Forensic Isotope Methodology for Discriminating among Hydrocarbon and Brine Sources in a Producing Oil and Gas Field*

Randy Bassett[1] and Terry Moore[2]

Search and Discovery Article #40998 (2012)**
Posted August 20, 2012

*Adapted from oral presentation at AAPG Annual Convention and Exhibition, Long Beach, California, April 22-25, 2012
**AAPG © 2012 Serial rights given by author. For all other rights contact author directly.

[1]Tetra Tech Inc., Fort Collins, CO (randy.bassett@tetratech.com)
[2]BP Remediation Management, Plano, TX

Abstract

Forensic methods were successful in discriminating among sources of fugitive hydrocarbons in groundwater by using stable isotopic measurements of $\delta^{11}B$, $\delta^{34}S$, $\delta^{13}C$, δD in co-migrating inorganic dissolved constituents, as well as the direct determination of $\delta^{13}C$, δD, $\delta^{18}O$, in HC gases, and HC components dissolved in groundwater. Groundwater from a deep water supply well adjacent to a producing gas well pad containing dissolved methane, low levels of BTEX, and elevated salinity in the vicinity of producing gas wells had as many as seven different hypotheses for source contribution, including: natural gas, produced water and condensate, leaching of near-surface organic-rich oil shale, natural brines, fluids from major faults connecting with productive HC reservoirs, reserve pits, or residual components in water well casing such as pipe sealers, and oil residue. The isotopic labels from all potential sources were used along with conventional measurements of concentration to systematically define the sources of each constituent. The dissolved gas was not thermogenic, eliminating the producing wells as a source, and was clearly biogenically derived from the shallow oil shale facies intersecting the well screens of the water well. In contrast the key BTEX components were isotopically different from the oil shale but clearly related to a thermogenic source. The elevated salinity was not derived from any know natural brine in the immediate vicinity nor did it correlate with produced water. The source of all dissolved constituents except for dissolved biogenic methane correlated with residual liquid from a closed reserve pit. The components in the pit were a mixture of produced water, natural brines and completion fluids with a combination of components providing a unique combination of isotopic labels. Following two limited pumping events in the affected groundwater well and continued monitoring, hydrocarbon concentrations have decreased dramatically, eliminating the need for extensive characterization and potential remediation. Additionally, the presence of biogenic methane derived from the shallow oil shale was found to be widely distributed in the groundwater within the producing gas field and further explained the anecdotal occurrences of gas in water wells and gas pockets encountered in drilling locally.

References

Collister, J.W., and J.M. Hayes, 1991, A preliminary study of the carbon and nitrogen isotopic biogeochemistry of lacustrine sedimentary rocks from the Green River Formation, Wyoming, Utah, and Colorado, *in* M.L. Tuttle (ed.), Geochemical, biogeochemical, and sedimentological studies of the Green River Formation, Wyoming, Utah, and Colorado: U.S. Geological Survey Bulletin, Report #B 1973-A-G, p. C1-C16.

Textoris, D.A., 1963, Stratigraphy of the Green River Formation in the Bridger Basin, Wyoming: Ohio Journal of Science, v.63/6, p. 241-258.

TETRA TECH

complex world | CLEAR SOLUTIONS™

Forensic Isotopic Methodologies for Discriminating Among Hydrocarbon and Brine Sources in a Producing Oil and Gas Field

April 25th, 2012

Presentation To

AAPG Annual Meeting
Theme 8: Petroleum, Groundwater, Geochemistry, and Forensics (DEG) Long Beach, CA

R.L. Bassett, Ph.D., Tetra Tech and Terry Moore, Ph.D., BP Remediation Management

TETRA TECH

complex world | CLEAR SOLUTIONS™

Thermal Ionization Mass Spectrometer

Isotopic Tools

Stable Isotopes

- δD - hydrogen
- $\delta^{18}O$ - oxygen
- $\delta^{11}B$ - boron
- $\delta^{13}C$ - carbon
- $\delta^{34}S$ - sulfur
- $\delta^{15}N$ - nitrogen

