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.

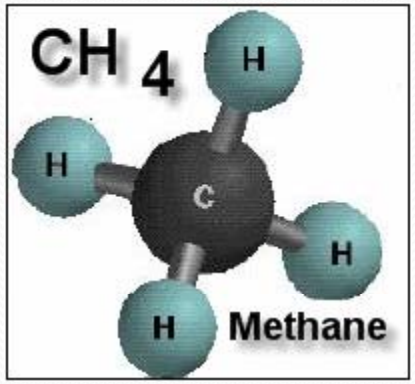
Environment of Deposition

Middle Devonian (385 MA)

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

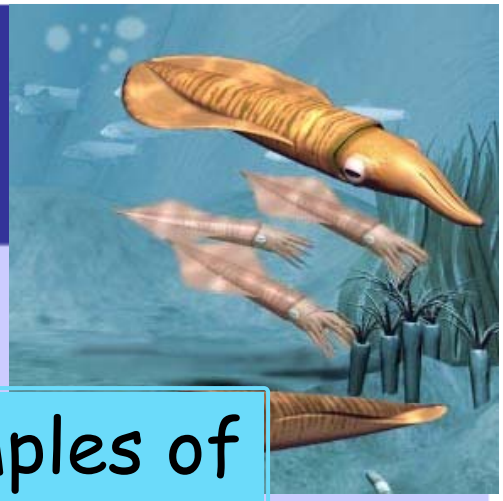
Methane is the principal hydrocarbon detected in all stray natural gas migration incidents

- Exposure limit (gas phase): TLV-TWA: 1,000 ppm (ACGIH, 10/2009)
- Methane (CH_4) 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



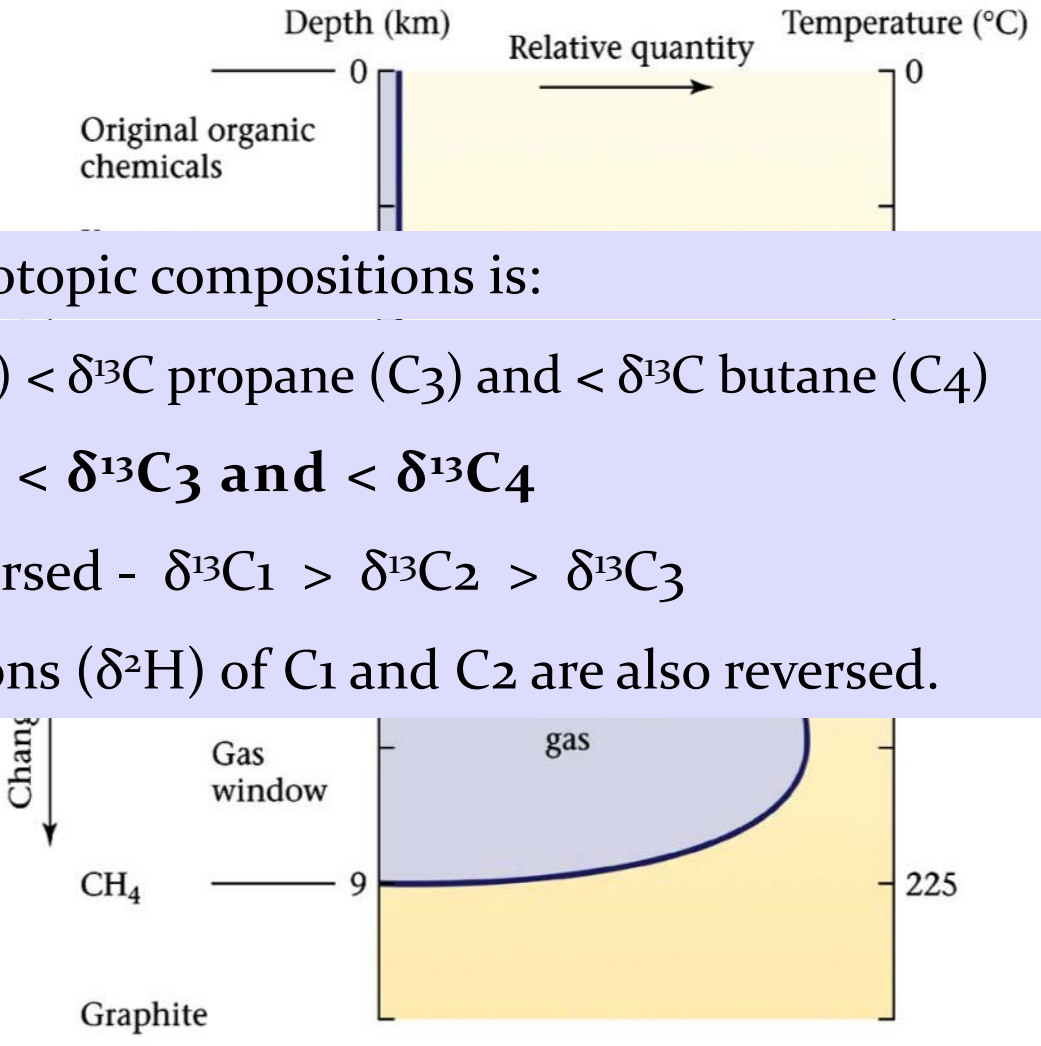
So by collecting numerous gas samples of known origin a database has been developed and fingerprinting of gas samples may performed.

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

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

Shale Gas

- Increasing formation temperature leads to diagnostic



The normal sequence of carbon isotopic compositions is:

$\delta^{13}C$ methane (C1) < $\delta^{13}C$ ethane (C2) < $\delta^{13}C$ propane (C3) and < $\delta^{13}C$ butane (C4)

$\delta^{13}C1 < \delta^{13}C2 < \delta^{13}C3$ and $< \delta^{13}C4$

In the Marcellus they are fully reversed - $\delta^{13}C1 > \delta^{13}C2 > \delta^{13}C3$

Also hydrogen isotopic compositions ($\delta^{2}H$) of C1 and C2 are also reversed.

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

Isotope Geochemistry

- Molecular: Methane/Ethane
- Isotopic: Carbon and Hydrogen isotopes ($\delta^{13}C$-CH_4, $\delta^{2}H$-CH_4, $\delta^{13}C$-C_2H_6)
- Noble Gases

Easily Distinguishes:

- ☑ 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?

ISOTECH
ISOTECH LABORATORIES INC

ANALYSIS REPORT

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

Component	Chemical mol. %	$\delta^{13}C$ ‰	δD ‰	$\delta^{18}O$ ‰
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

Total BTU/cu.ft. dry @ 60deg F & 14.7psia, calculated: 590 Specific gravity, calculated: 0.736

