

# Isotech - Stable Isotope Analysis

Determining the origin of methane  
and its effect on the aquifer.



# Agenda

- Geologic history
- Methane characteristics
- The ratio of carbon isotopes in methane.
- The unique ratio of hydrocarbons in the Marcellus Formation
- Identifying the age of the methane.
- The effects methane and drilling have on the aquifer and trend over time.
- Conclusions.

# Environment of Deposition Middle Devonian (385 MA)





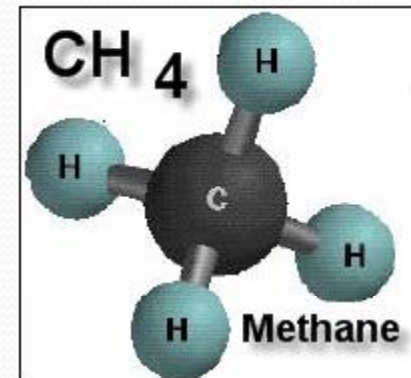


**Osborn S G et al. PNAS 2011;108:8172-8176**



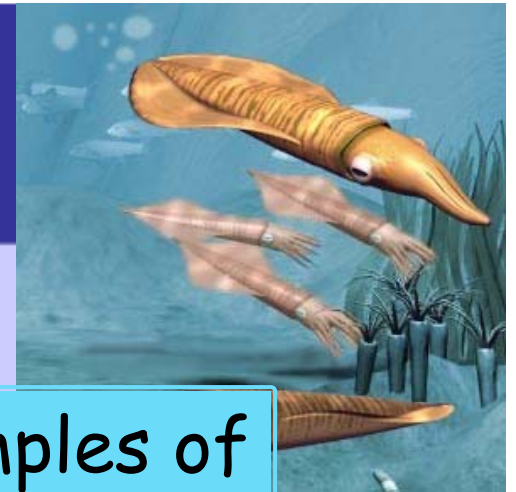
## Methane is the principal hydrocarbon detected in all stray natural gas migration incidents

- Exposure limit (gas phase): TLV-TWA: 1,000 ppm (ACGIH, 10/2009)
- Methane (CH<sub>4</sub>) is the simplest paraffin hydrocarbon gas
- Methane is generated by microbial & thermogenic processes
- Flammable, colorless, odorless.
- Specific gravity: 0.555 (NTP) air = 1
- Explosive range: 5-15% in ambient air
- Solubility in water: 26-32 mg/l (1 atm.)
- Non toxic, no ingestion hazard
- Simple asphyxiant, explosion hazard



Methane can migrate as free gas or dissolved in the groundwater

# Delta notation



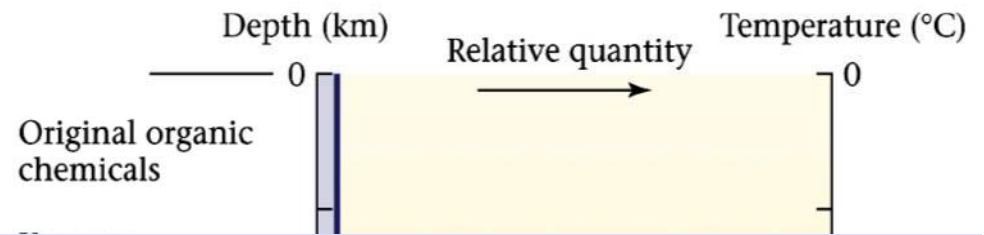
So by collecting numerous gas samples of known origin a database has been developed and fingerprinting of gas samples may be performed.

$R_{reference} = \text{VPDB (Vienna Pee Dee Belemnite)}$

$$\delta^{13}\text{C} = \delta(^{13}\text{C}) = \delta(^{13}\text{C}/^{12}\text{C}) = \frac{n_X(^{13}\text{C})/n_X(^{12}\text{C}) - n_{\text{ref}}(^{13}\text{C})/n_{\text{ref}}(^{12}\text{C})}{n_{\text{ref}}(^{13}\text{C})/n_{\text{ref}}(^{12}\text{C})}$$

# Shale Gas

- Increasing formation temperature leads to diagnostic



The normal sequence of carbon isotopic compositions is:

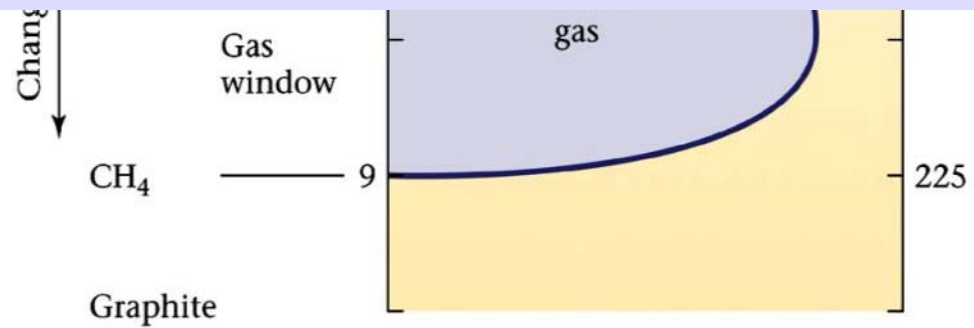
$\delta^{13}\text{C}$  methane ( $\text{C}_1$ ) <  $\delta^{13}\text{C}$  ethane ( $\text{C}_2$ ) <  $\delta^{13}\text{C}$  propane ( $\text{C}_3$ ) and <  $\delta^{13}\text{C}$  butane ( $\text{C}_4$ )

$$\delta^{13}\text{C}_1 < \delta^{13}\text{C}_2 < \delta^{13}\text{C}_3 \text{ and } < \delta^{13}\text{C}_4$$

In the Marcellus they are fully reversed -  $\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3$

Also hydrogen isotopic compositions ( $\delta^2\text{H}$ ) of  $\text{C}_1$  and  $\text{C}_2$  are also reversed.

- Uniquely identifiable when paired with additional proxies (e.g. noble gases)





# Isotope Geochemistry

## Easily Distinguishes:

- Molecular: Methane/Ethane
- Isotopic: Carbon and Hydrogen isotopes ( $\delta^{13}\text{C}-\text{CH}_4$ ,  $\delta^2\text{H}-\text{CH}_4$ ,  $\delta^{13}\text{C}-\text{C}_2\text{H}_6$ )
- Noble Gases

☑ Biogenic vs. Thermogenic  
(e.g. Schoell, 1983; Coleman et al, 1991; Baldassare and Laughrey, 1998)

☑ Distinguishing different thermogenic gases  
(e.g. Schoell et al, 1983; Jenden et al, 1993; Revesz et al, 2010; Tilley et al, 2010)

? What's best for distinguishing thermally mature gases?





Lab #: 235488 Job #: 17407  
 Sample Name/Number: HW02z  
 Company: TechLaw, Inc.  
 Date Sampled: 1/25/2012  
 Container: Dissolved Gas Bottle  
 Field/Site Name: A3TA  
 Location:  
 Formation/Depth:  
 Sampling Point:  
 Date Received: 2/03/2012 Date Reported: 2/20/2012

<sup>13</sup>C fractionation

<sup>2</sup>H fractionation

% argon

% nitrogen

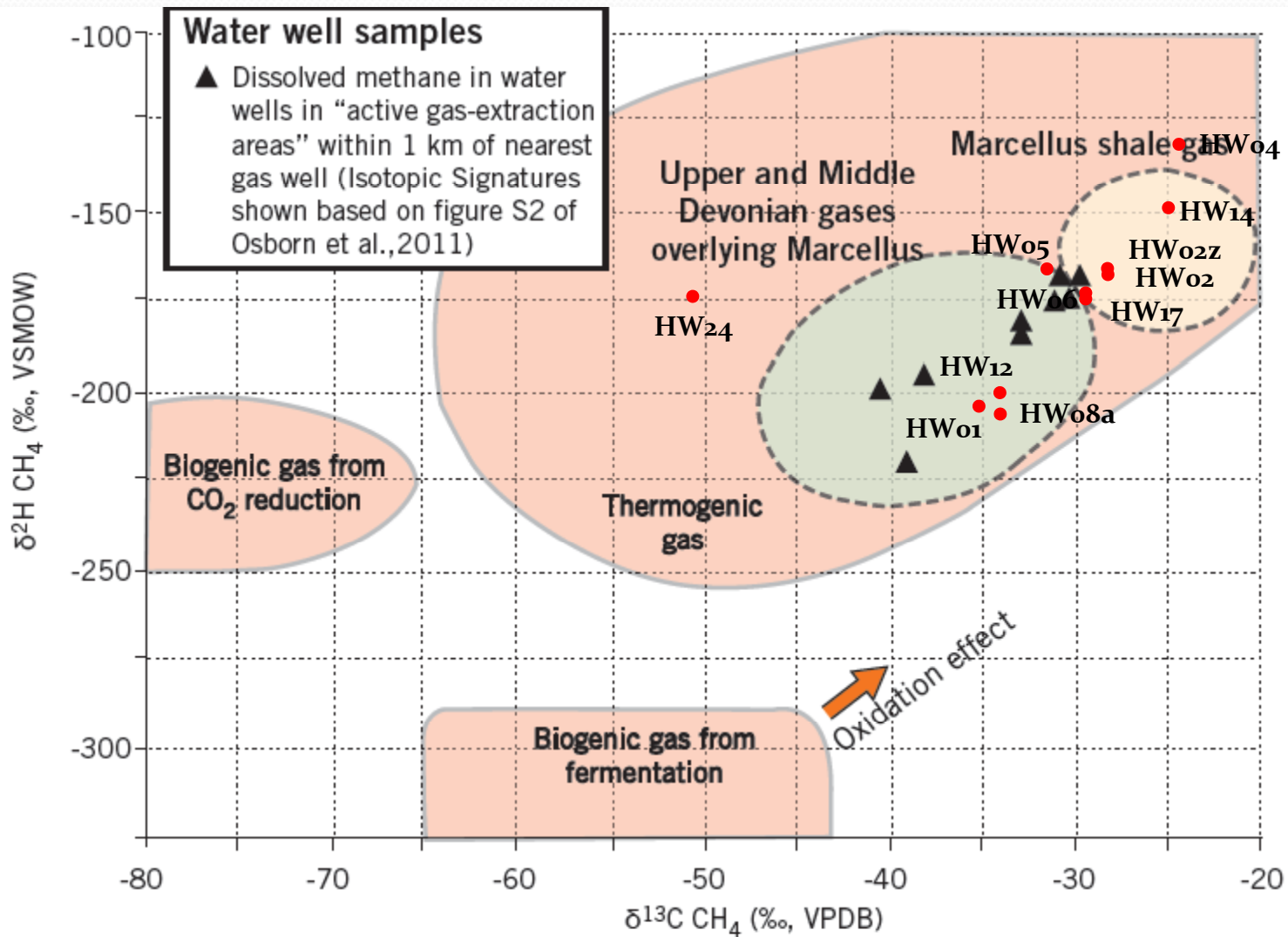
Component	Chemical mol. %	$\delta^{13}\text{C}$ ‰	$\delta\text{D}$ ‰	$\delta^{18}\text{O}$ ‰
Carbon Monoxide -----	nd			
Hydrogen Sulfide -----	na			
Helium -----	0.0112			
Hydrogen -----	nd			
Argon -----	0.628			
Oxygen -----	0.80			
Nitrogen -----	40.72			
Carbon Dioxide -----	0.094			
Methane -----	57.06	-29.30	-160.6	
Ethane -----	0.687			
Ethylene -----	nd			
Propane -----	nd			
Propylene -----	0.0001			
Iso-butane -----	nd			
N-butane -----	nd			
Iso-pentane -----	nd			
N-pentane -----	nd			
Hexanes + -----	nd			
Water -----			-64.6	-9.66

