< 2 mg/L
Not Detected
65% OF ALL SITES SAMPLED CONTAIN MEASURABLE AMOUNTS OF DISSOLVED METHANE



Denver Basin Case Study

CASE STUDY DENVER BASIN



OXIDATION

- Oxidation gradients set up within invaded zone
  - Well bore air/water interface
  - Shallow alluvial sediment vadose/phreatic interface
  - Phreatic electron donor zones
- Oxidation mediated by bacteria
- Observed temporal effects are rate dependent
  - Rate of bacterially mediated oxidation vs. Rate of fresh gas delivery
    - Preferential consumption of higher homologs
    - Preferential consumption of straight chain isomers
    - Preferential consumption of light isotopes

BUBBLING HYDROCARBONS CAN ACCELERATE THE FOLLOWING NATURAL REACTIONS

SRBs

Sulfuric Acid (corrosion)

AIR

SO_4 + Organics -> Sulfide + CO_2

IRBs

Rust Stain
Poor Taste

Dissolved Iron

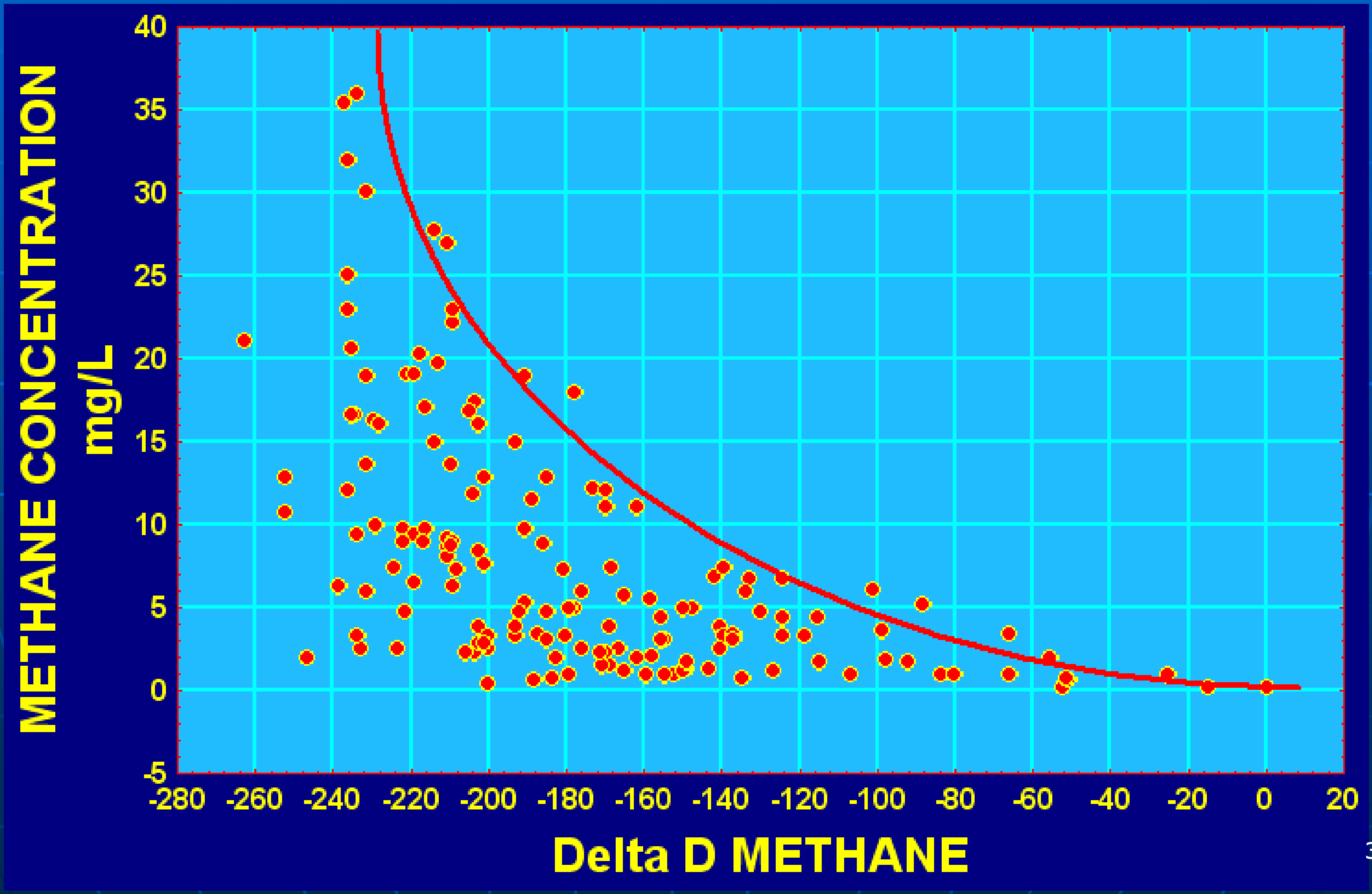
+ Hardness

Iron Sulfide
Gray Color
Poor Taste

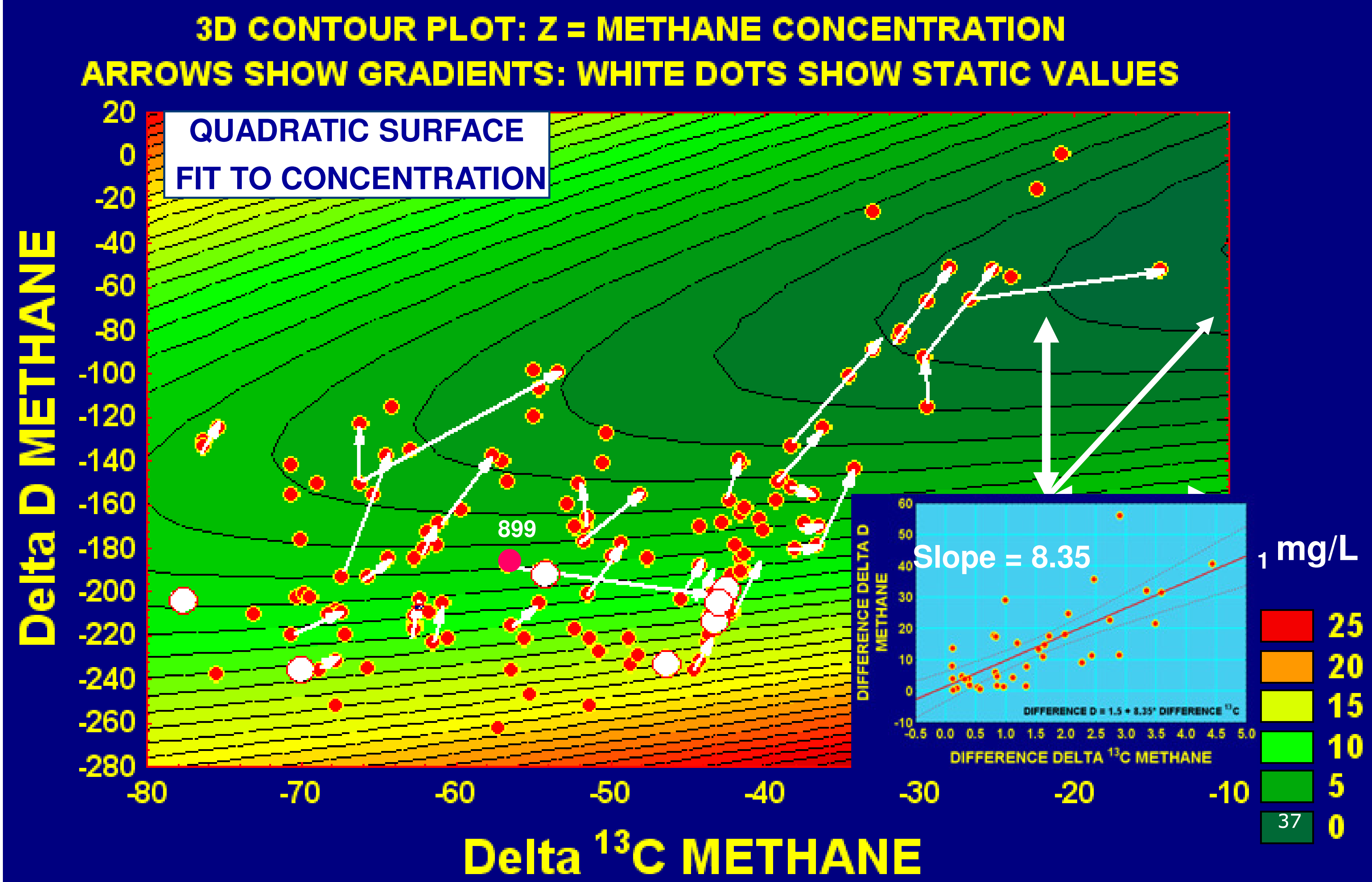
AIR

Mineral Scale
PRECIPITATION
Increasing SAR

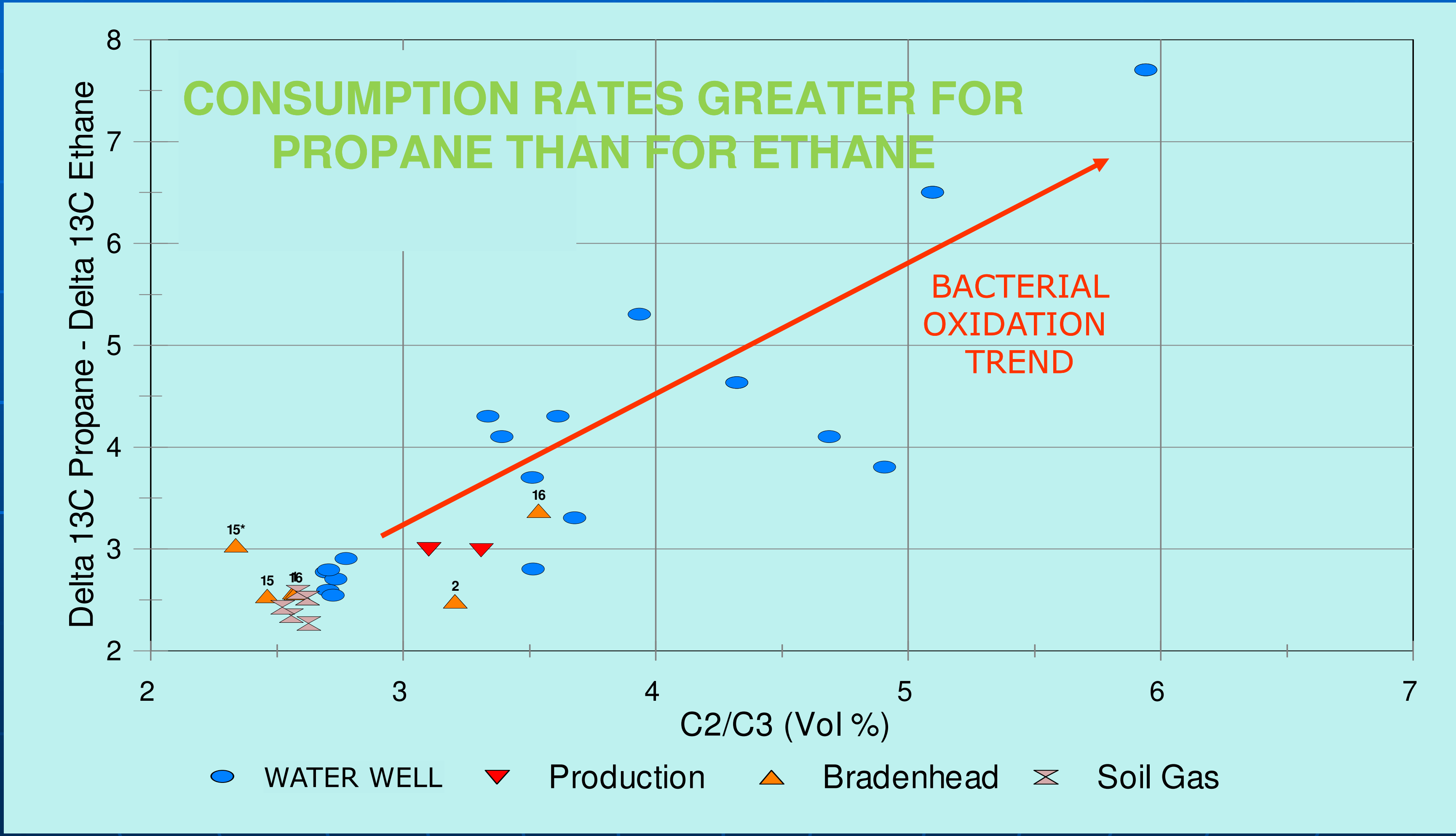
DECREASING CONCENTRATION CHARACTERISITIC OF HYDROCARBON OXIDATION e.g. SAN JUAN BASIN