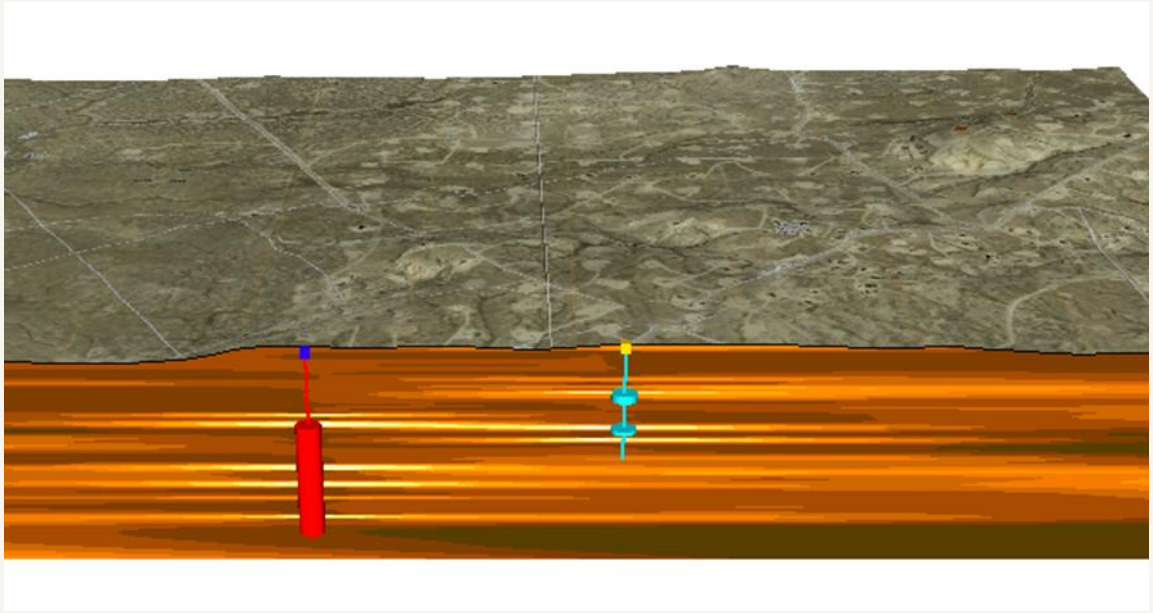
Radiogenic Isotopes

- ^{14}C - radiocarbon
- ^{3}H - tritium
- ^{36}Cl - chlorine
- $^{87/86}Sr$ - strontium
- $^{234/238}U$ - uranium

Introduction

Context:

BTEX: benzene+
HC Gas: methane
TDS: elevated



Key Questions:

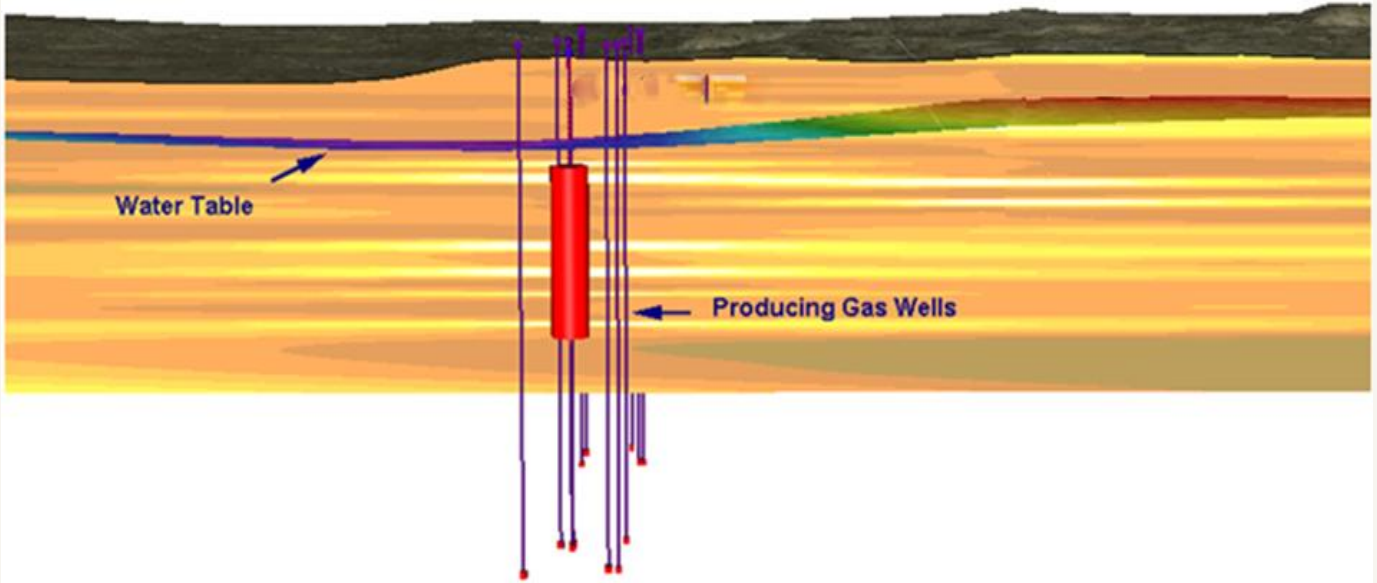
- Origin
- Extent
- Source Options
- Forensic Approach