**-29**

**-160**

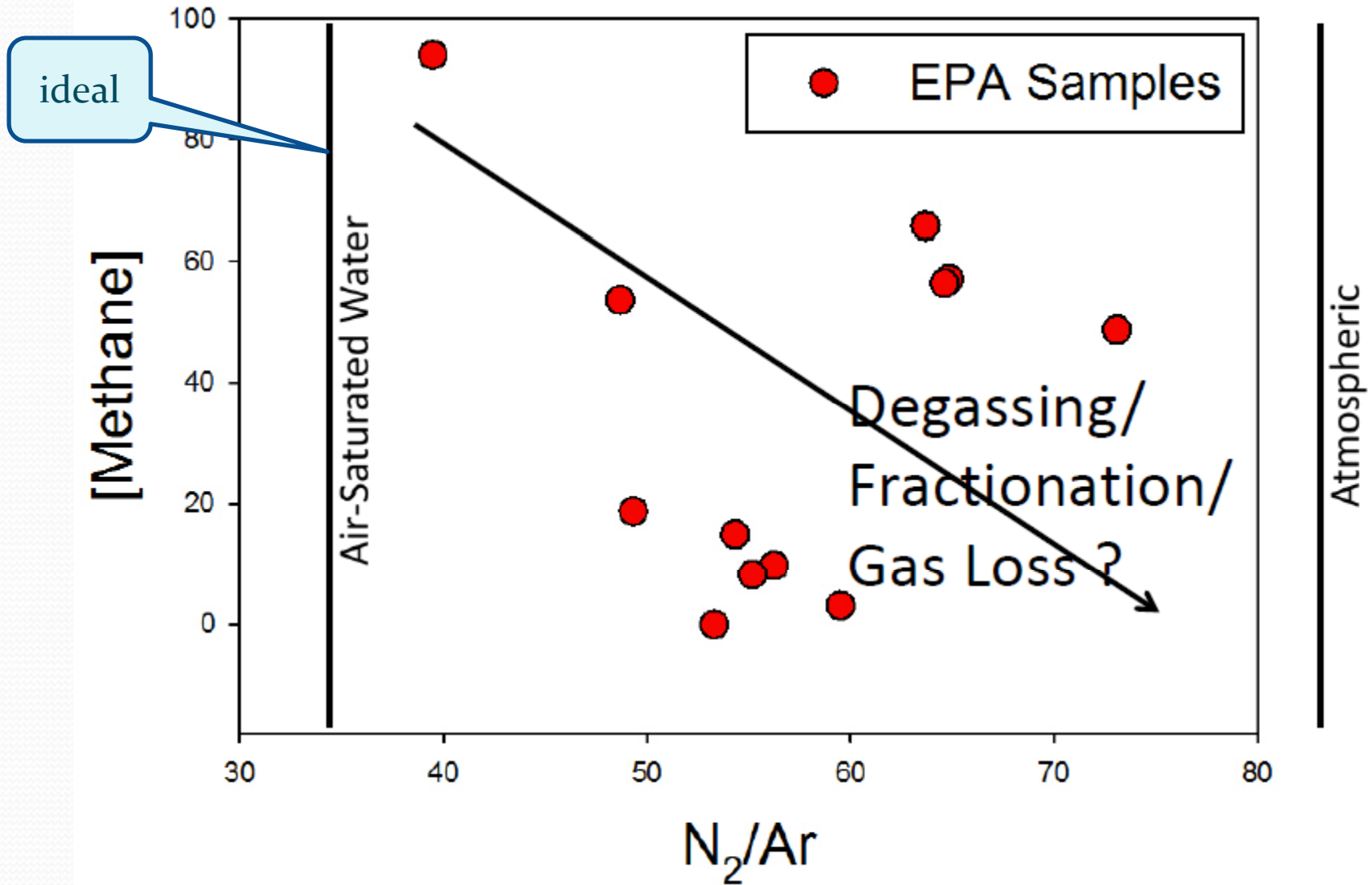
Total BTU/cu.ft. dry @ 60deg F & 14.7psia, calculated: 590

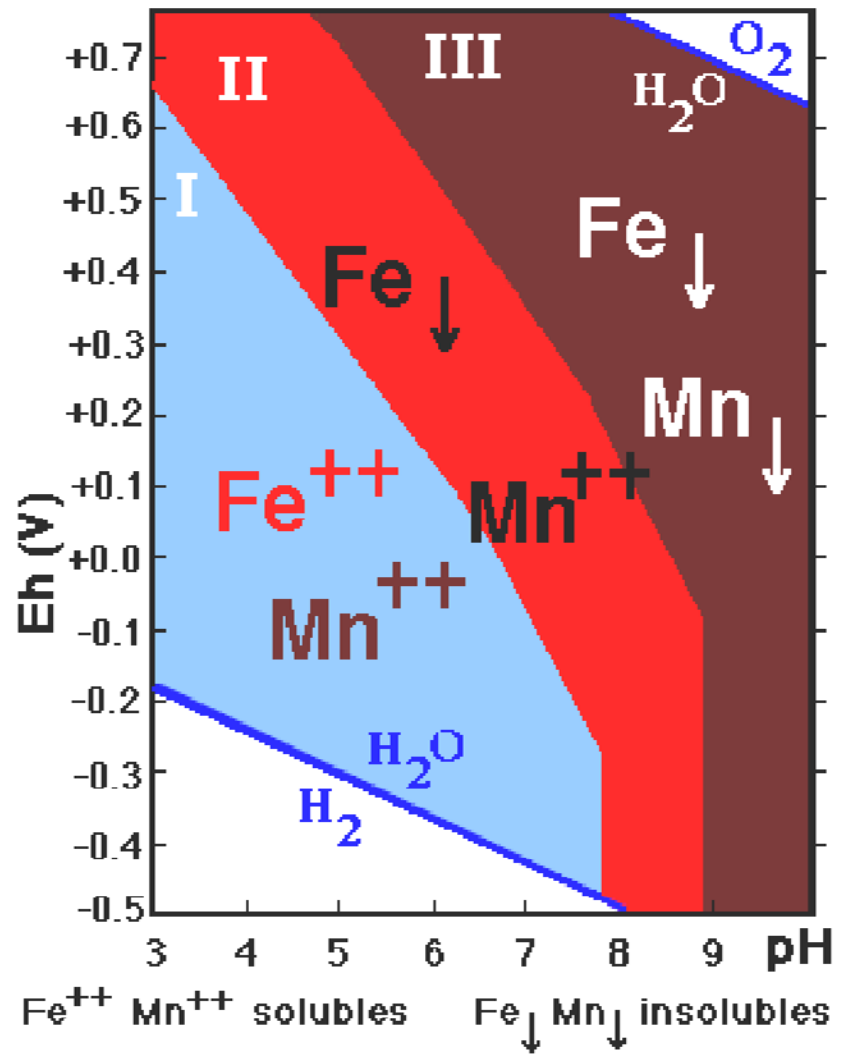
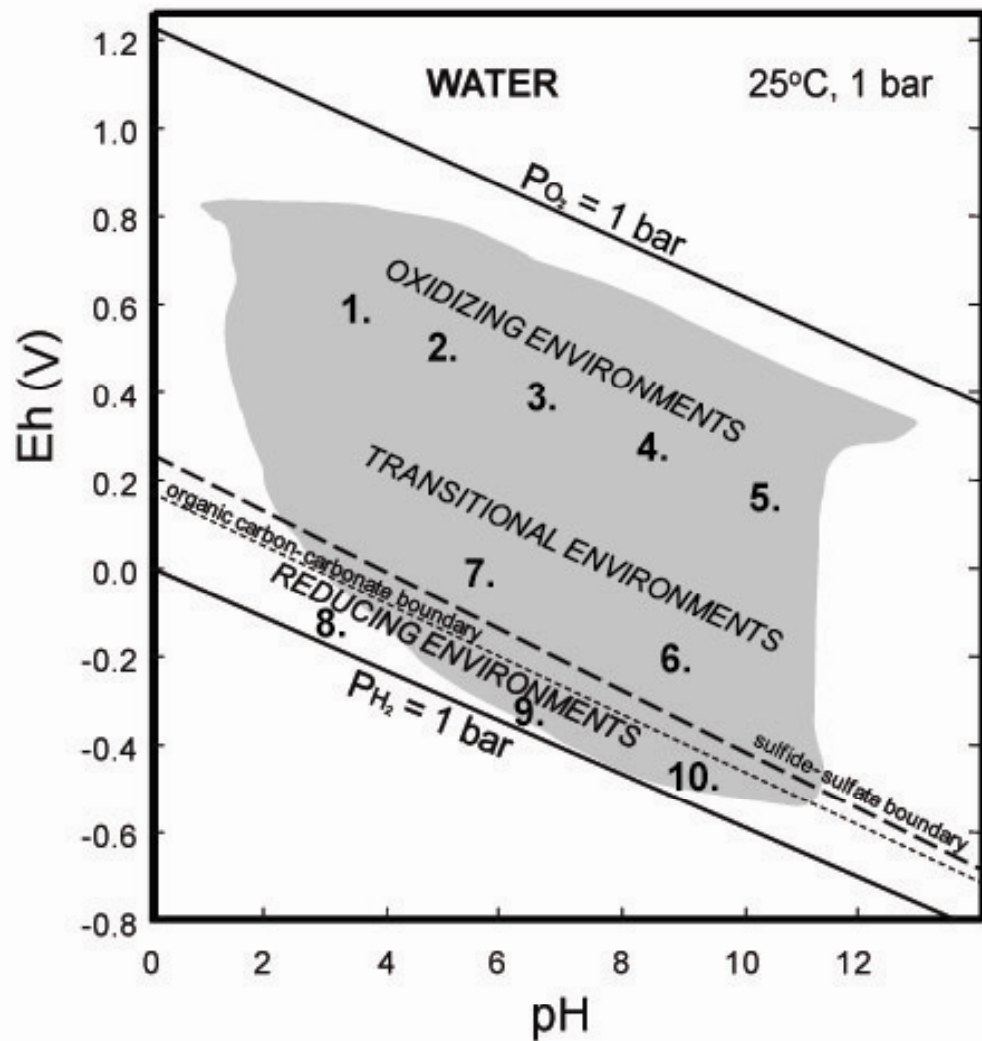
Specific gravity, calculated: 0.736





