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

Randy Bassett¹ and Terry Moore²

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

Abstract

Forensic methods were successful in discriminating among sources of fugitive hydrocarbons in groundwater by using stable isotopic measurements of δ¹¹B, δ³⁴S, δ¹³C, δD in co-migrating inorganic dissolved constituents, as well as the direct determination of δ¹³C, δD, δ¹⁸O, 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


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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
Thermal Ionization Mass Spectrometer
Isotopic Tools

**Stable Isotopes**

- $\delta D$ - 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

GW Well Location
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

1. Oil shale source
2. Migration along faults
3. Production pit backflow
4. Pit leakage
Anomalous Concentrations: Sulfate and TDS

![Graph showing concentration levels of sulfate and TDS across different sources such as Abandoned Reserve Pit, GW Well Composition, Background Groundwater, and Produced Water.]
## Source of Methane

### Methane Isotopic Composition

<table>
<thead>
<tr>
<th>Sample</th>
<th>Biogenic Gas</th>
<th></th>
<th>Thermogenic Gas</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C‰</td>
<td>$\delta^D$‰</td>
<td>$\delta^{13}$C‰</td>
<td>$\delta^D$‰</td>
</tr>
<tr>
<td></td>
<td>-45 to -100</td>
<td>-150 to -350</td>
<td>&gt; -45</td>
<td>&gt; -150</td>
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<tr>
<td>GW Well</td>
<td>-56.48</td>
<td>-245.23</td>
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<tr>
<td>GW Well</td>
<td>-58.27</td>
<td>-157.14</td>
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<tr>
<td>Produced Water</td>
<td>-42.68</td>
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<td>-38.57</td>
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<tr>
<td>Produced Water</td>
<td>-42.1</td>
<td></td>
<td>-133.57</td>
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</tr>
</tbody>
</table>
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,” *chgtVgzvtlu.3; 85+
Source of Benzene (BTEX) 
(C\textsubscript{6}H\textsubscript{6} use $\delta^{13}$C) eliminates oil shale

Produced Water

Groundwater Well

Oil Shale Formation
(Collister and Hayes, 1991)

$\delta^{13}$C per mil

-40,0 -38,0 -36,0 -34,0 -32,0 -30,0 -28,0 -26,0 -24,0 -22,0 -20,0
Water (H\textsubscript{2}O) Isotopes (δD and δ\textsuperscript{18}O) Distinct

![Graph showing δD and δ\textsuperscript{18}O values for different water types.]

- Produced Water
- Groundwater Well
- Background groundwater

Corona 1-11
Corona 2-14
PW 2-14
PW 7-14
MWL
PW 1-14
Sulfate ($\delta^{34}\text{SO}_4$) Isotope Distribution

![Graph showing sulfate distribution in groundwater well and closed reserve pit compared to gas well produced water and background sulfate.](image-url)
Boron Isotope Mixing Curve
($\delta^{11}$B) off the mixing line

![Graph showing boron isotope mixing curve with data points for background groundwater, produced water, and ground and gas well produced water.](image-url)
Conclusions

SOURCES of BENZENE, CH₄ 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 δ¹³C is biogenic from oil shale; no thermogenic gas detected in GW well;

• δ¹³C of benzene in GW well different and distinct from oil shale;

• δD, δ¹⁸O indicate GW well is different from Background GW or Produced Water, but slightly evaporated, consistent with Pit Water source;
Sources of benzene, CH₄ and TDS in GW well in producing gas field?
- Produced water/gas/condensate from gas wells?
- Oil shale?
- Abandoned reserve pit?

- δ³⁴SO₄ eliminates mixing of produced water and background GW to yield GW well composition; GW well sulfate matches the pit water;
- δ¹¹B 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