^{13}C fractionation

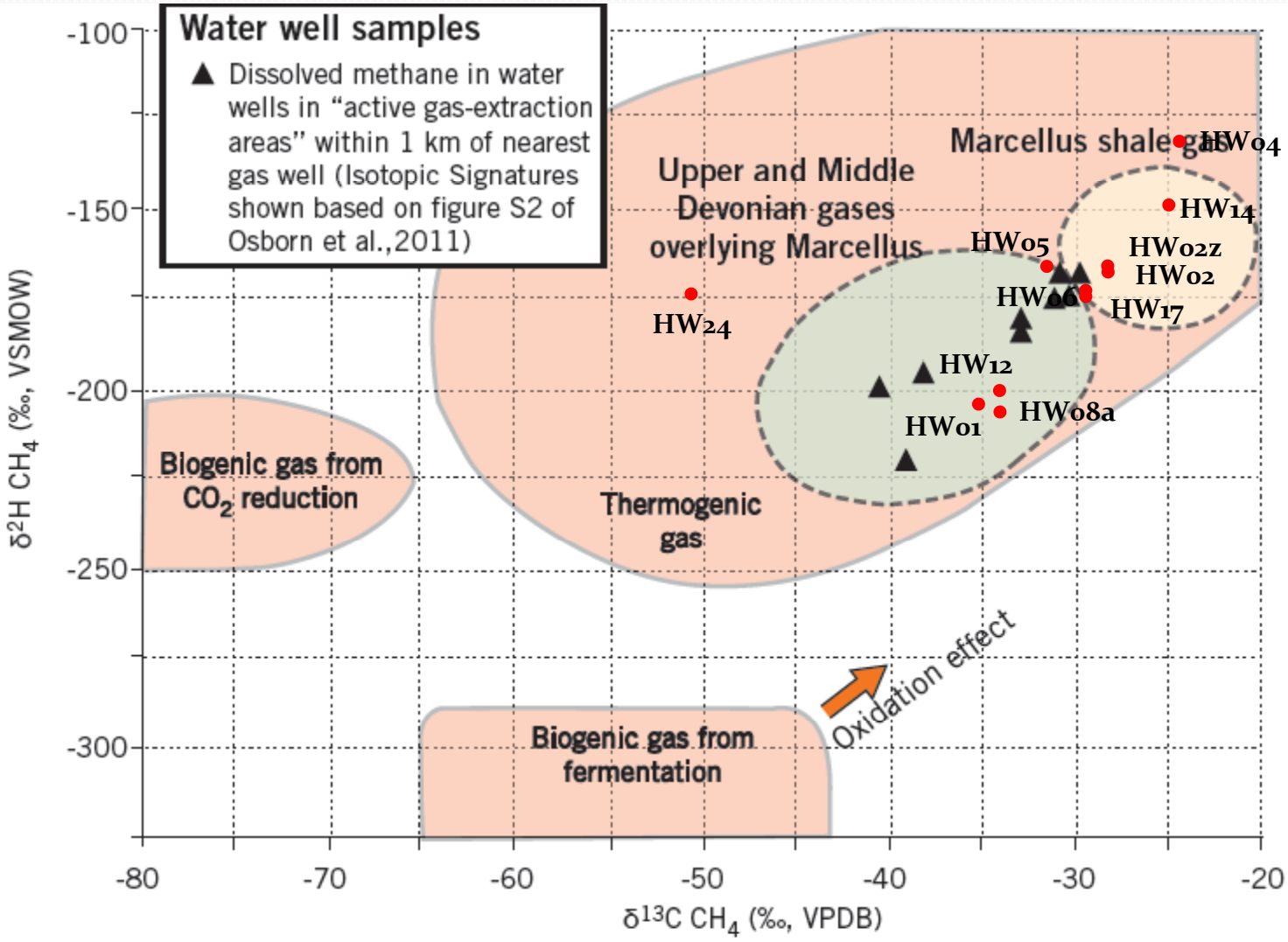
^{2}H fractionation

% argon

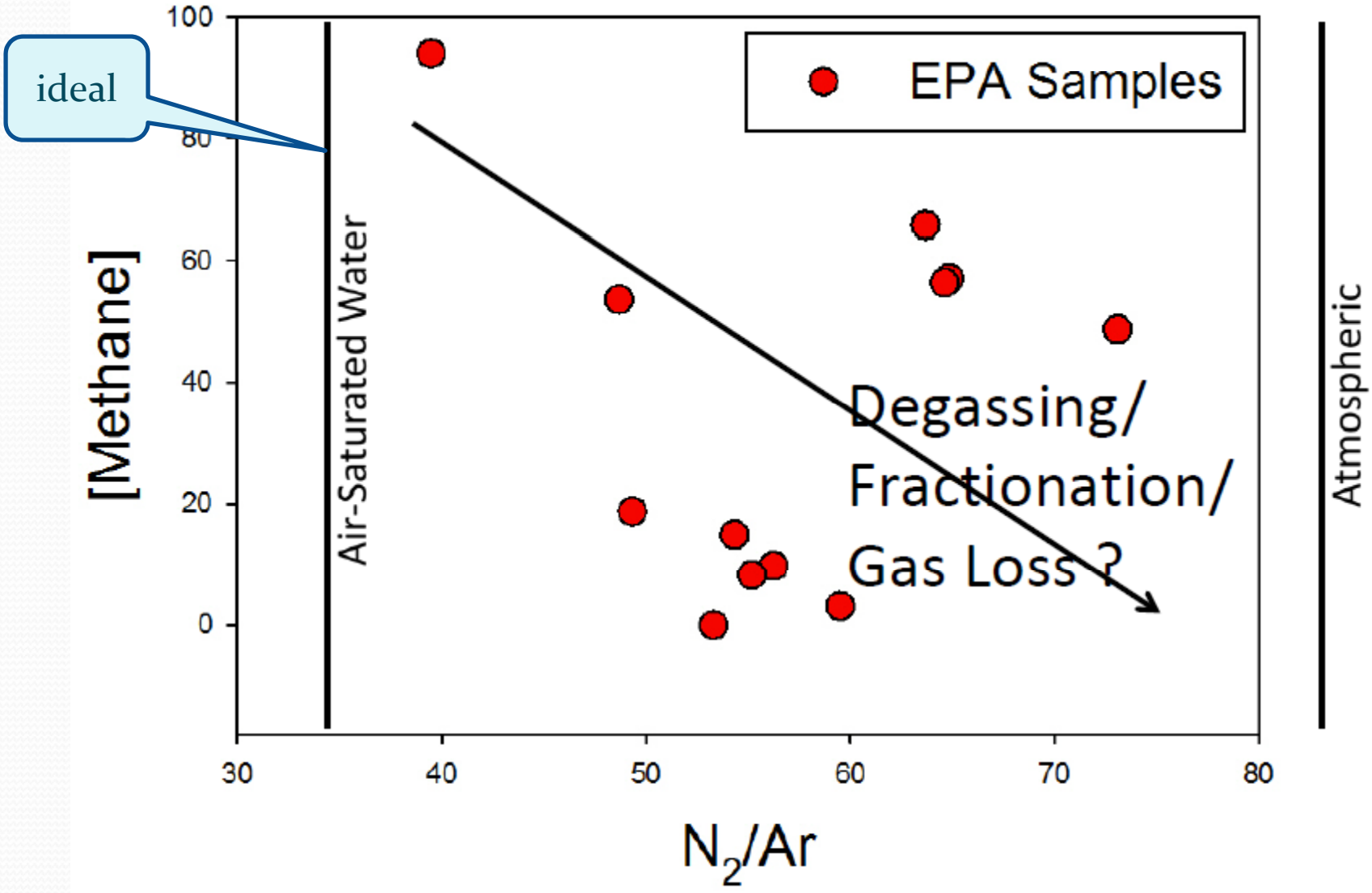
% nitrogen

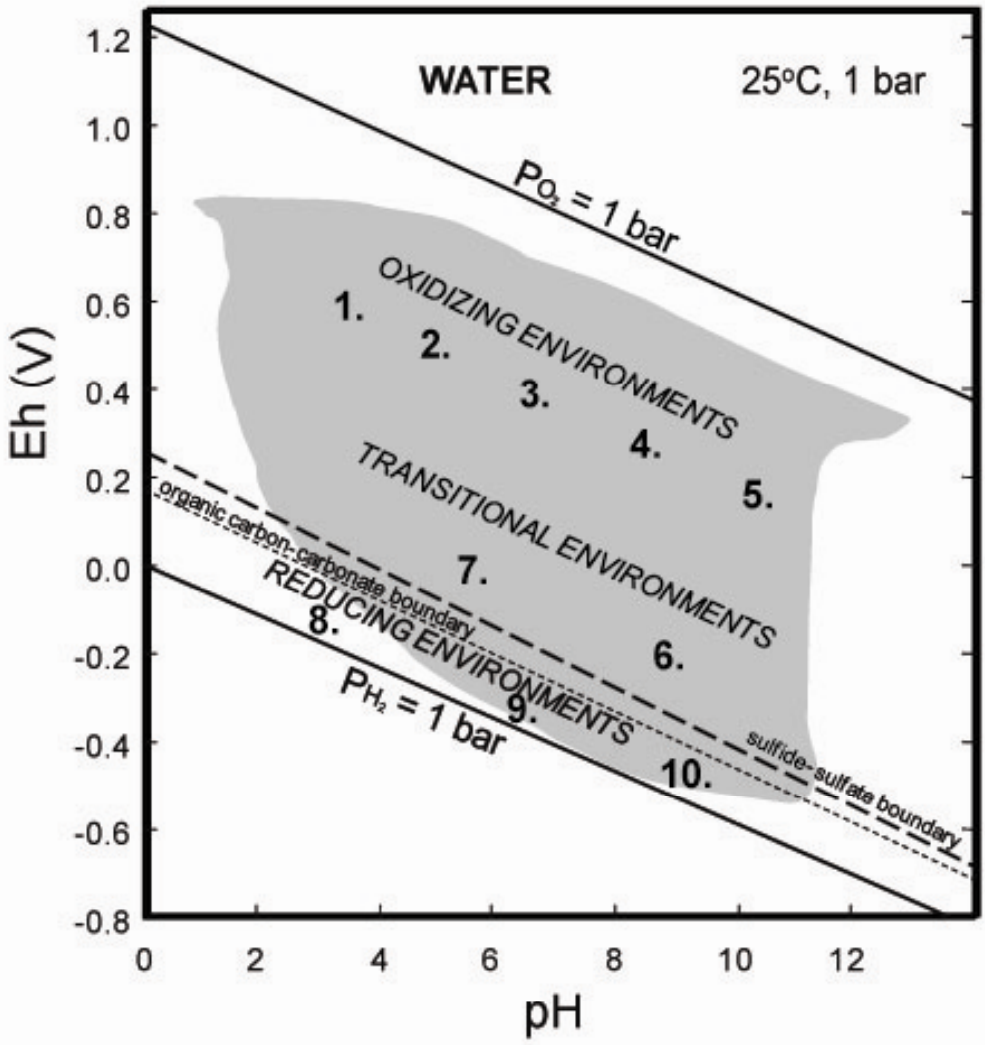
-29

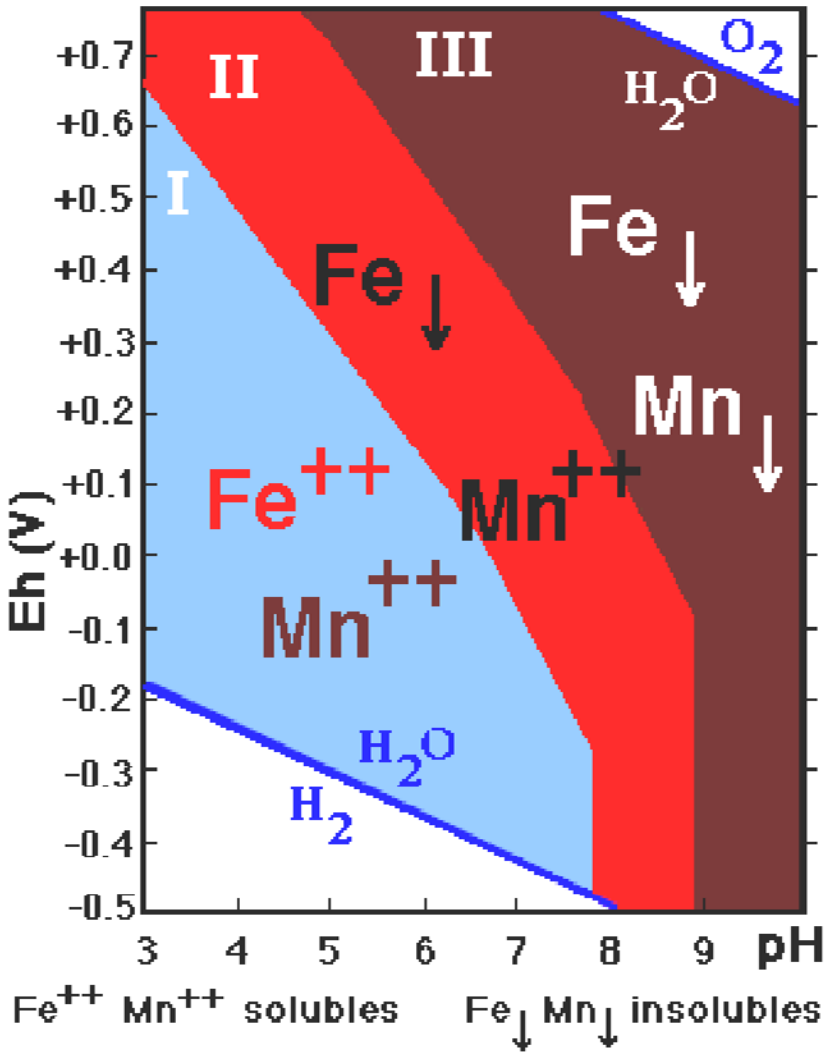
-160


Water well samples
▲ Dissolved methane in water wells in "active gas-extraction areas" within 1 km of nearest gas well (Isotopic Signatures shown based on figure S2 of Osborn et al.,2011)
Marcellus shale gas
Upper and Middle Devonian gases overlying Marcellus
Biogenic gas from CO_2 reduction
Thermogenic gas
Biogenic gas from fermentation