# Sample Quality - degassing?









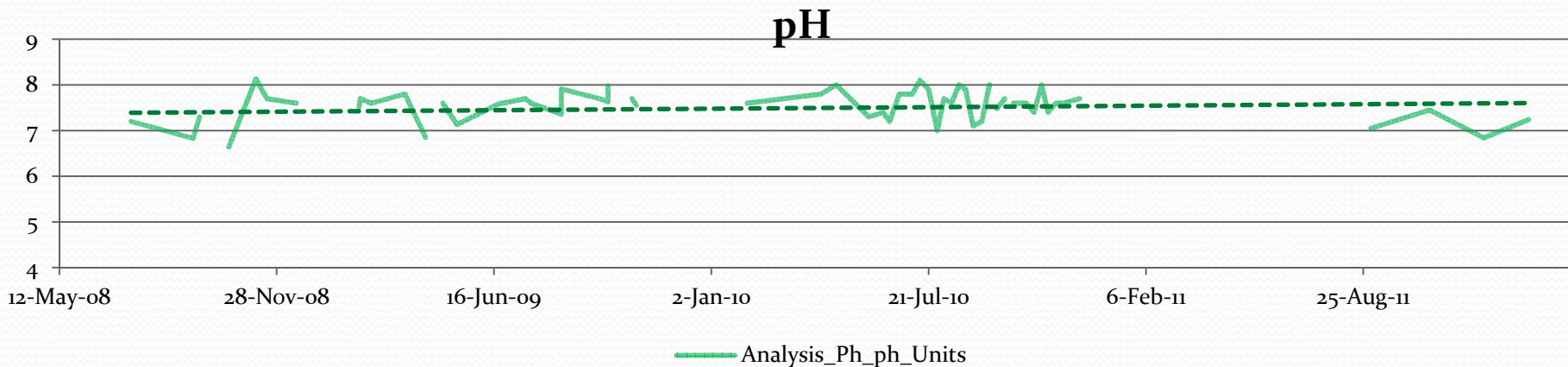
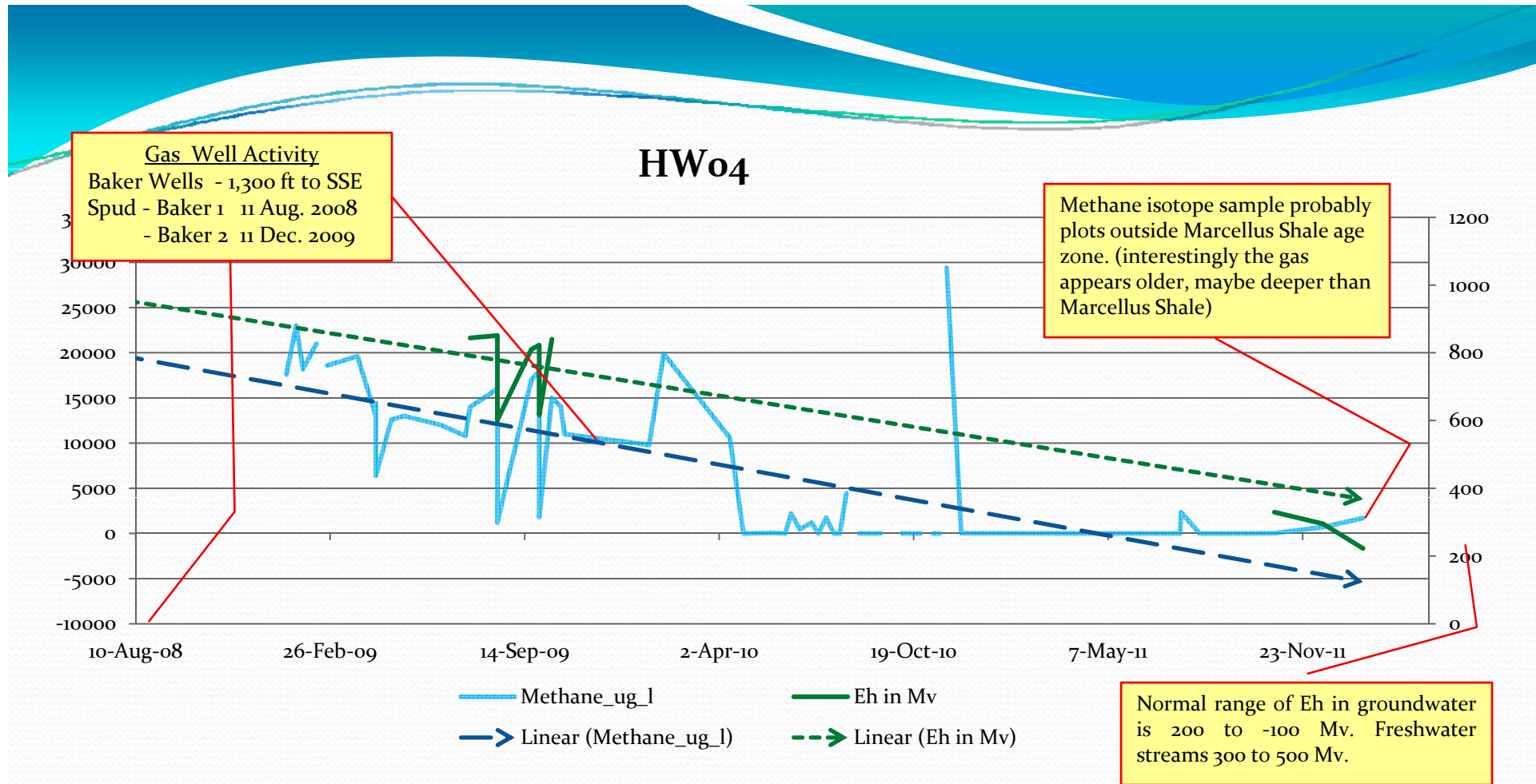
# Three Patterns of Contamination