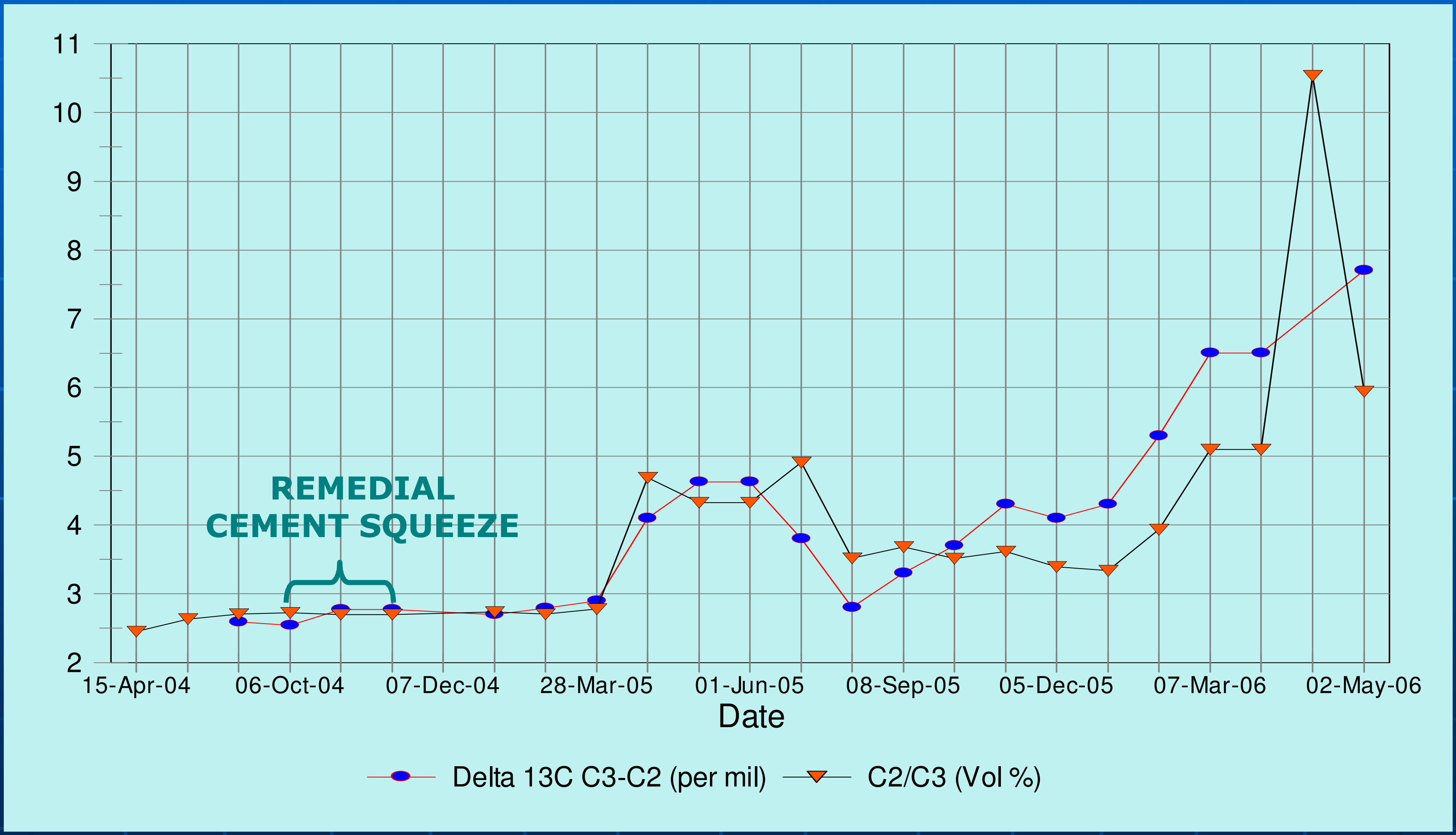
STABLE ISOTOPIC ENRICHMENT ASSOCIATED WITH BACTERIALLY-MEDIATED OXIDATION



MULTIPLE SAMPLES OF DISSOLVED GASES IN CONTAMINATED WATER WELL



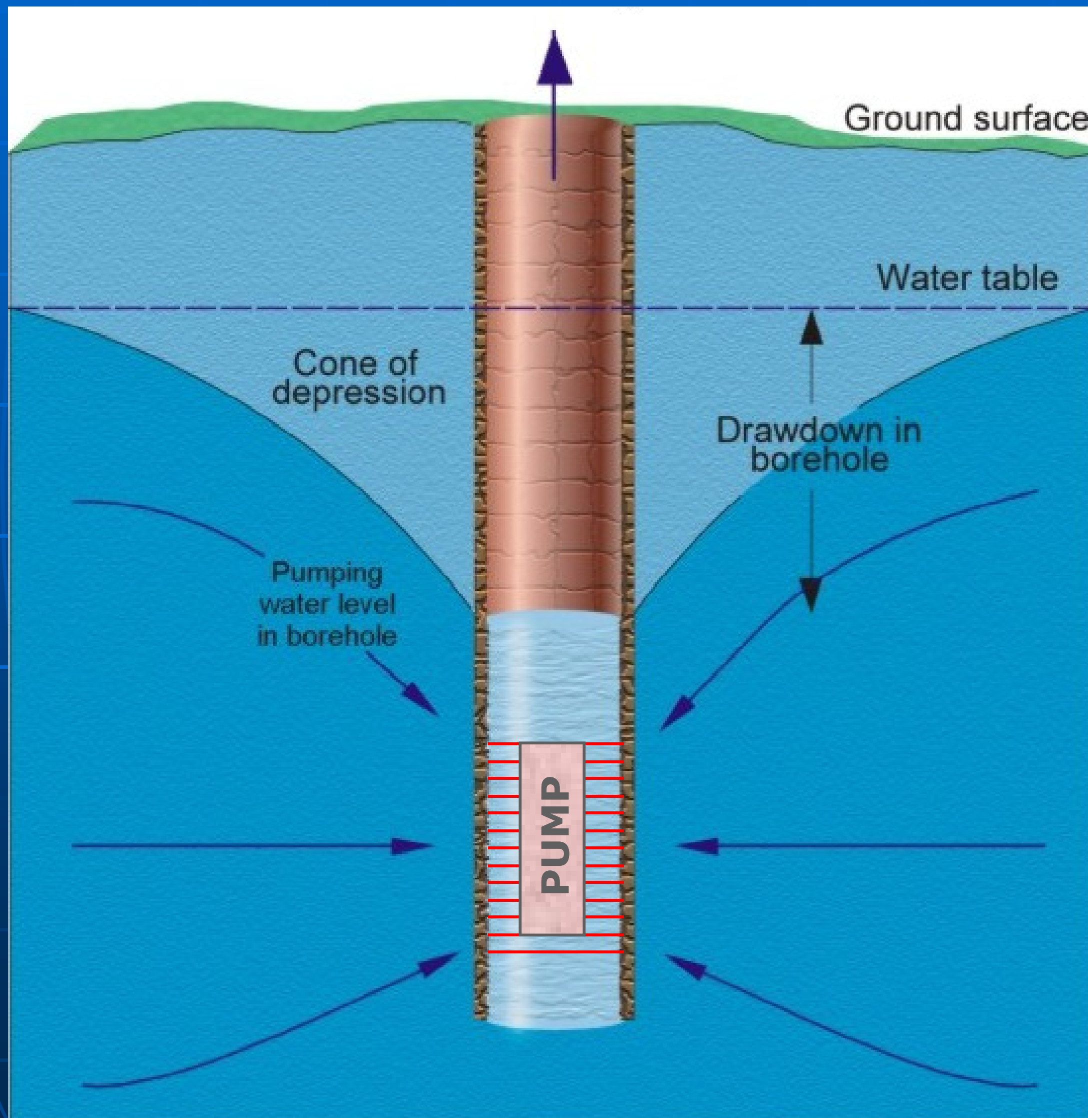
TEMPORAL CHANGES IN COMPOSTION AND STABLE ISOTOPES CORRELATED