Oxidation effect
HW04
HW14
HW05
HW02z
HW02
HW06
HW17
HW24
HW12
HW08a
HW01
-100
-150
-200
-250
-300
-80
-70
-60
-50
-40
-30
-20
$\delta^2H\ CH_4$ (‰, VSMOW)
$\delta^{13}C\ CH_4$ (‰, VPDB)

Sample Quality - degassing?



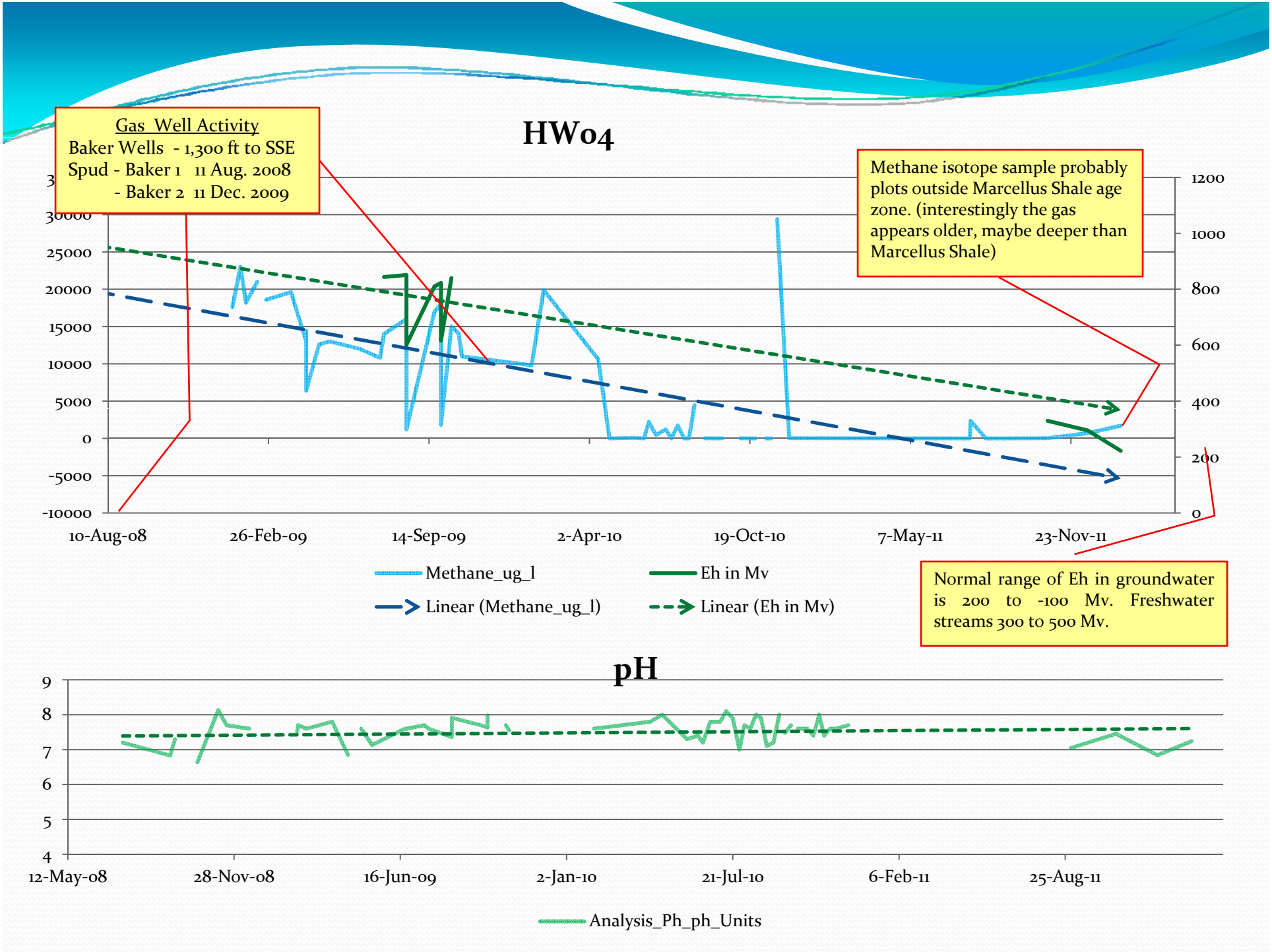

WATER
25°C, 1 bar
P_{O_2} = 1 bar
OXIDIZING ENVIRONMENTS
1.
2.
3.
4.
5.
TRANSITIONAL ENVIRONMENTS
organic carbon-carbonate boundary
7.
REDUCING ENVIRONMENTS
8.
6.
9.
P_{H_2} = 1 bar
sulfide-sulfate boundary
10.
Eh (V)
pH
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
-0.4
-0.6
-0.8
0
2
4
6
8
10
12