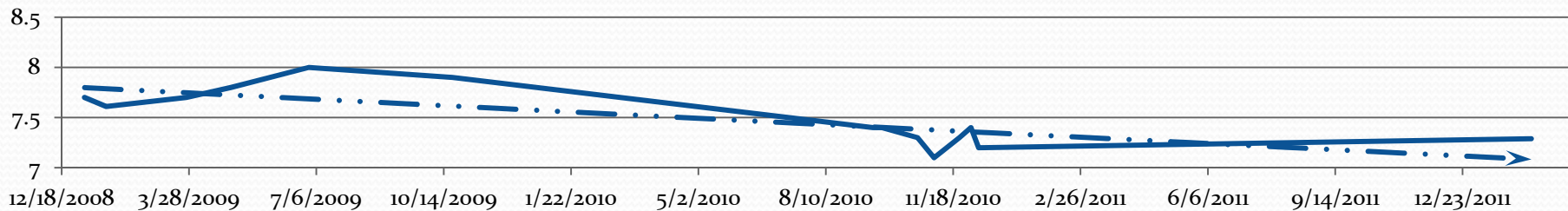
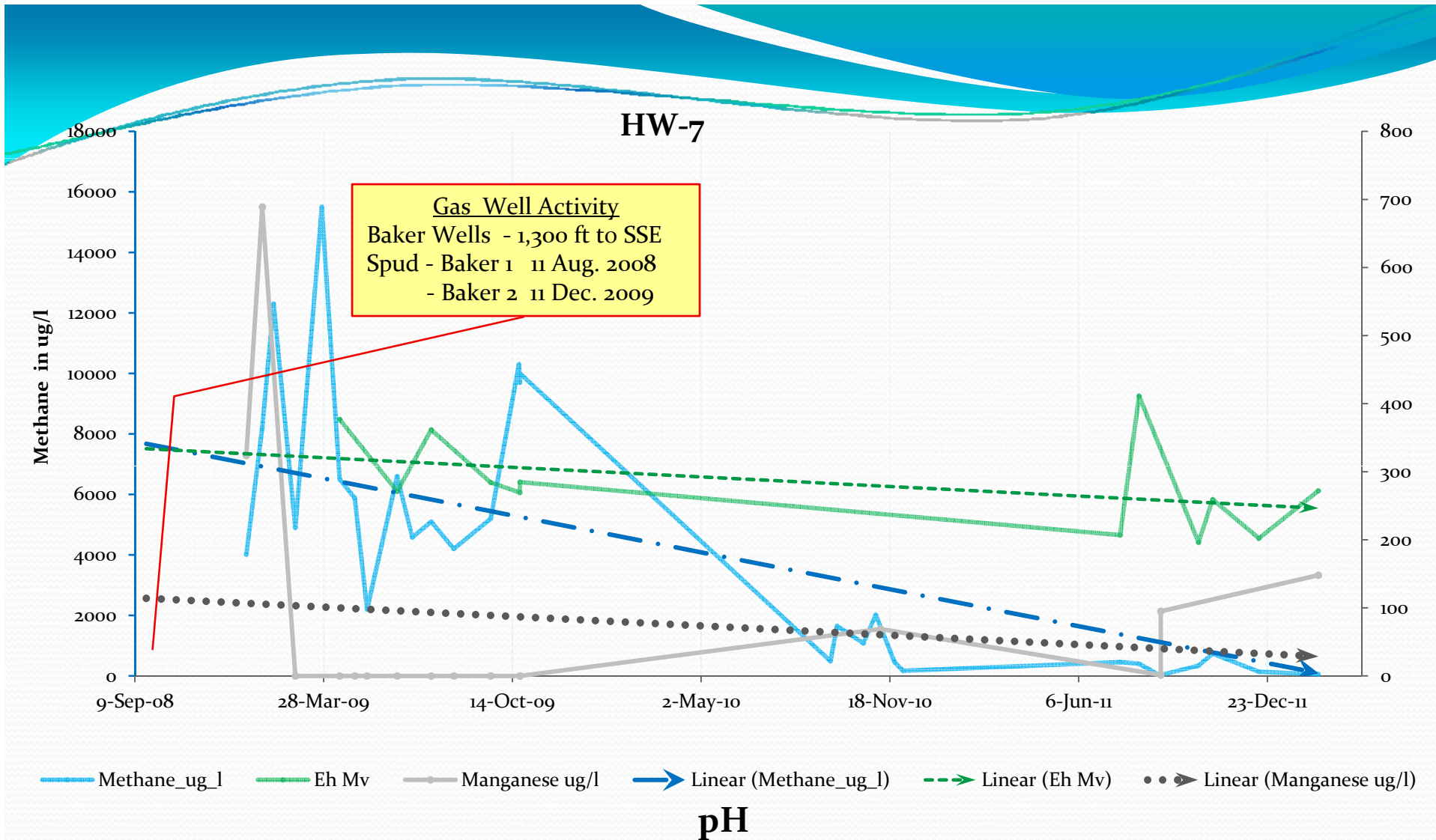
1. **Short term** (< 1 year) disruption to the aquifer caused by drilling.
2. **Long term** (> 3-4 year) disruption or contamination of the aquifer caused by drilling/fracking, releases or other situations.
3. **Natural Background Conditions** with high levels of metals and anions.