Well Site

SOURCES OF BTEX, HC GAS, TDS

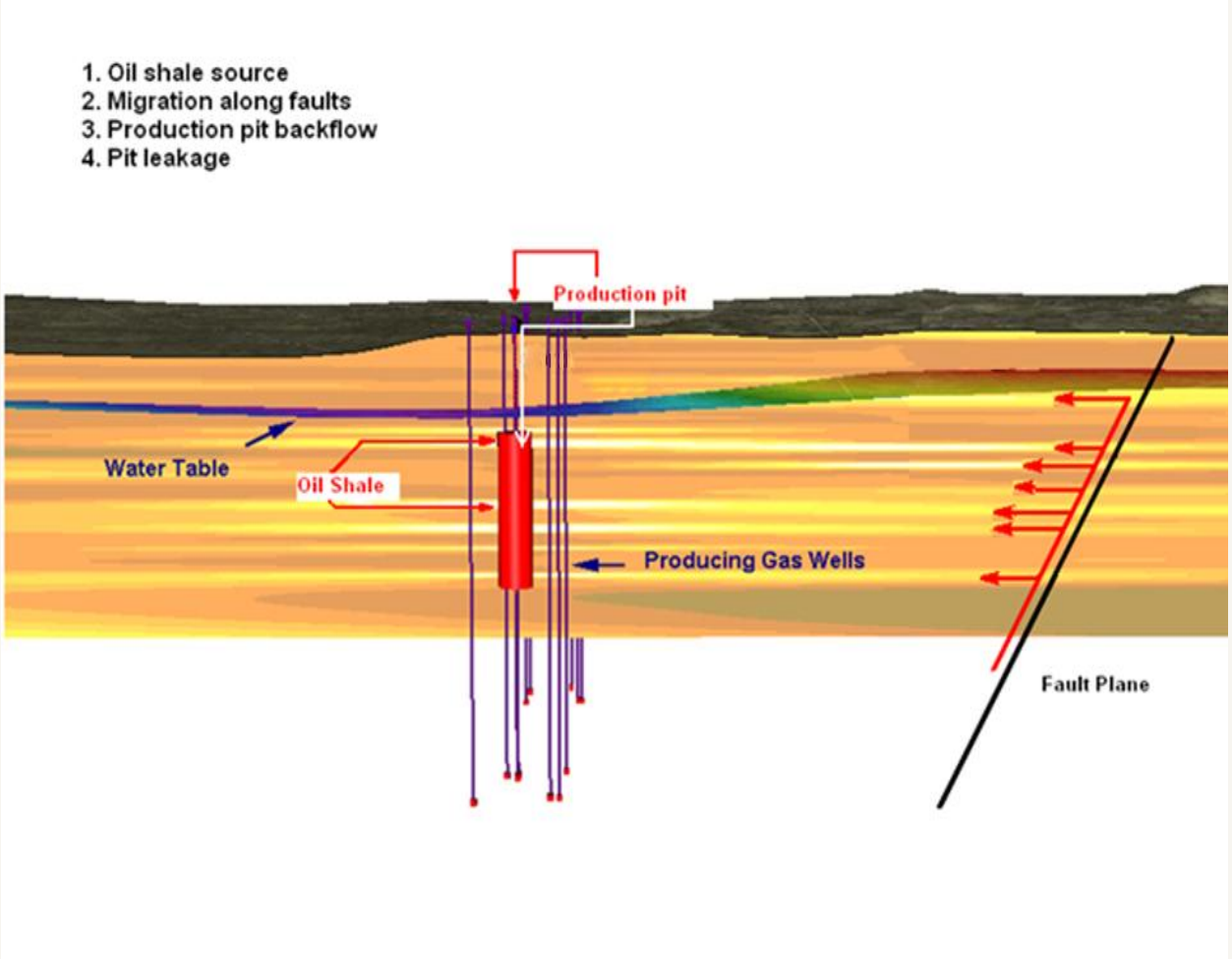
From Mechanical/Treatment Processes

1. Casing leak from producing gas well
2. Used Casing
3. Water well completion products

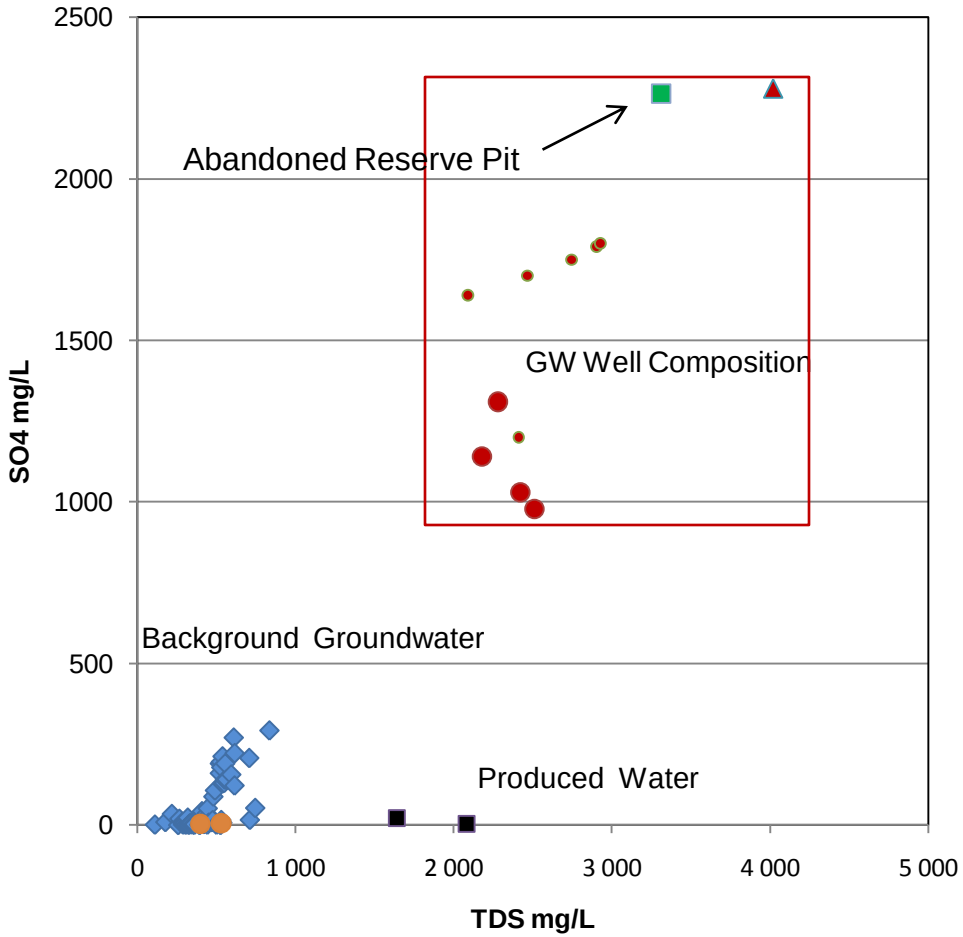


SOURCES OF BTEX, HC GAS, TDS