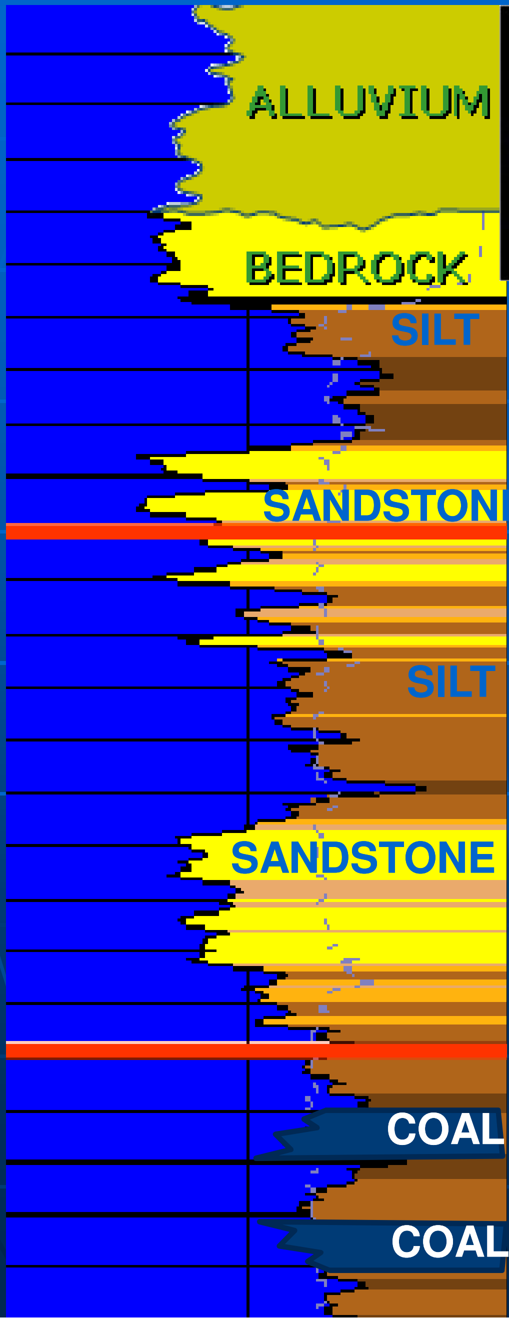
DILUTION

- Screened intervals do not define water sources
  - Mixing via open hole or gravel pack common
- Mixing affects oxidation rates and dilution
  - Address remediation efficiency/rates

PUMPING AND DRAWDOWN: WHERE DOES THE WATER COME FROM?