# Type 1: Short Term Disruption

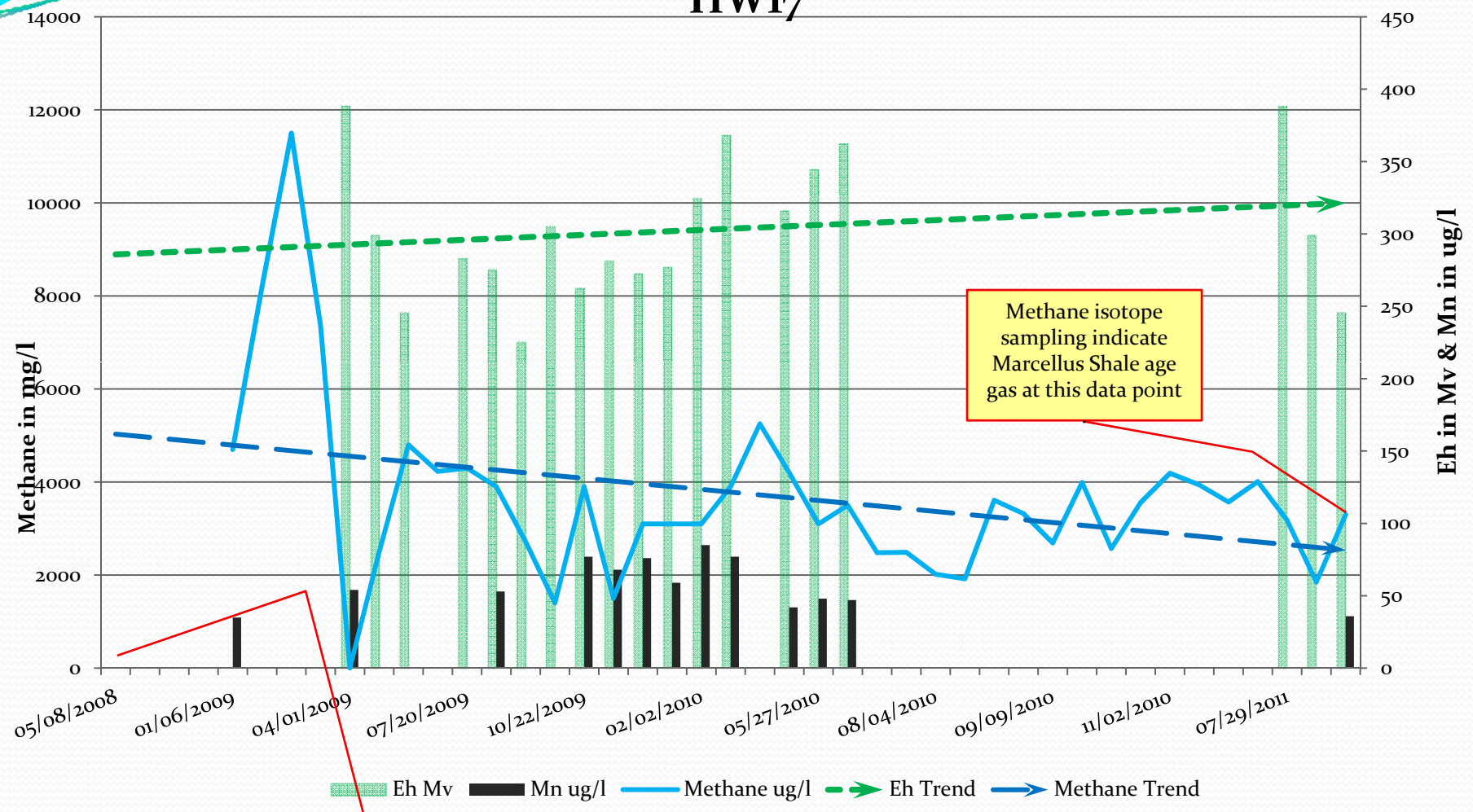








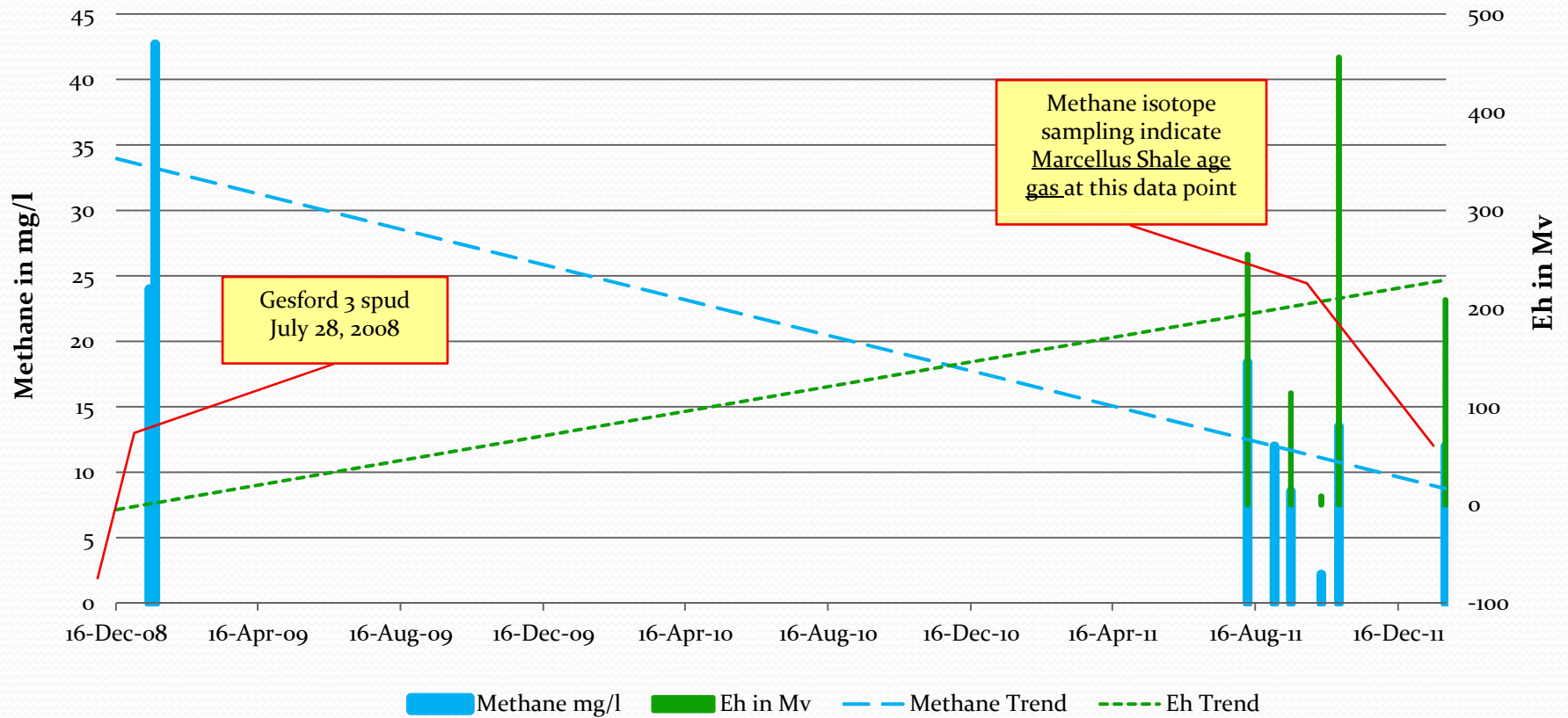
# HW17



<u>Gas Well</u>	<u>Date Spud</u>	<u>Distance to HW17</u>
Lewis	5/28/2008	670 ft.
Ely 4H & 6H	3/27/2008	1,360 ft.
Costello 1	7/16/2008	1,350 ft.

Note incomplete data set

# HW<sub>1</sub> - Hubert



HW<sub>1</sub> lacked data for nearly all constituents, particularly for the years 2009-2010