Site Preparation/HydroGeologic Processes



Anomalous Concentrations: Sulfate and TDS



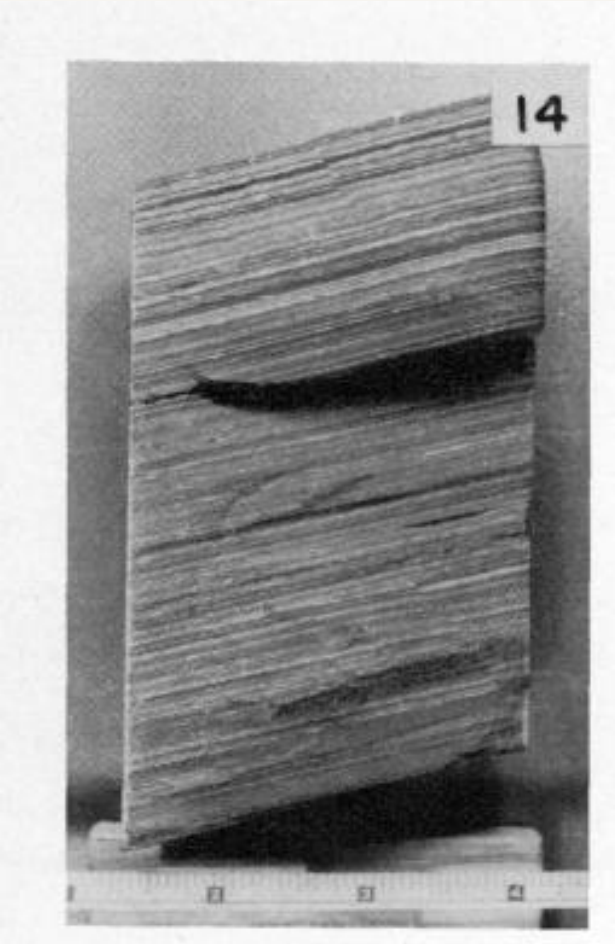
Source of Methane

Methane Isotopic Composition

Sample	Biogenic Gas		Thermogenic Gas	
	$\delta^{13}C$ ‰	δD ‰	$\delta^{13}C$ ‰	δD ‰