PRINCIPAL COMPONENTS OF GROUNDWATER IN ROCKIES



LIME : CALCIUM AND MAGNESIUM BICARBONATE

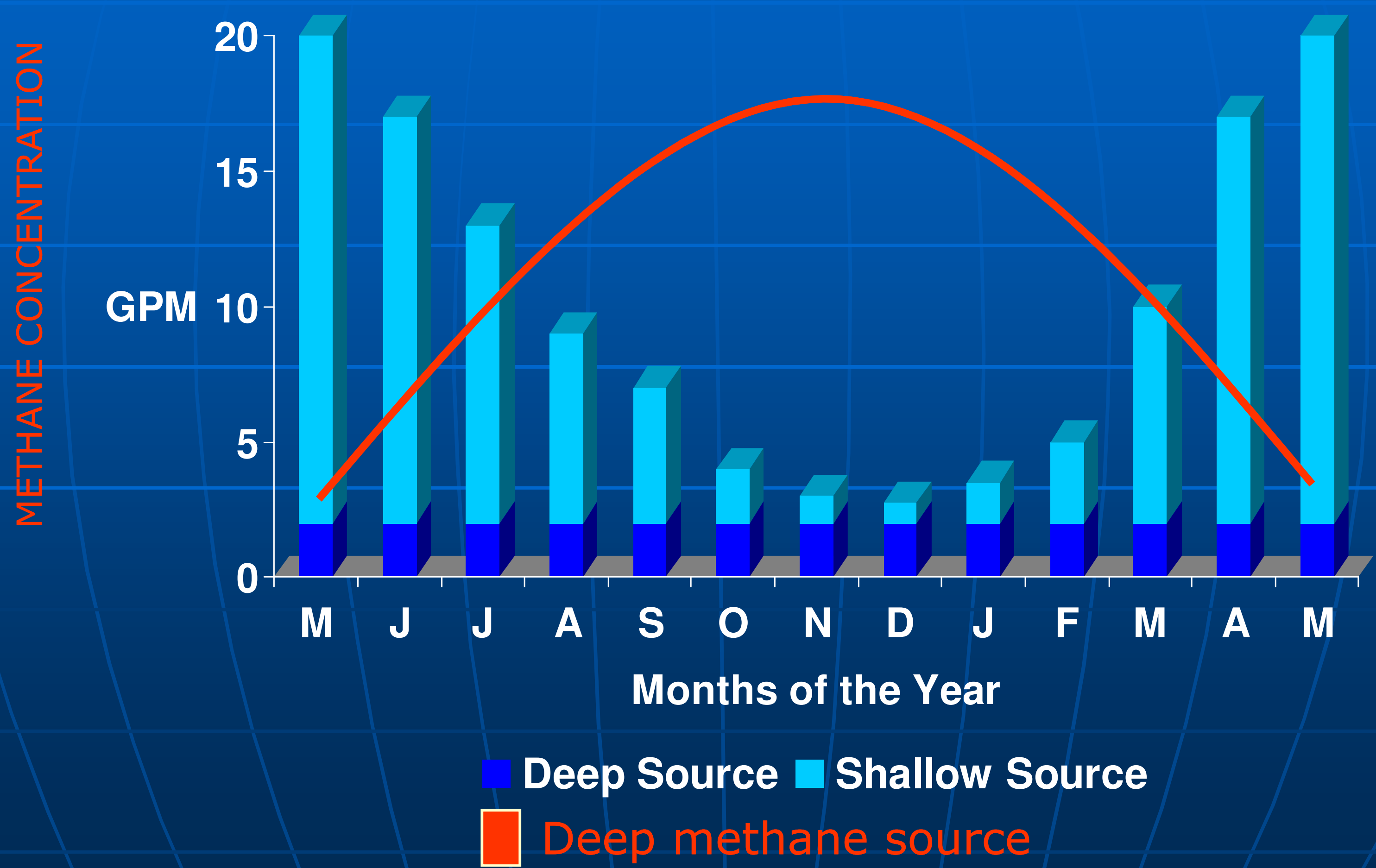
THERNARDITE – SODIUM SULFATE

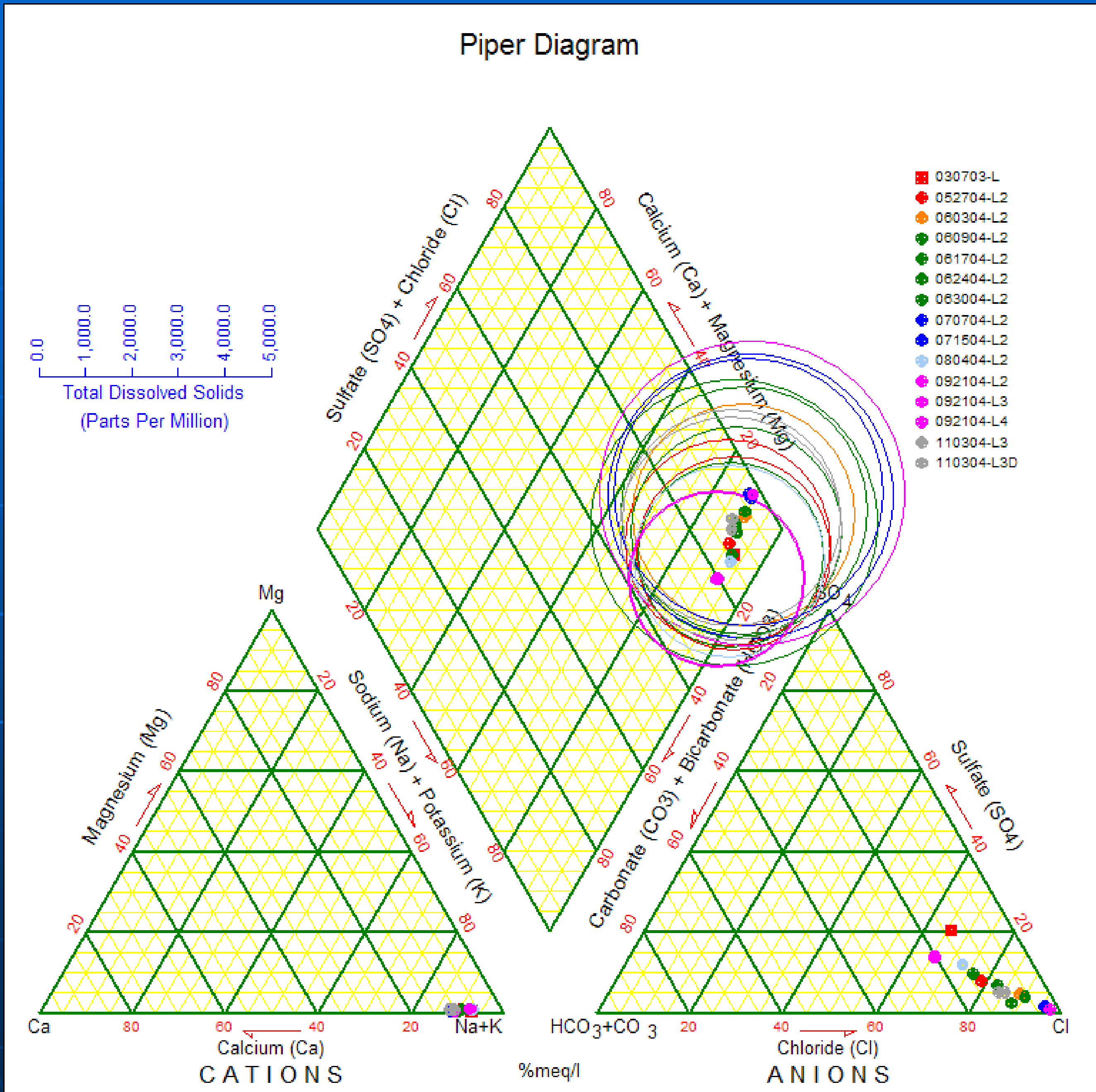
GYPSUM – CALCIUM SULFATE

SODIUM BICARBONATE

SODIUM CHLORIDE

RELATIVE AMOUNTS OF WATER FROM EACH SOURCE CAN CHANGE

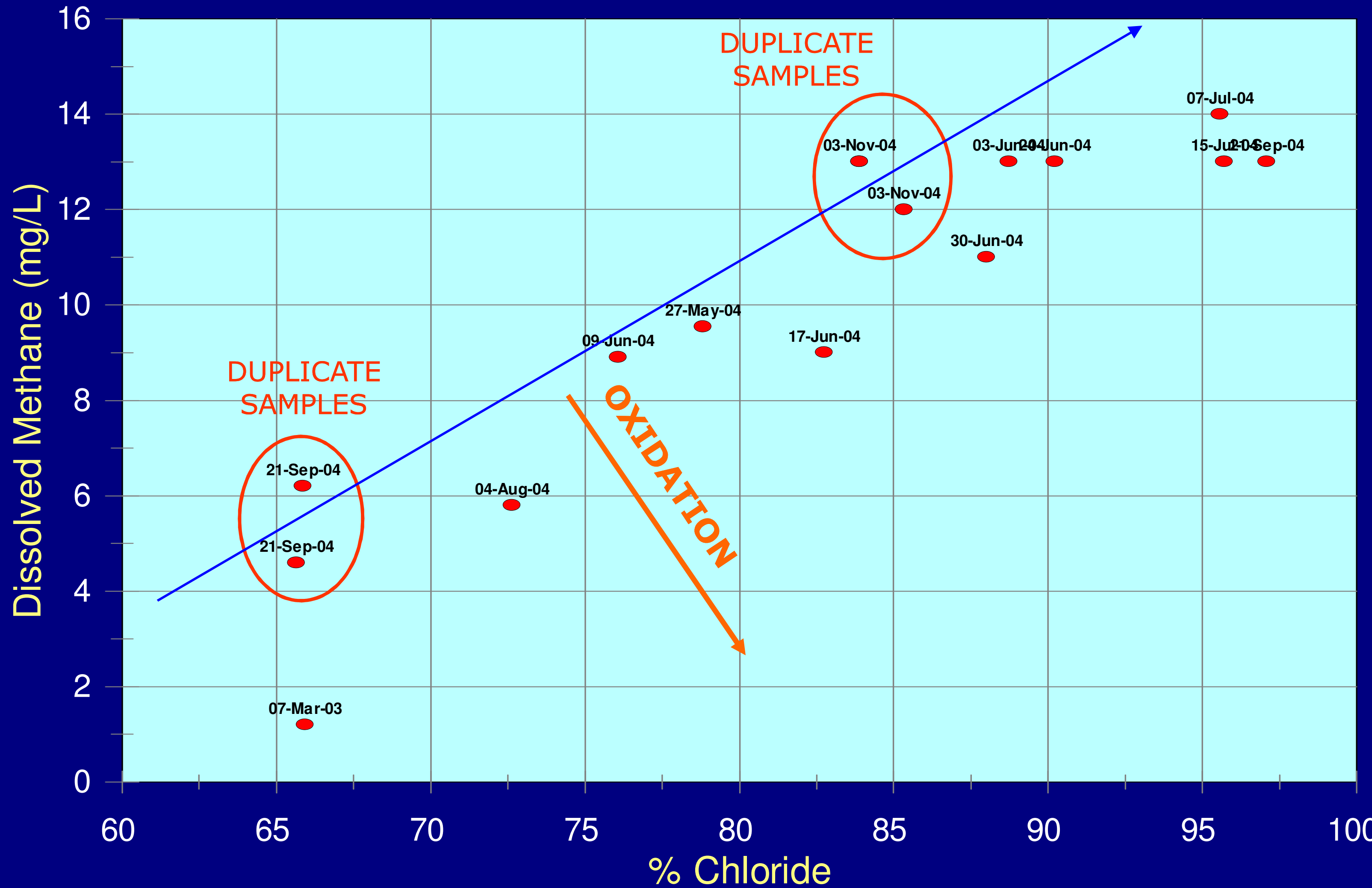




TIME SERIES OF WATER WELL DATA FROM A SINGLE WELL

WHAT IS THE BEST PLOTTING PARAMETER?

DISSOLVED METHANE CONCENTRATION VARIES LINEARLY WITH % CHLORIDE



CONCLUSIONS

- Gas ratios and stable isotopes most useful for identifying gas well point sources
  - Differentiate free and dissolved gas samples
- Immediate sampling is best
  - Sample producing wells and casing head gas within ½ mile radius down dip or along strike of discharge
- Use repeated sampling to examine remediation, and effects of oxidation and dilution
  - Always standard set of water quality analytes both inorganic and organic
- Baseline sampling essential to support forensics
  - Abandoned wells
  - Historical contamination

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QUESTIONS AND ANSWERS

http://www.worldofstock.com/slides/TAU2752.jpg

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