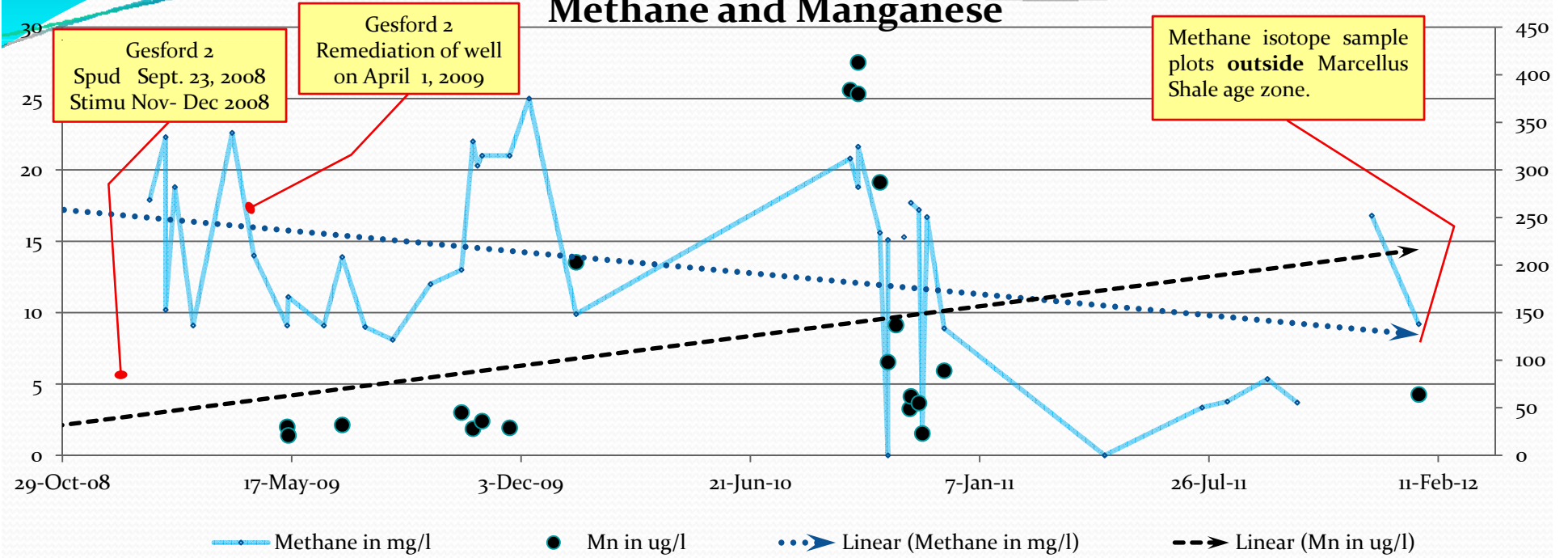


# Type 2: Long Term Disruption

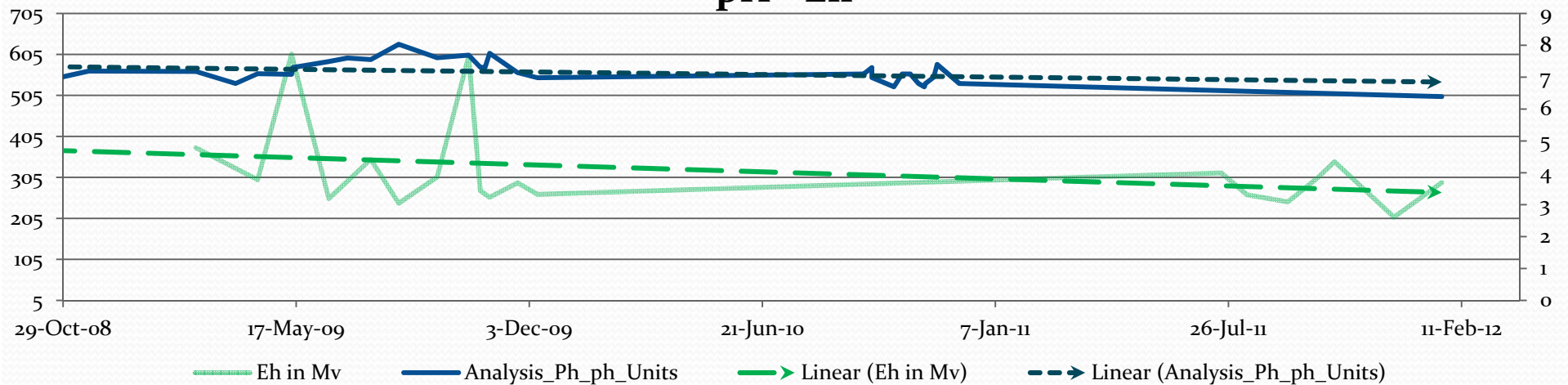


# HW8

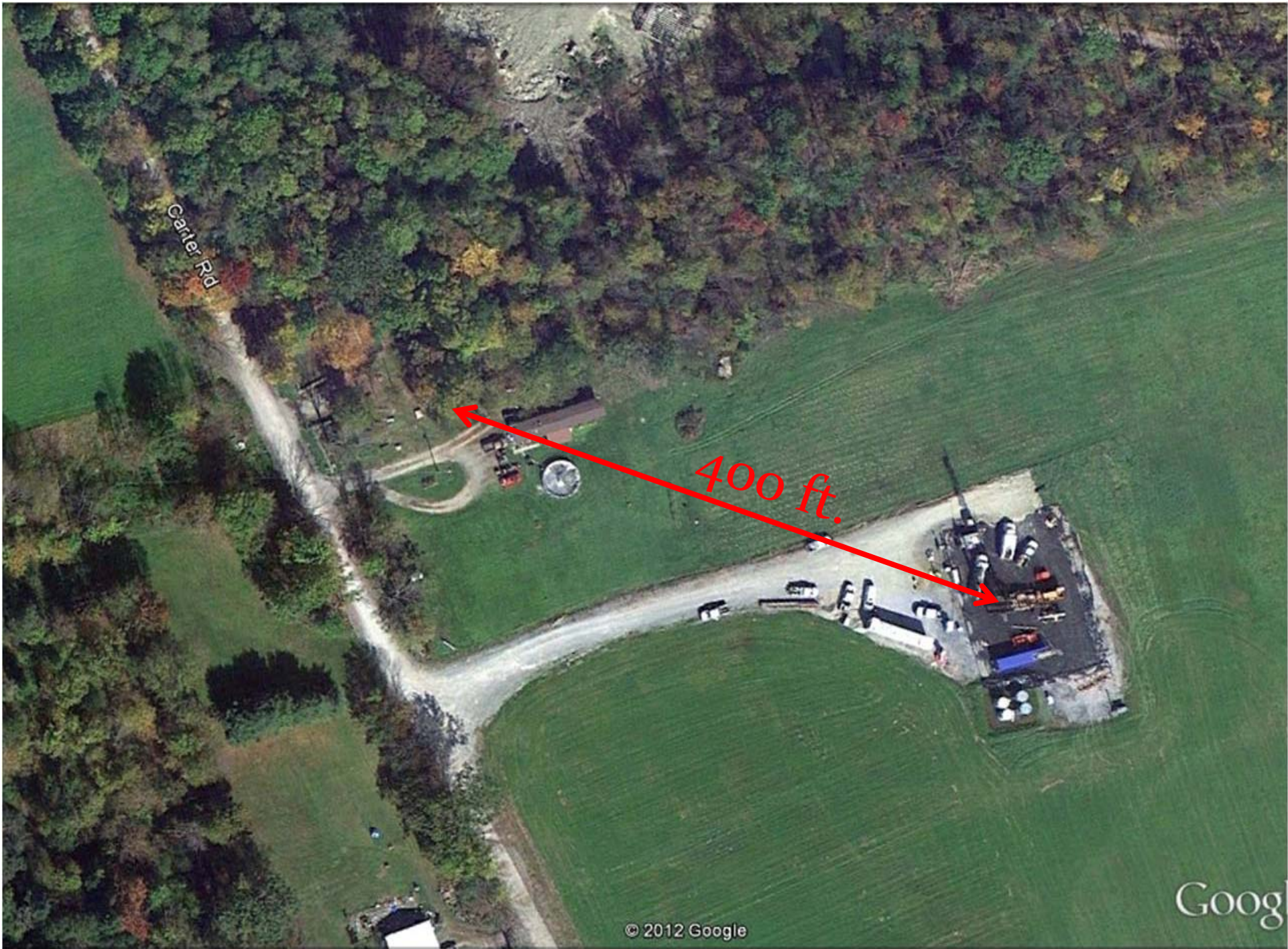
## Methane and Manganese



## pH - Eh



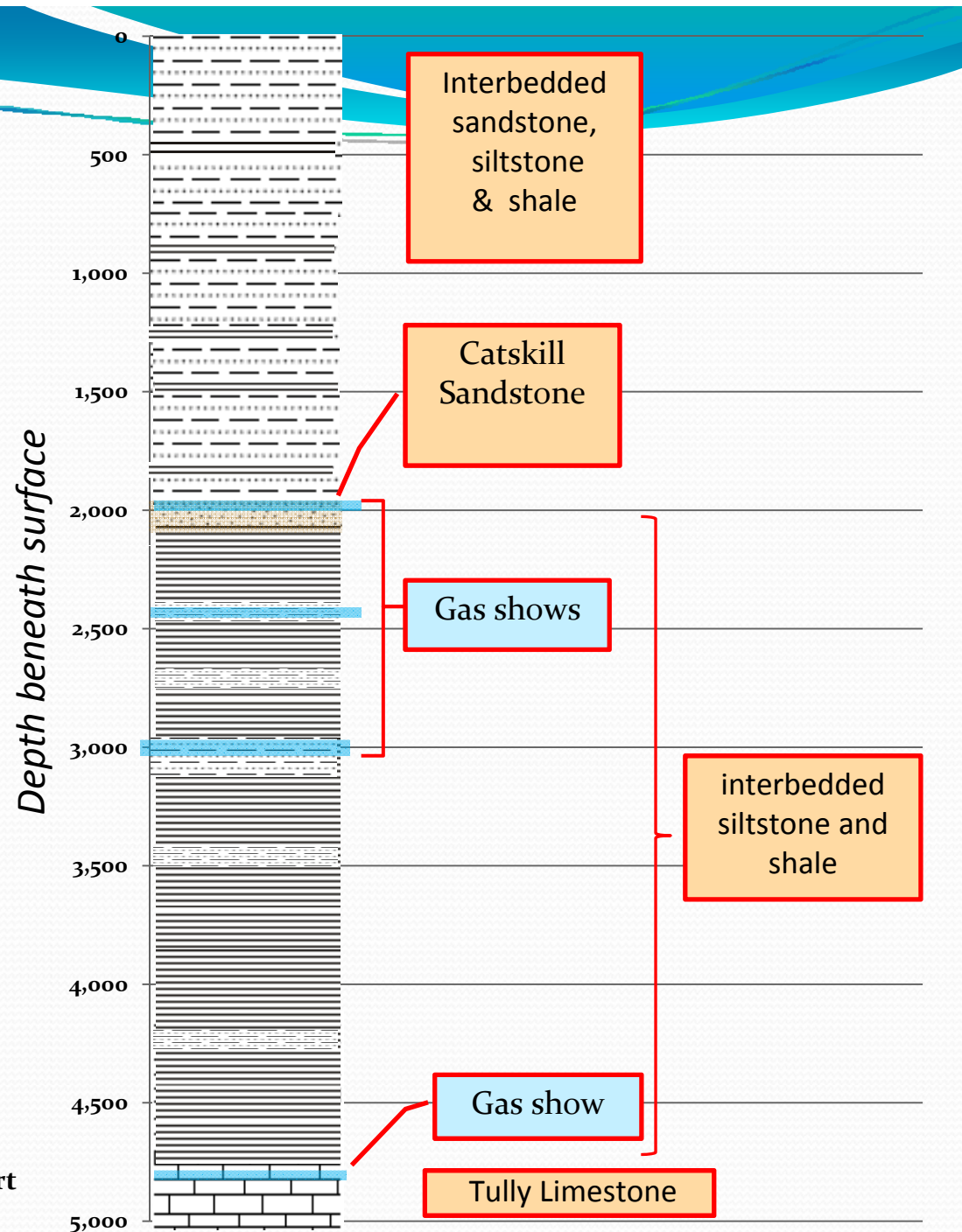






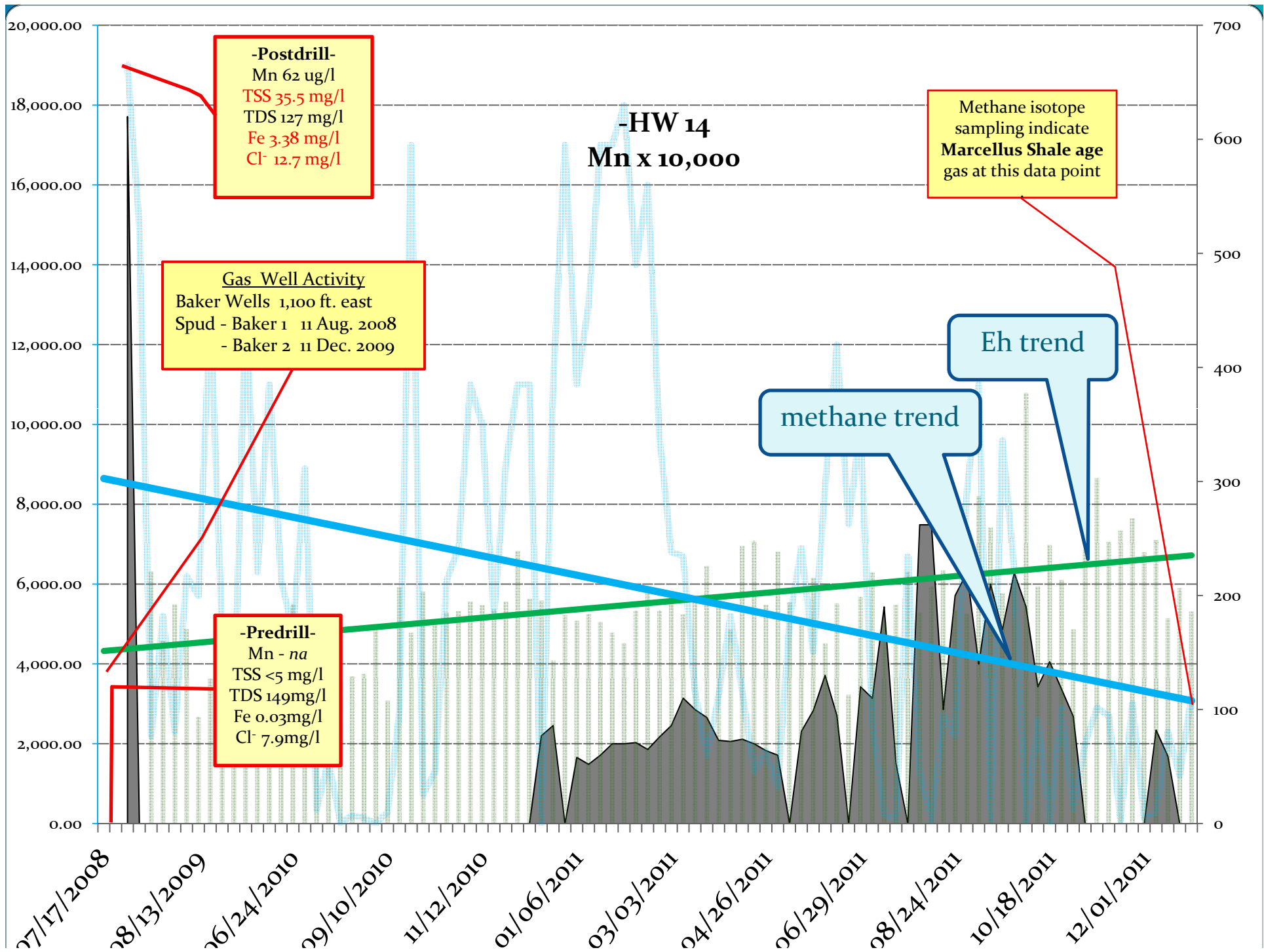
# Gas is Gas

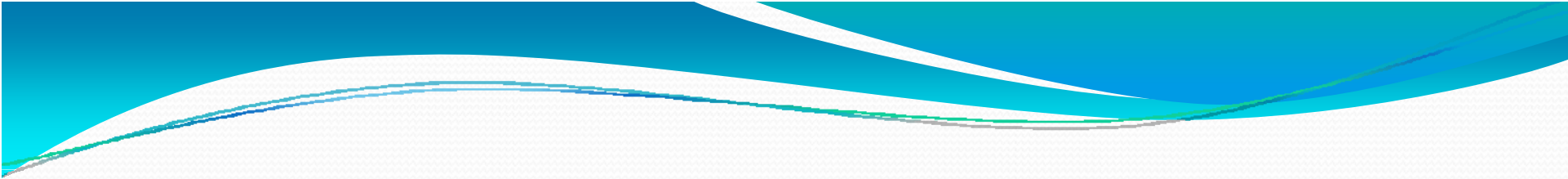
- Thermogenic gas is present throughout the upper Devonian formations. Drilling creates pathways, either temporary or permanent, that allows gas to migrate to the shallow aquifer near surface.
- Shallower (non Marcellus) gas may also include higher amounts of H<sub>2</sub>S which can have a greater impact on groundwater.
- In some cases, these gases disrupts groundwater quality