	-45 to -100	-150 to -350	> -45	> -150
GW Welll	-56.48	-245.23		
GW Well	-58.27	-157.14		
Produced Water			-42.68	-130.88
Produced Water			-38.57	-101.94
Produced Water			-42.1	-133.57

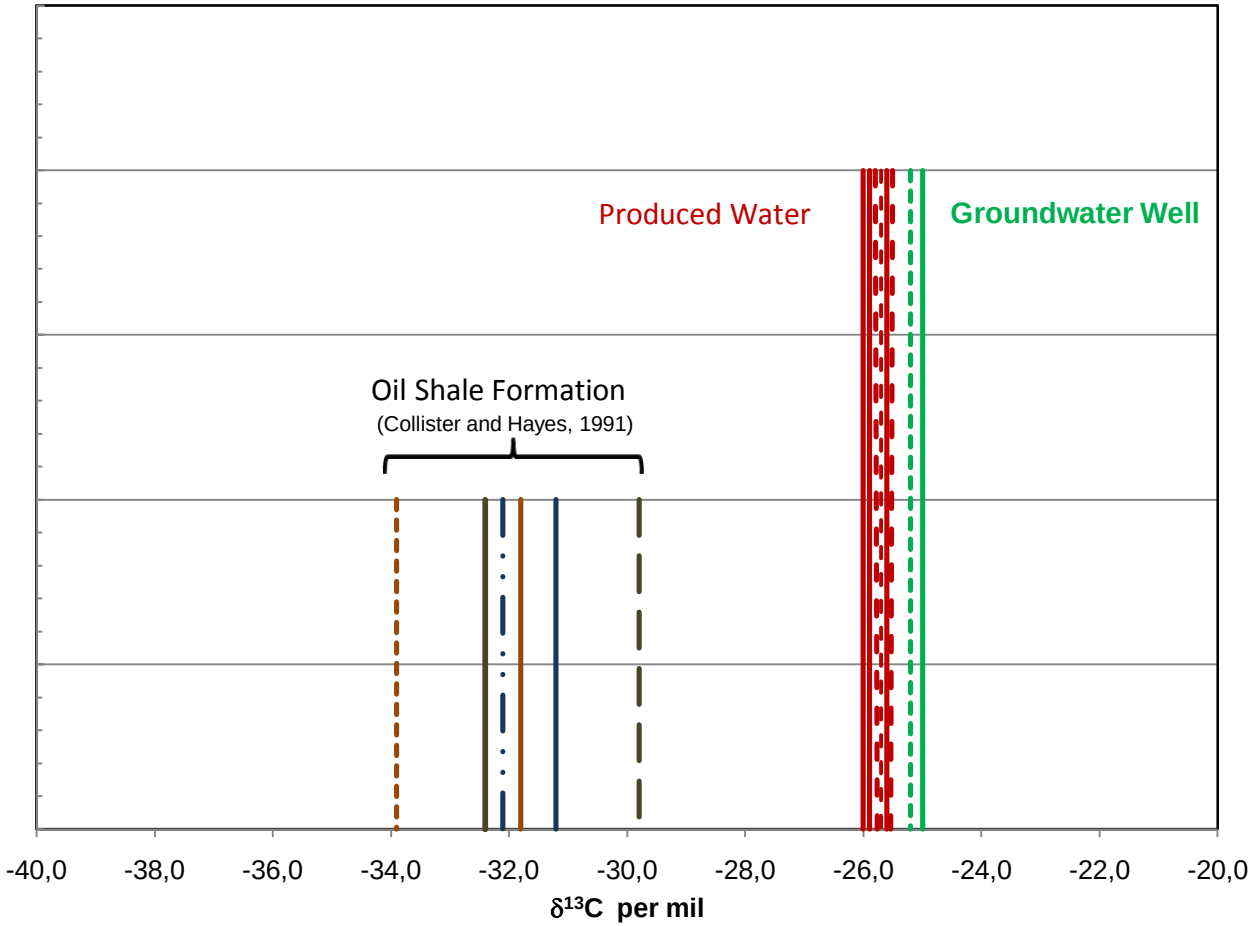
Potential Natural Benzene (BTEX) Source - Oil Shale