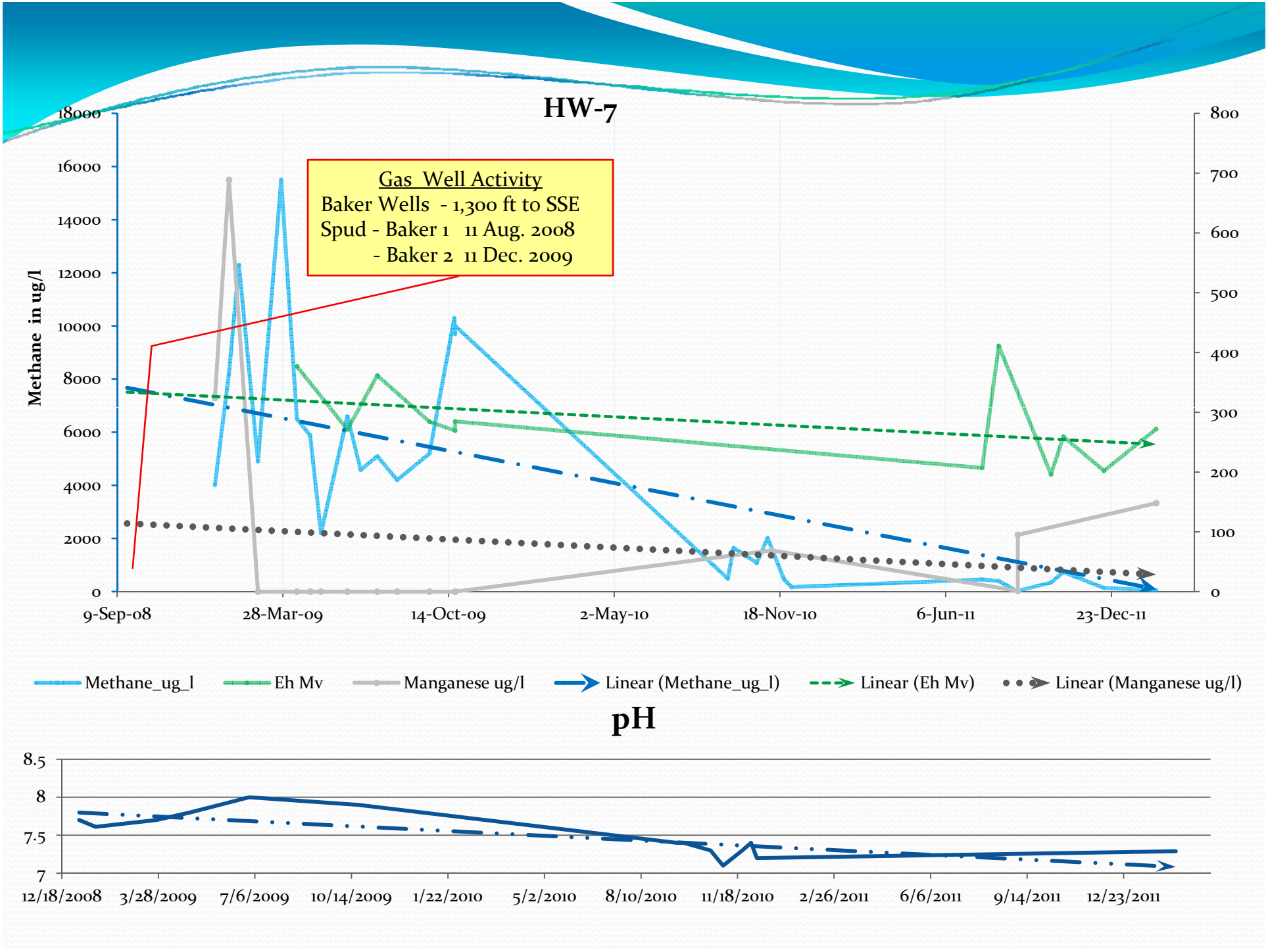

II
III
O_2
H_2O
I
$Fe_{\downarrow}$
$Mn_{\downarrow}$
Fe^{++}
Mn^{++}
Mn^{++}
H_2O
H_2
Eh (V)
+0.7
+0.6
+0.5
+0.4
+0.3
+0.2
+0.1
+0.0
-0.1
-0.2
-0.3
-0.4
-0.5
3
4
5
6
7
8
9
pH
Fe^{++} Mn^{++} solubles
$Fe_{\downarrow}$ $Mn_{\downarrow}$ insolubles

Three Patterns of Contamination

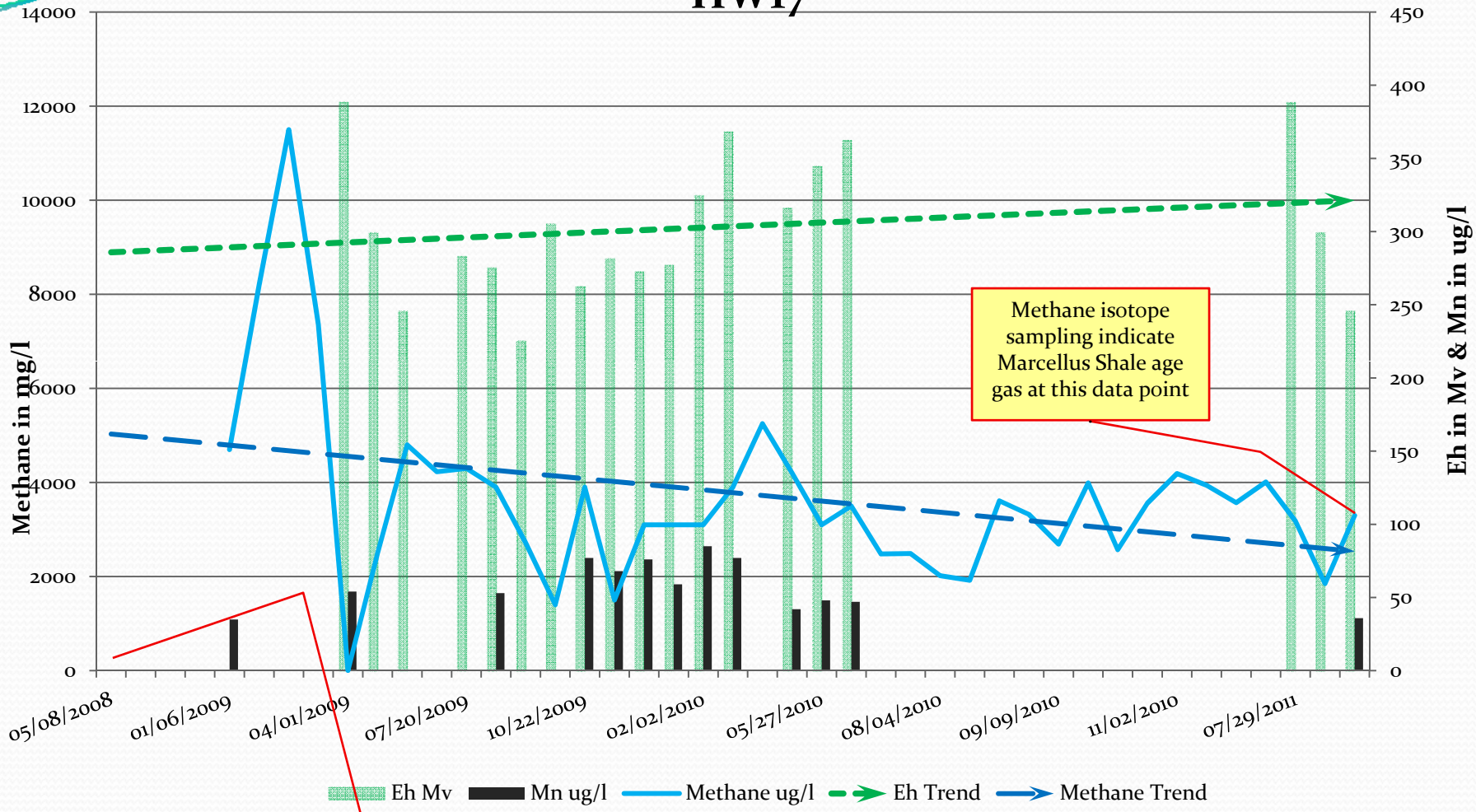
1. **Short term** (< 1 year) disruption to the aquifer caused by drilling.
2. **Long term** (> 3-4 year) disruption or contamination of the aquifer caused by drilling/fracking, releases or other situations.
3. **Natural Background Conditions** with high levels of metals and anions.

Type 1: Short Term Disruption


HW04
Gas Well Activity
Baker Wells - 1,300 ft to SSE
Spud - Baker 1 11 Aug. 2008
- Baker 2 11 Dec. 2009
Methane isotope sample probably plots outside Marcellus Shale age zone. (interestingly the gas appears older, maybe deeper than Marcellus Shale)
30000
25000
20000
15000
10000
5000
0
-5000
-10000
1200
1000
800
600
400
200
0
10-Aug-08
26-Feb-09
14-Sep-09
2-Apr-10
19-Oct-10
7-May-11
23-Nov-11
Methane_ug_l
Eh in Mv
Linear (Methane_ug_l)
Linear (Eh in Mv)
Normal range of Eh in groundwater is 200 to -100 Mv. Freshwater streams 300 to 500 Mv.
pH
9
8
7
6
5
4
12-May-08
28-Nov-08
16-Jun-09
2-Jan-10
21-Jul-10
6-Feb-11
25-Aug-11
Analysis_Ph_ph_Units


HW-7
Gas Well Activity
Baker Wells - 1,300 ft to SSE
Spud - Baker 1 11 Aug. 2008
- Baker 2 11 Dec. 2009
Methane in ug/l
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
800
700
600
500
400
300
200
100
0
9-Sep-08
28-Mar-09
14-Oct-09
2-May-10
18-Nov-10
6-Jun-11
23-Dec-11
Methane_ug_l
Eh Mv
Manganese ug/l
Linear (Methane_ug_l)
Linear (Eh Mv)
Linear (Manganese ug/l)
pH
8.5
8
7.5
7
12/18/2008
3/28/2009
7/6/2009
10/14/2009
1/22/2010
5/2/2010
8/10/2010
11/18/2010
2/26/2011
6/6/2011
9/14/2011
12/23/2011