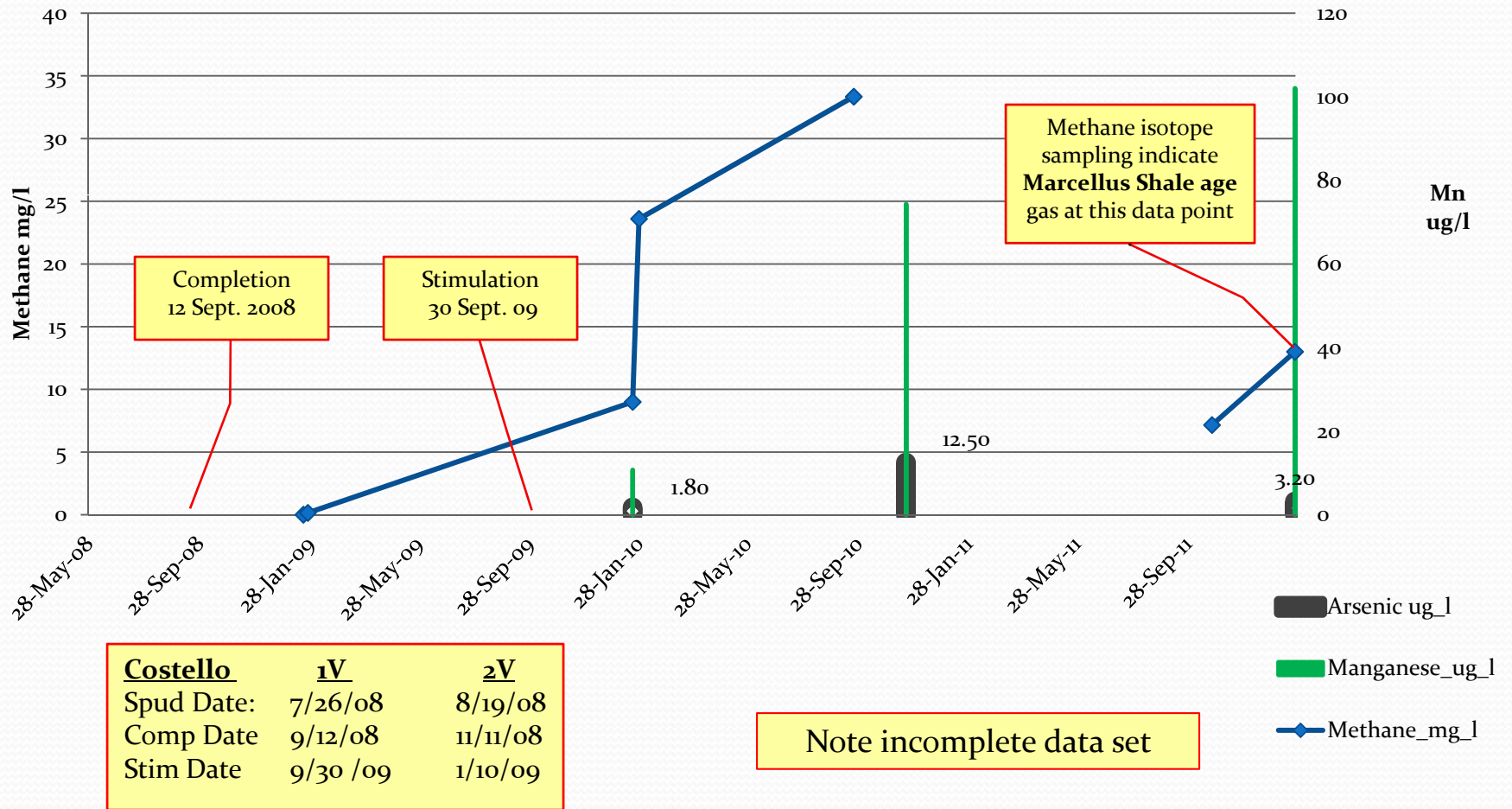
From Gesford 2 Well Record and Completion Report



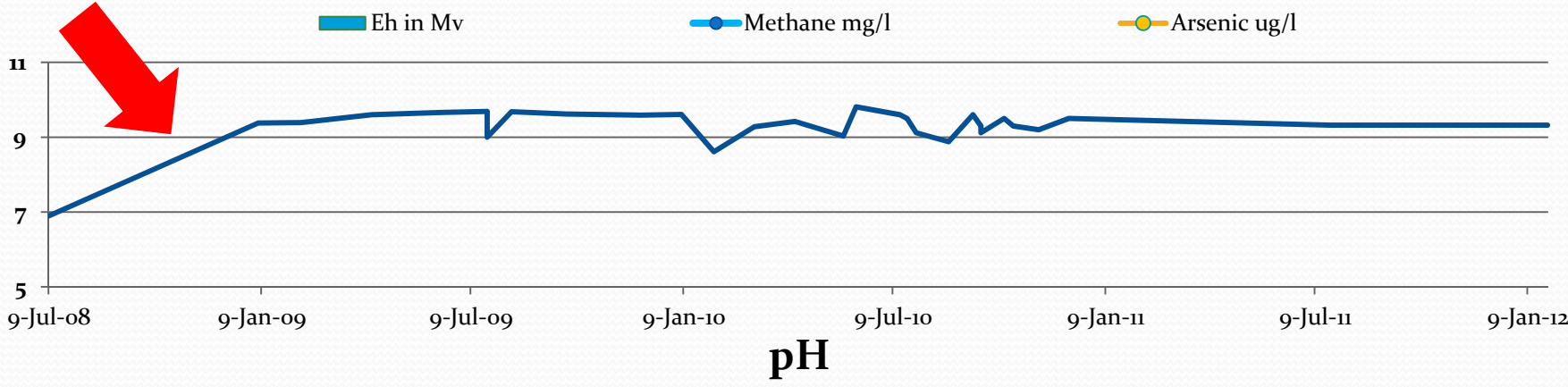
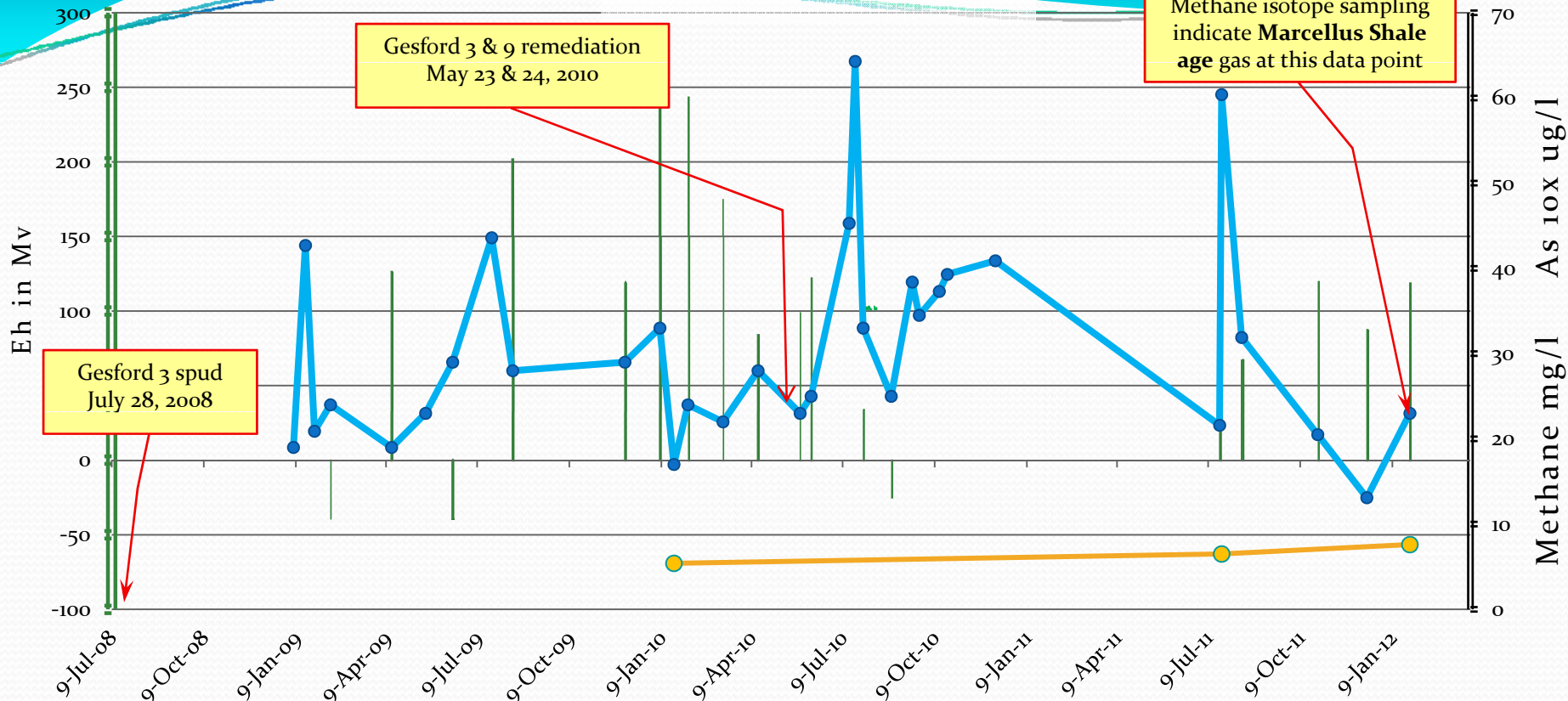