Left: “Gray fissile shale grading into a low-grade varved oil shale,”
Right: “Black and buff varved shale,” (afterTextoris,1963)

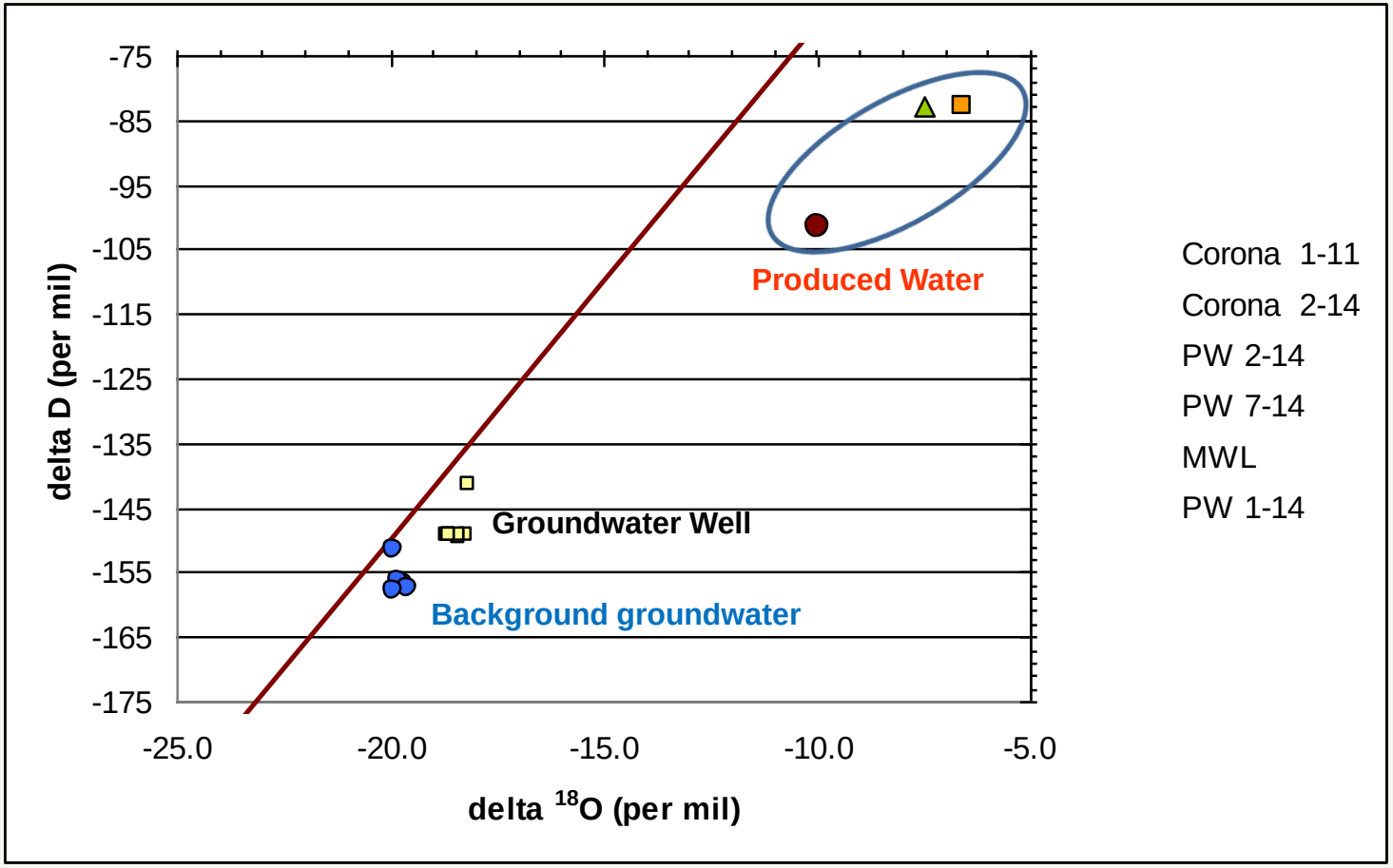


Source of Benzene (BTEX)

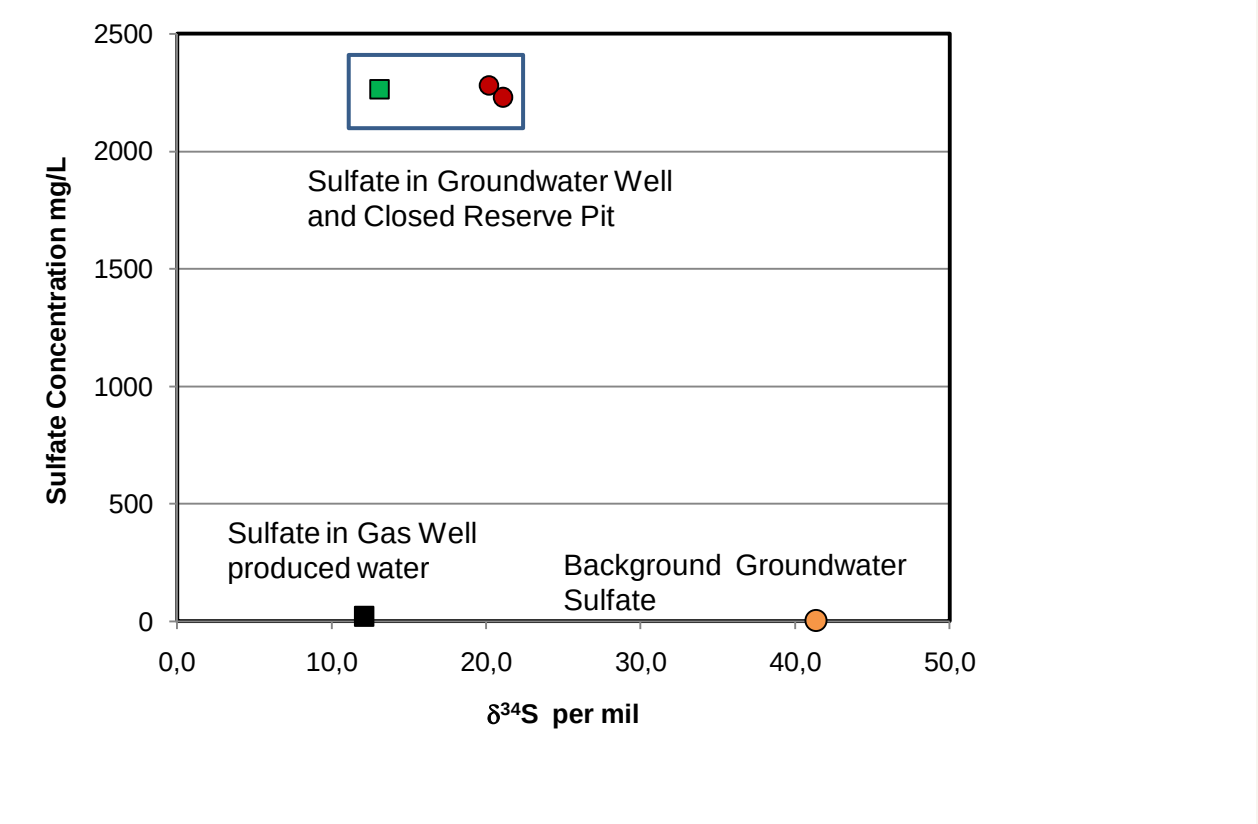
(C_6H_6 use $\delta^{13}C$) eliminates oil shale