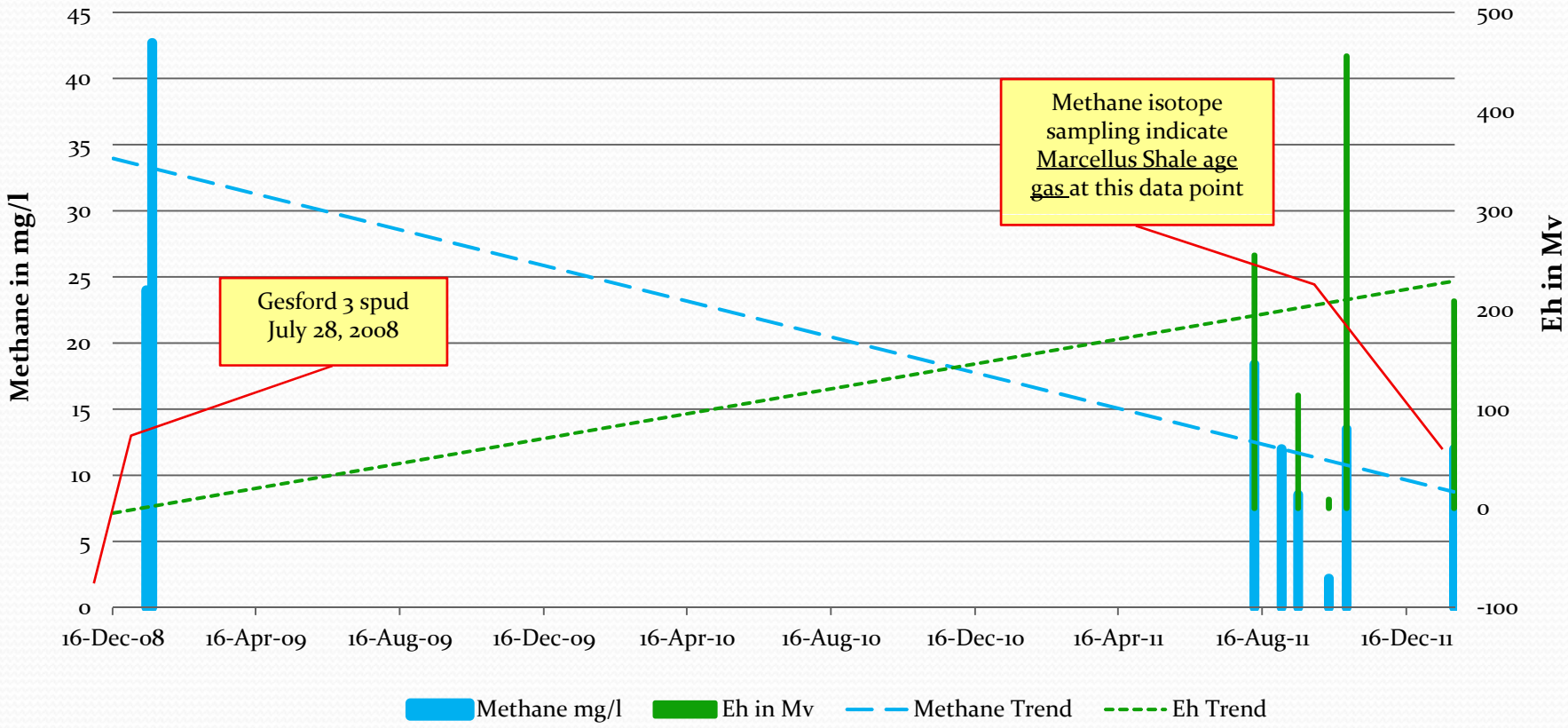
HW17



Gas Well	Date Spud	Distance to HW17
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

HW1 - Hubert

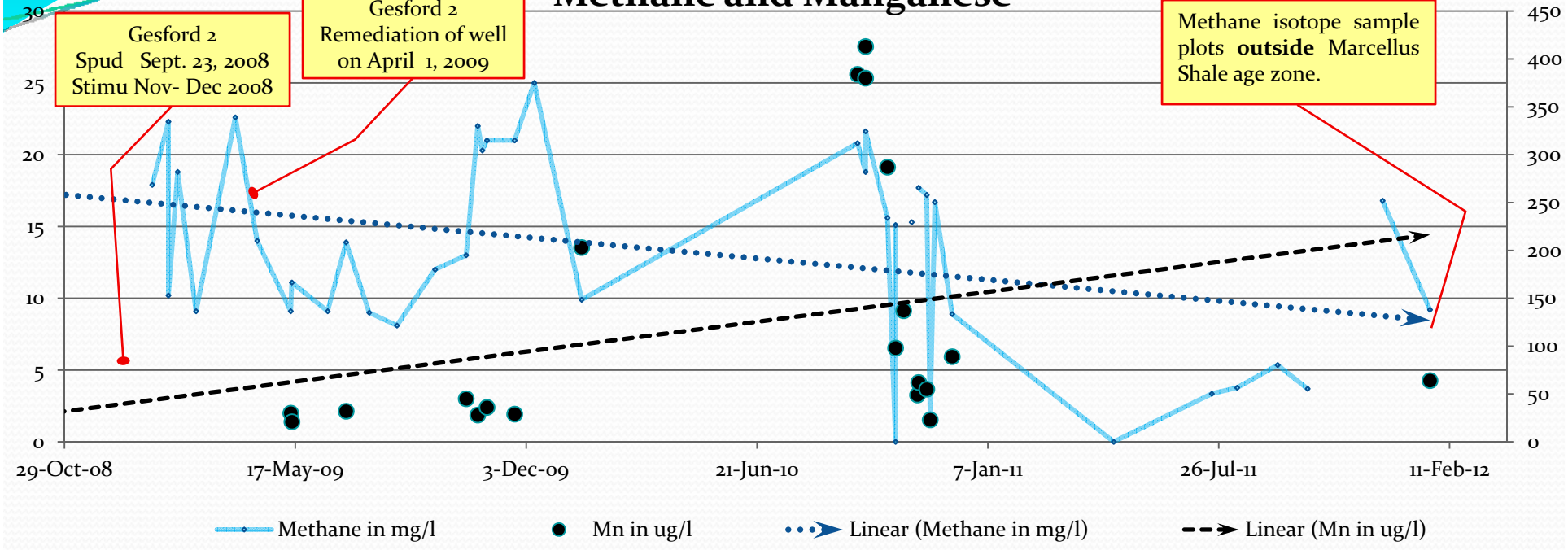


HW1 lacked data for nearly all constituents, particularly for the years 2009-2010