## HW-2

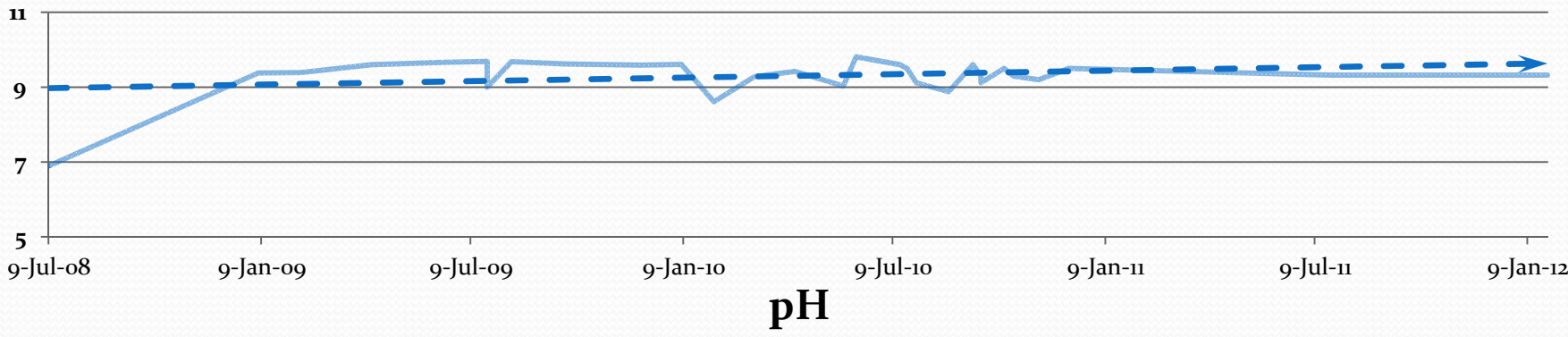
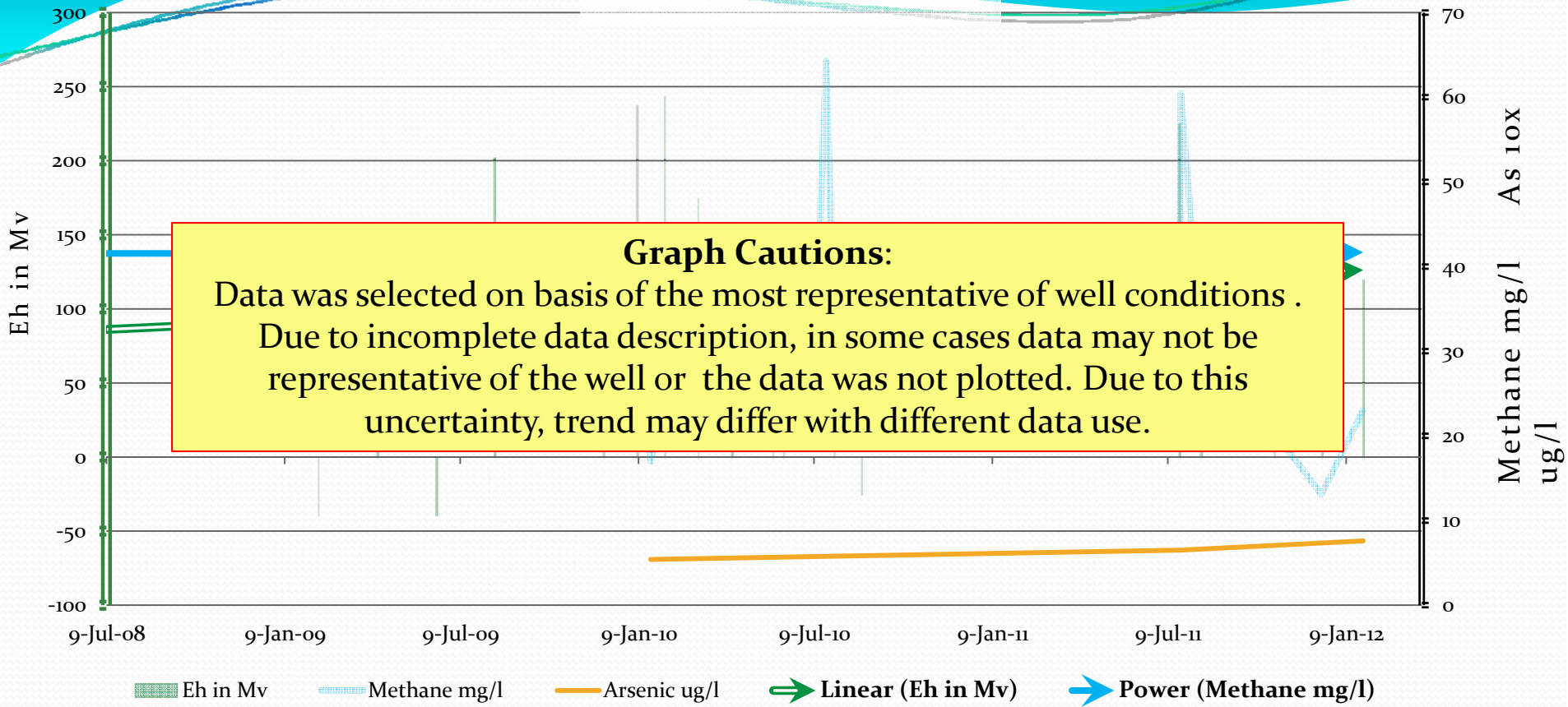


# HW6





# HW6

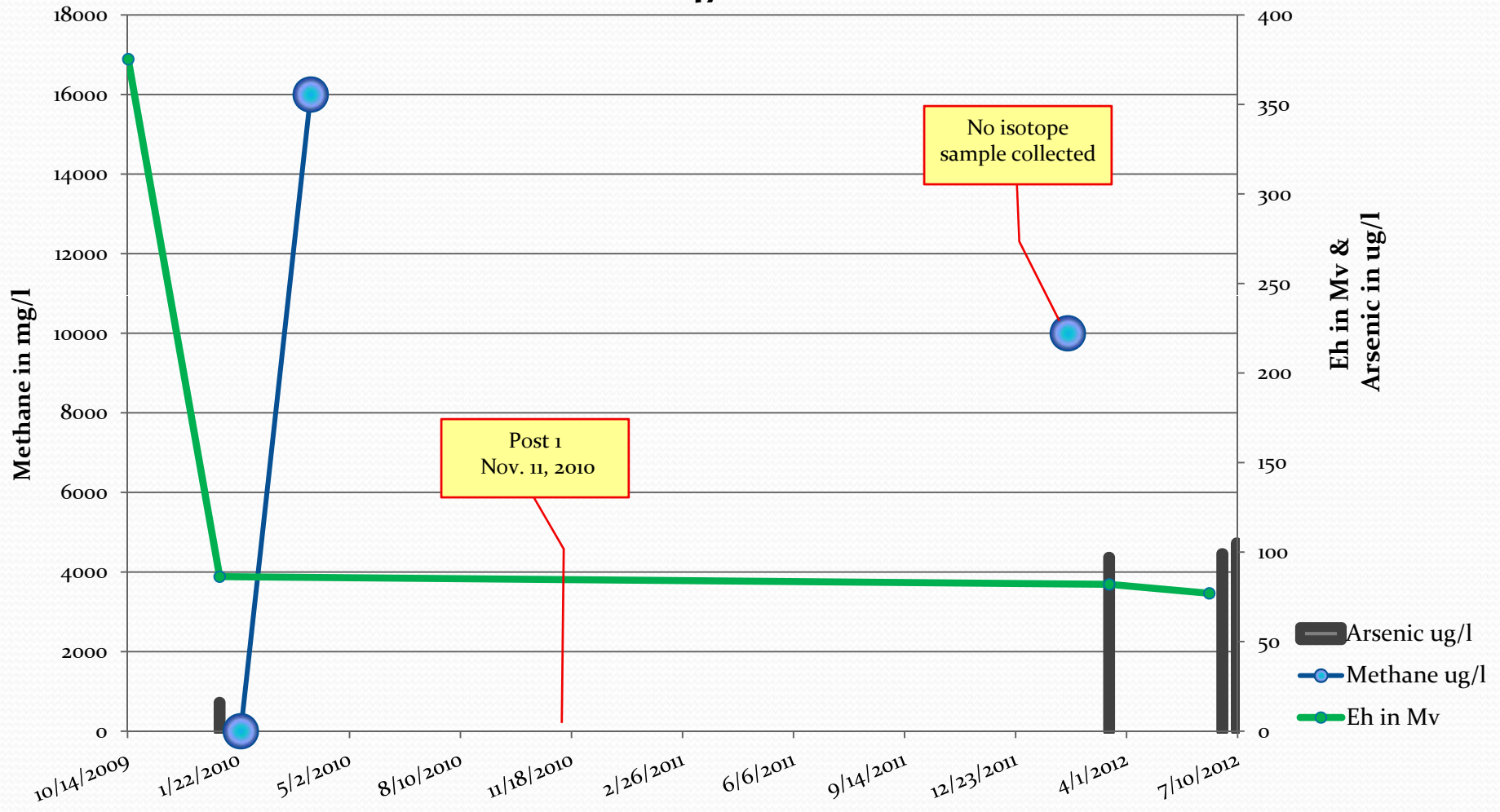




# Type 3: Naturally Occurring Contamination



# HW47 -



Post 1  
Nov. 11, 2010

No isotope  
sample collected

When no data is plotted,  
no data was available.

- Arsenic ug/l
- Methane ug/l
- Eh in Mv





# Conclusions

- Methane is released during the drilling and perhaps during the fracking process and other gas well work.
- Methane is at significantly higher concentrations in the aquifers after gas drilling and perhaps as a result of fracking and other gas well work.
- The methane migrating into the aquifer is both from the shallower (younger age) formations and older Marcellus Shale (and perhaps even older formations).
- Methane and other gases released during drilling (including air from the drilling) apparently cause significant damage to the water quality.
- In some cases the aquifers recover (under a year) but, in others cases the damage is long term (greater than 3 years).