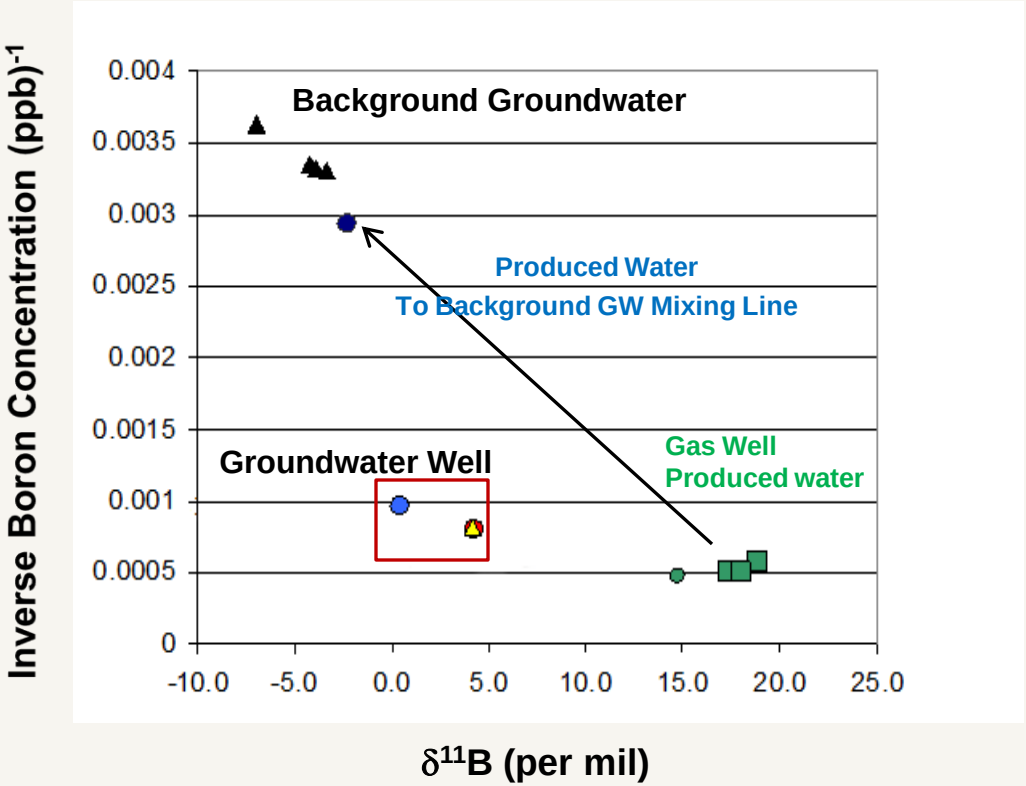
Water (H_2O) Isotopes
(δD and $\delta^{18}O$) Distinct



Sulfate ($\delta^{34}SO_4$) Isotope Distribution



Boron Isotope Mixing Curve
($\delta^{11}B$) off the mixing line



Conclusions

SOURCES of BENZENE, CH_4 and TDS in GW Well in Producing Gas Field?

- Produced Water/Gas/Condensate from Gas Wells?

- Oil Shale?

- Abandoned Reserve Pit?

- **Pit Water extract matches GW well concentrations/compositions; Produced Water does not;**
- **Methane in GW well is w/o higher gas fractions and $\delta^{13}C$ is biogenic from oil shale; no thermogenic gas detected in GW well;**
- **$\delta^{13}C$ of benzene in GW well different and distinct from oil shale;**
- **δD, $\delta^{18}O$ indicate GW well is different from Background GW or Produced Water, but slightly evaporated, consistent with Pit Water source;**

Conclusions

SOURCES of BENZENE, CH_4 and TDS in GW Well in Producing Gas Field?

- **Produced Water/Gas/Condensate from Gas Wells?**
- **Oil Shale?**
- **Abandoned Reserve Pit?**

- **$\delta^{34}SO_4$ eliminates mixing of Produced Water and Background GW to yield GW well composition; GW well sulfate matches the Pit Water;**
- **$\delta^{11}B$ eliminates a mixture of Produced Water and Background GW to yield GW;**
- **Reserve pit located in immediate proximity to the GW well; migration pathway would be laterally from the pit to the annulus of the well then down through the gravel pack to upper perforations of the well.**

Contaminated GW well is uniquely related to the previously unknown closed reserve pit – which was pumped & contaminant issue contained