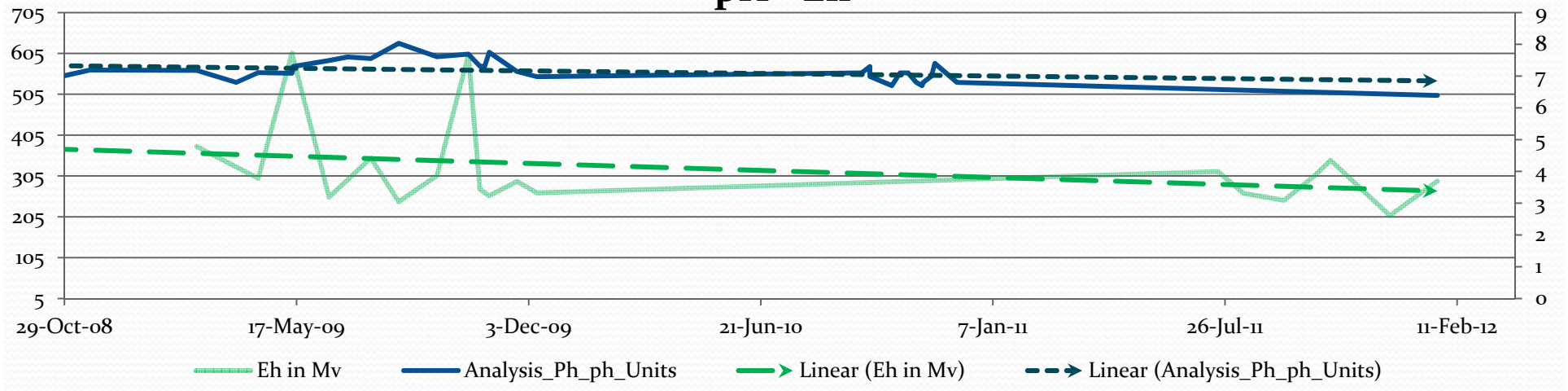
Type 2: Long Term Disruption

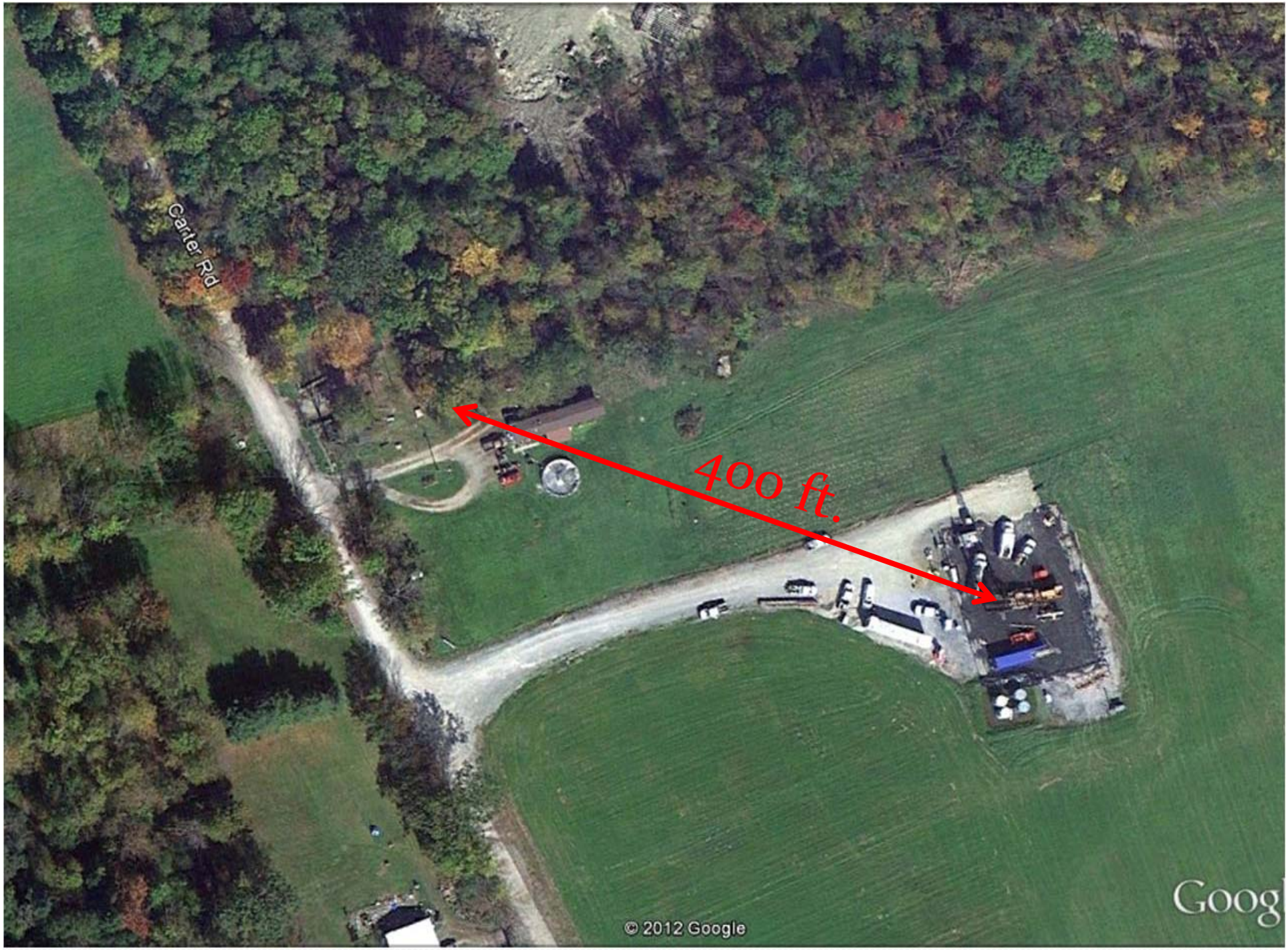
HW8

Methane and Manganese



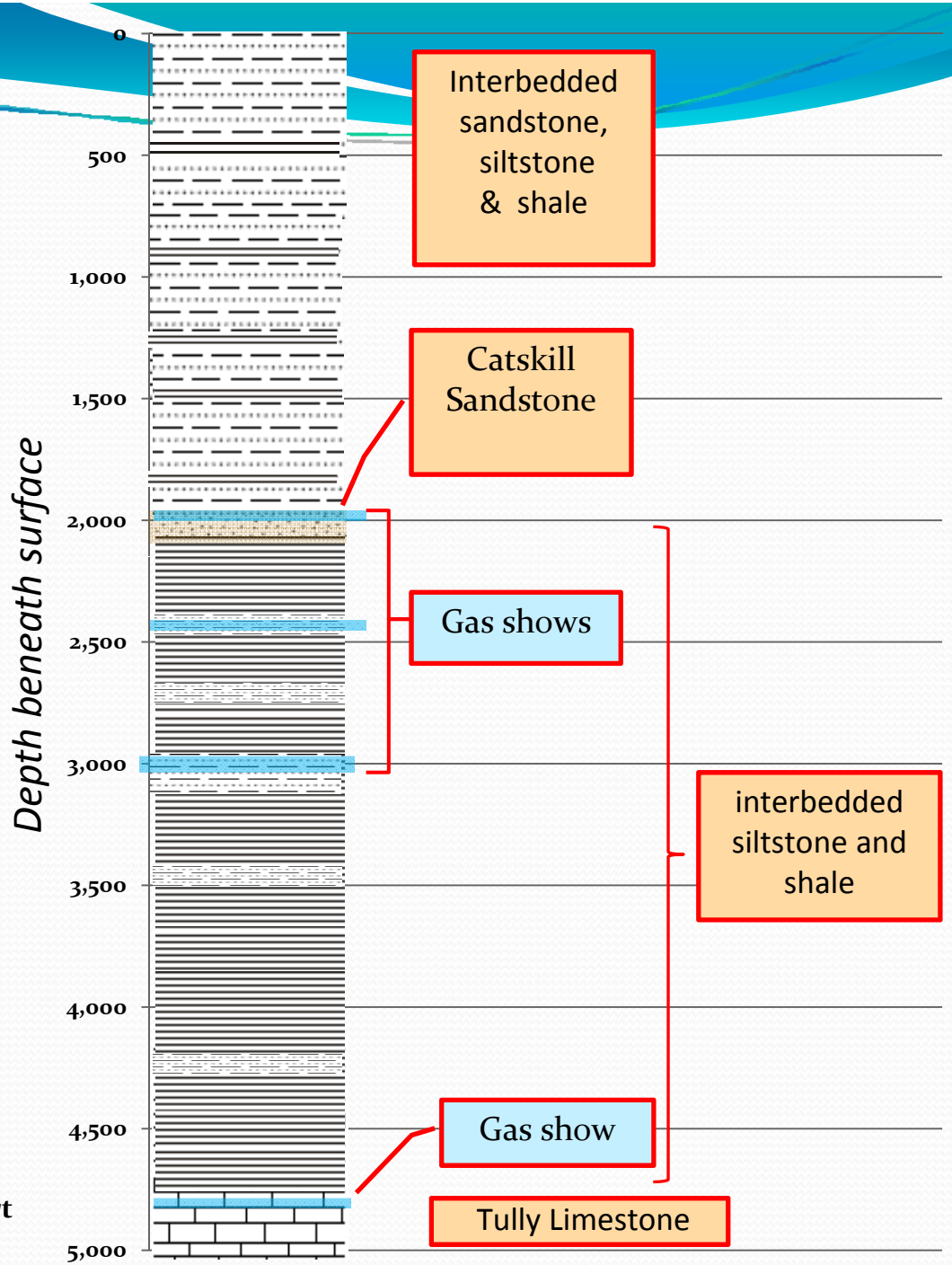
pH - Eh



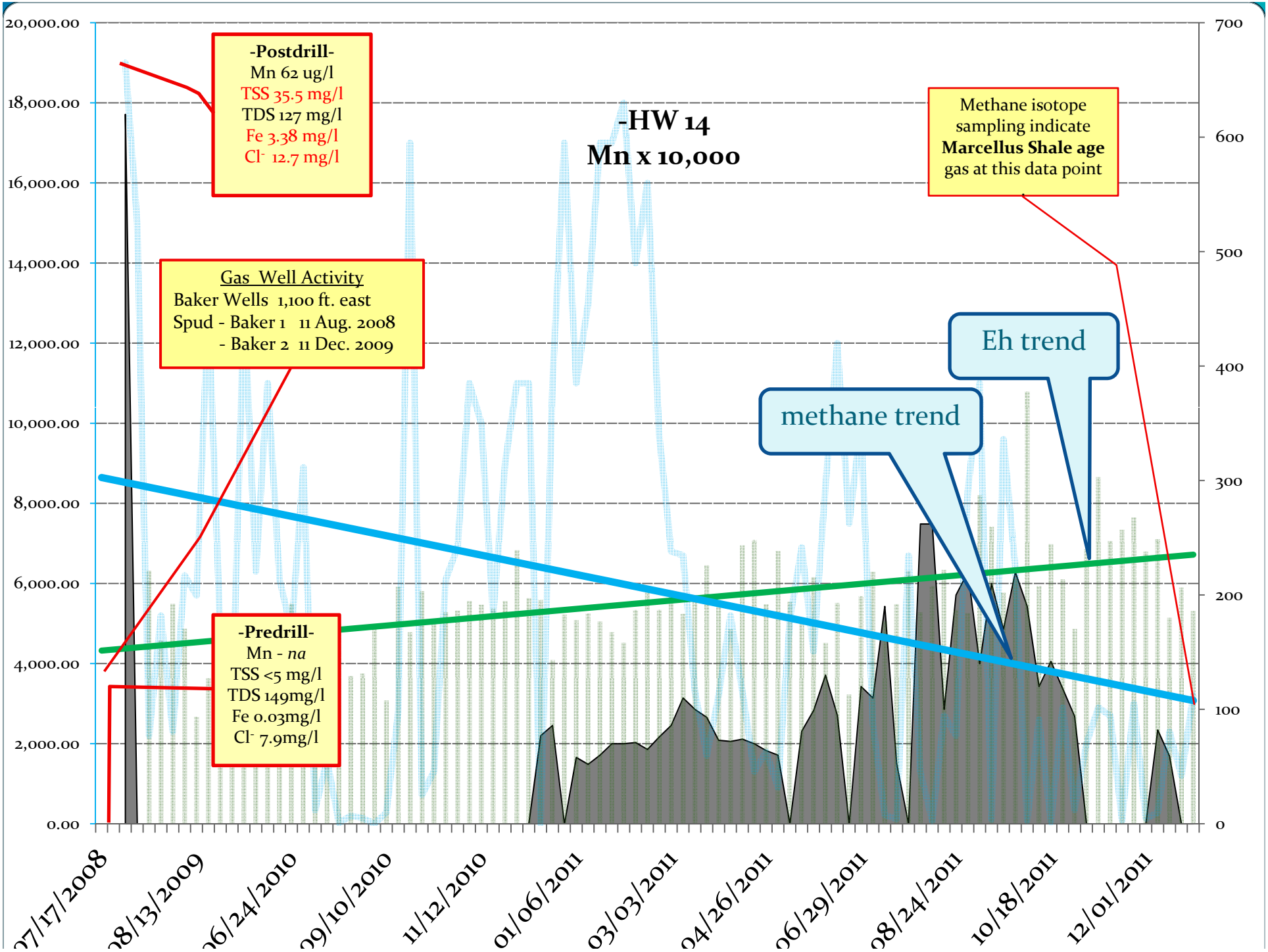

Carter Rd
400 ft.
© 2012 Google

Gas is Gas

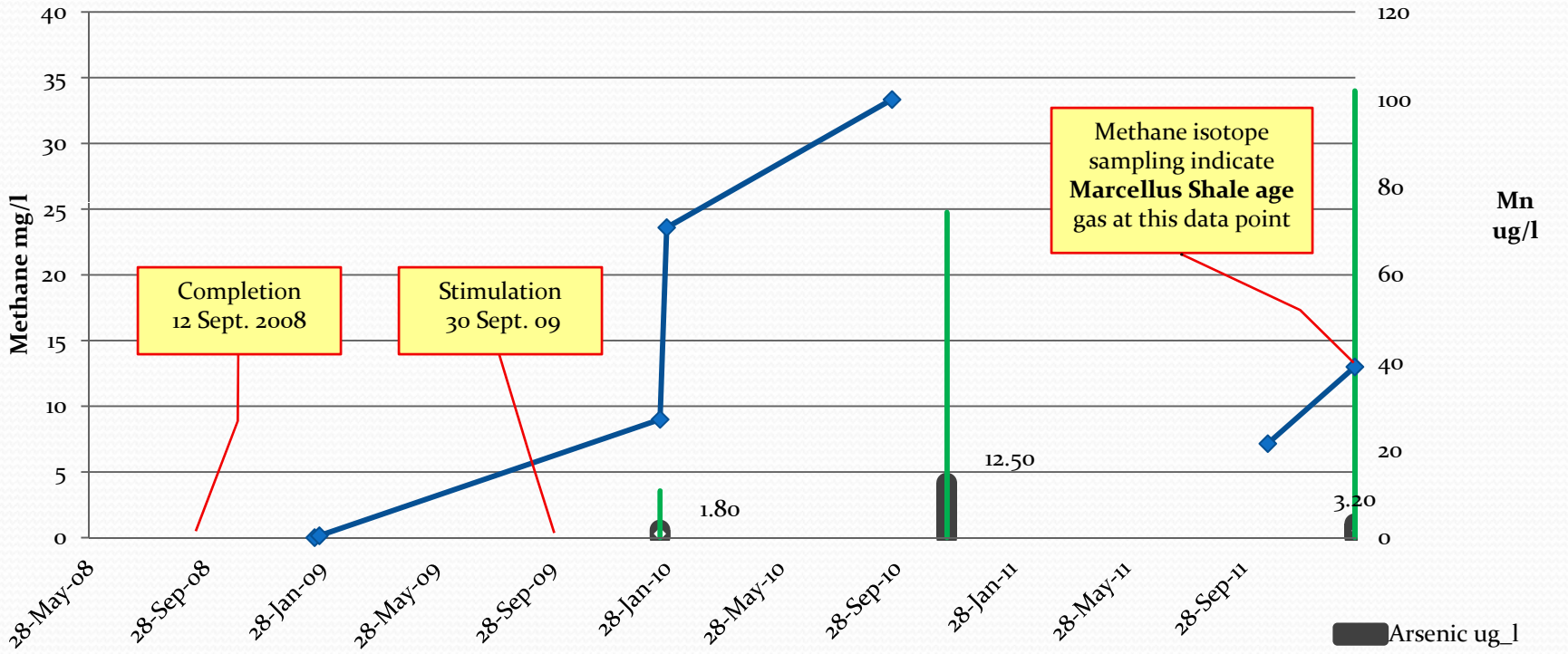
- Thermogenic gas is present throughout the upper Devonian formations. Drilling creates pathways, either temporary or permanent, that allows gas to migrate to the shallow aquifer near surface.
- Shallower (non Marcellus) gas may also include higher amounts of H_2S which can have a greater impact on groundwater.
- In some cases, these gases disrupts groundwater quality



From Gesford 2 Well Record and Completion Report

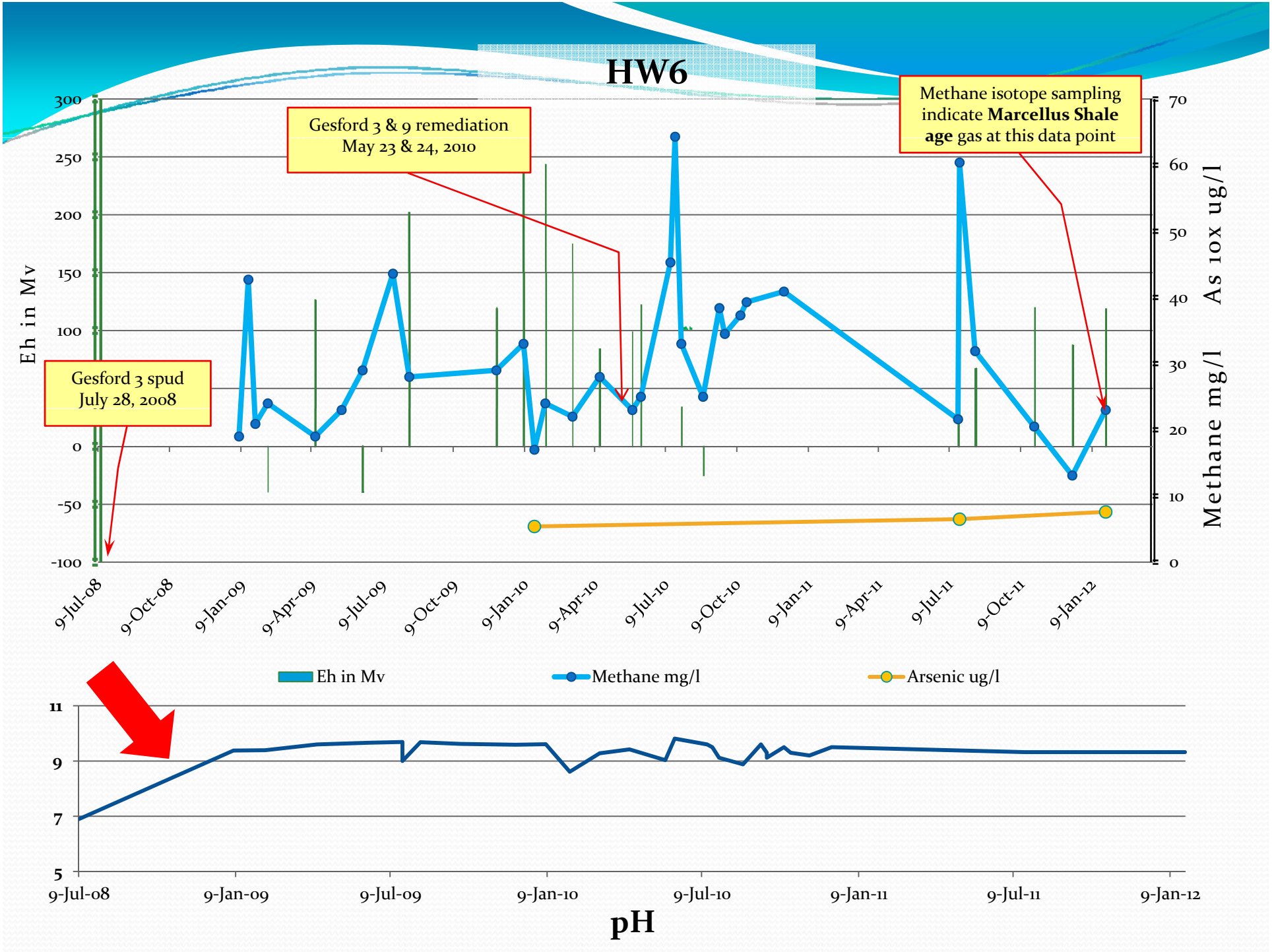

-Postdrill-
Mn 62 ug/l
TSS 35.5 mg/l
TDS 127 mg/l
Fe 3.38 mg/l
Cl- 12.7 mg/l
-HW 14
Mn x 10,000
Methane isotope sampling indicate Marcellus Shale age gas at this data point
Gas Well Activity
Baker Wells 1,100 ft. east
Spud - Baker 1 11 Aug. 2008
- Baker 2 11 Dec. 2009
Eh trend
methane trend
-Predrill-
Mn - na
TSS <5 mg/l
TDS 149mg/l
Fe 0.03mg/l
Cl- 7.9mg/l
20,000.00
18,000.00
16,000.00
14,000.00
12,000.00
10,000.00
8,000.00
6,000.00
4,000.00
2,000.00
0.00
700
600
500
400
300
200
100
0
07/17/2008
08/13/2009
06/24/2010
09/10/2010
11/12/2010
01/06/2011
03/03/2011
04/26/2011
06/29/2011
08/24/2011
10/18/2011
12/01/2011

HW-2

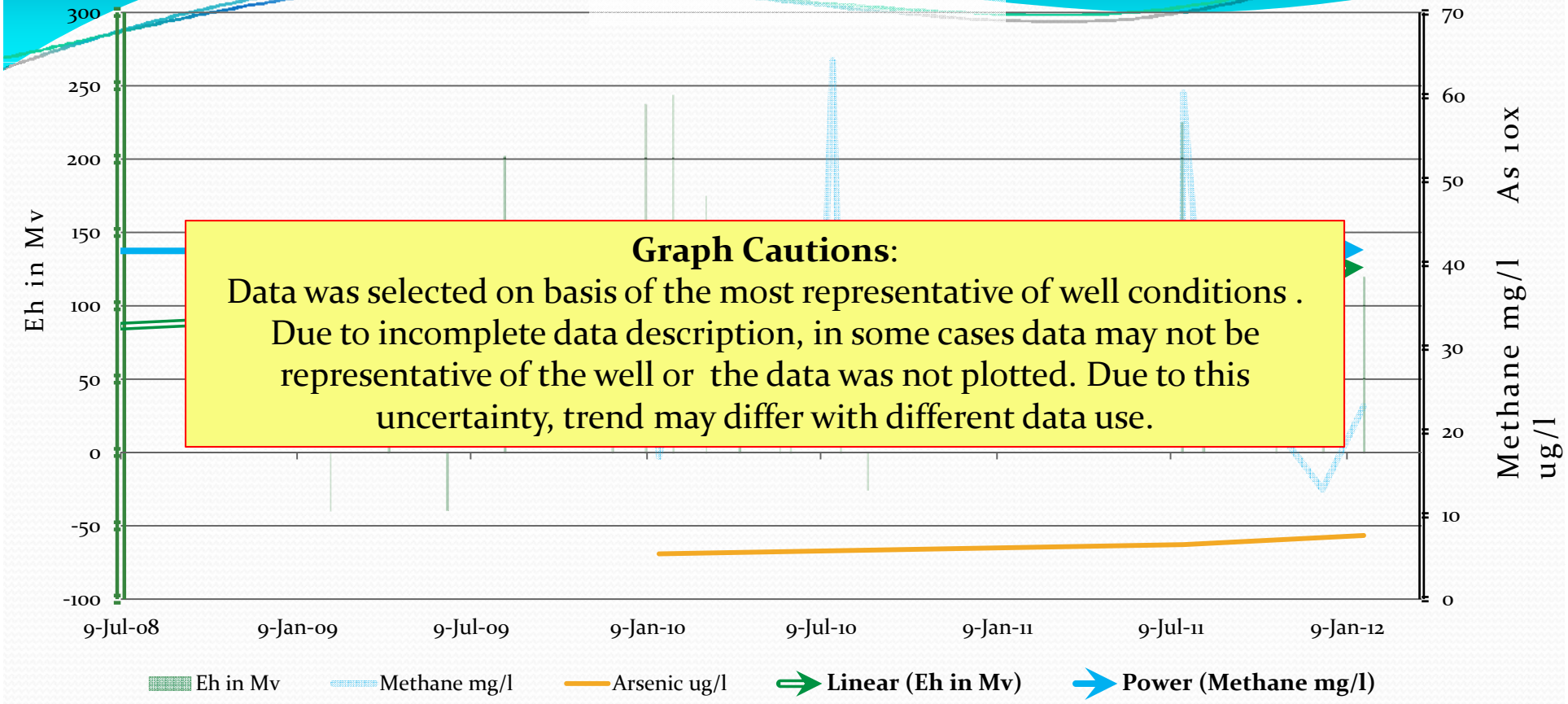


Costello	**1V**	**2V**
Spud Date:	7/26/08	8/19/08
Comp Date	9/12/08	11/11/08
Stim Date	9/30 /09	1/10/09

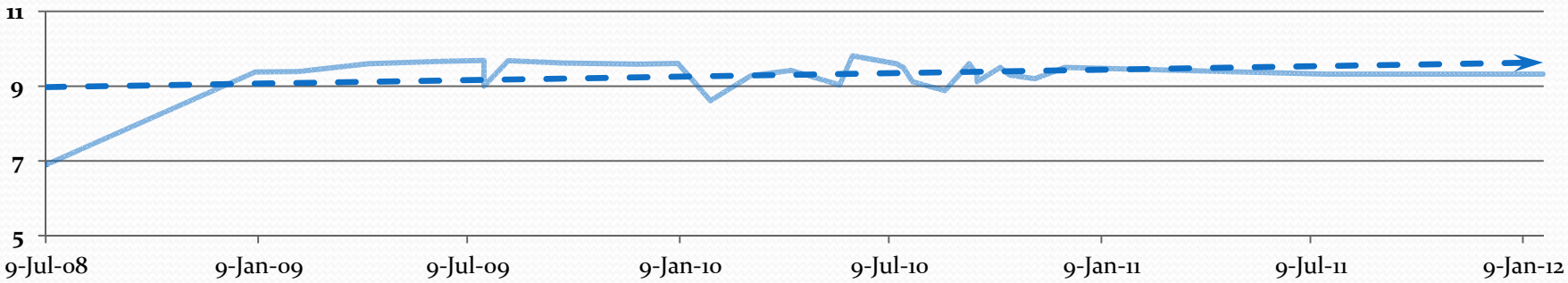
Note incomplete data set


HW6
Gesford 3 & 9 remediation
May 23 & 24, 2010
Methane isotope sampling indicate **Marcellus Shale age** gas at this data point
Gesford 3 spud
July 28, 2008
Eh in Mv
Methane mg/l
As 10x ug/l
300
250
200
150
100
0
-50
-100
70
60
50
40
30
20
10
0
9-Jul-08
9-Oct-08
9-Jan-09
9-Apr-09
9-Jul-09
9-Oct-09
9-Jan-10
9-Apr-10
9-Jul-10
9-Oct-10
9-Jan-11
9-Apr-11
9-Jul-11
9-Oct-11
9-Jan-12
Eh in Mv
Methane mg/l
Arsenic ug/l
11
9
7
5
9-Jul-08
9-Jan-09
9-Jul-09
9-Jan-10
9-Jul-10
9-Jan-11
9-Jul-11
9-Jan-12
pH

HW6



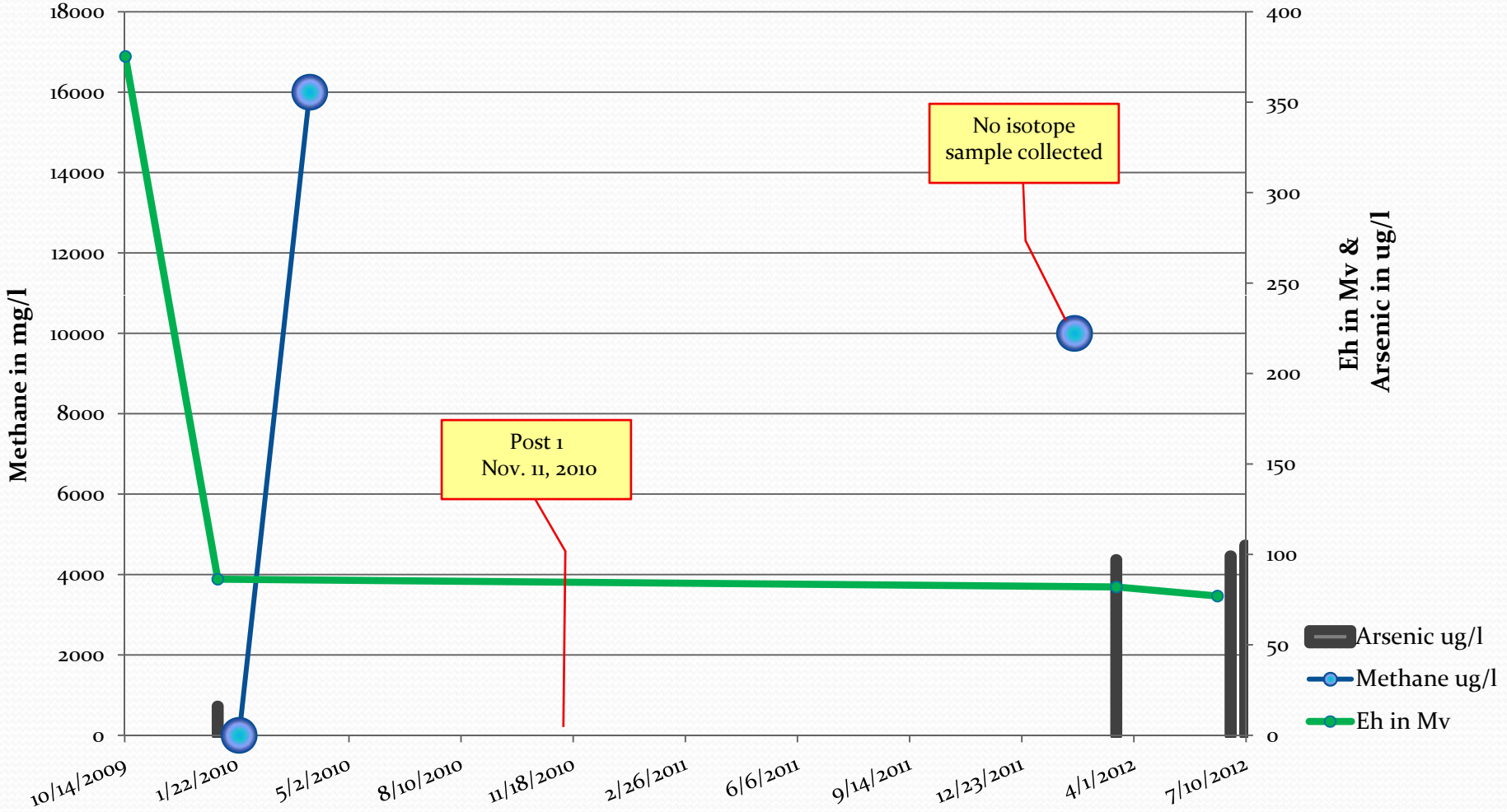
Graph Cautions:
Data was selected on basis of the most representative of well conditions . Due to incomplete data description, in some cases data may not be representative of the well or the data was not plotted. Due to this uncertainty, trend may differ with different data use.



pH

Type 3: Naturally Occurring Contamination

HW47 -



When no data is plotted, no data was available.

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).