Isotech - Stable Isotope Analysis

Determining the origin of methane

DIM0289725

Environment of Deposition

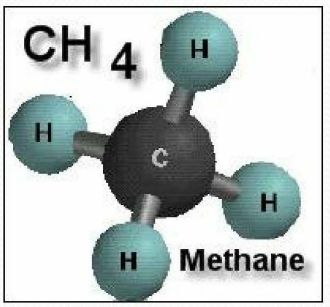
Middle Devonian (385 MA)

DIM0289725

DIM0289727

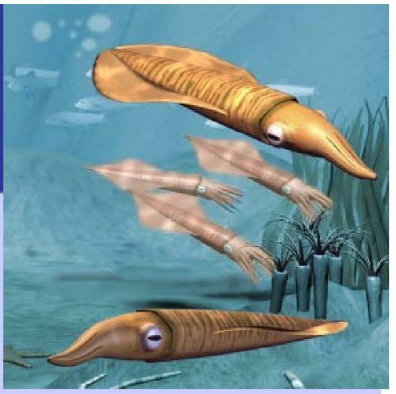
Methane is the principal hydrocarbon detected in all stray natural gas migration incidents

- 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



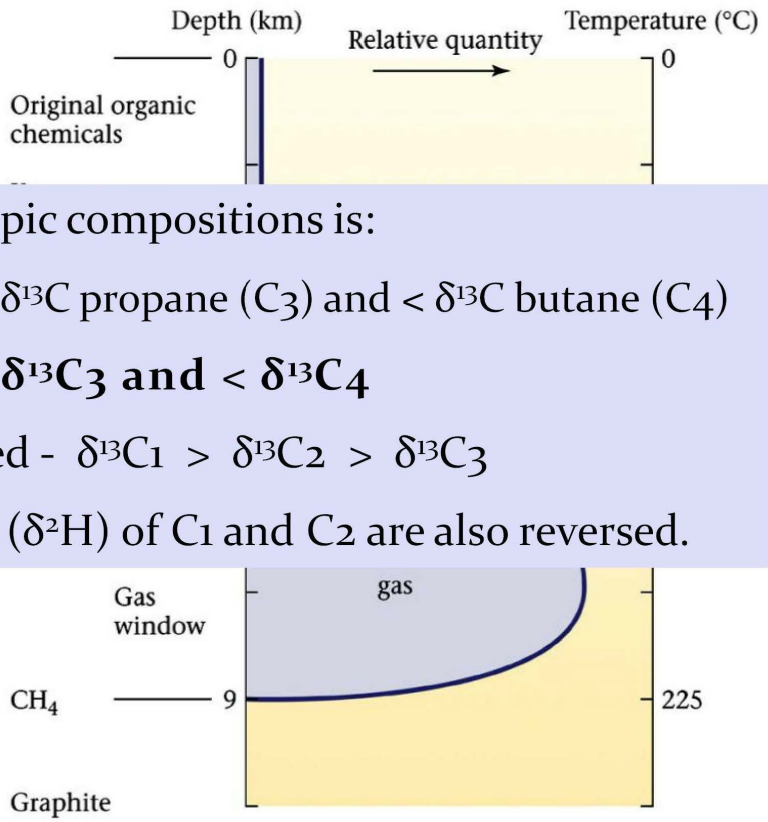
$$\delta^{13}C = \frac{R_{sample} - R_{reference}}{R_{reference}}$$

Where R = $^{13}C/^{12}C$,
$R_{reference}$= 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?

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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

^{13}C fractionation

^{2}H fractionation

% argon

% nitrogen

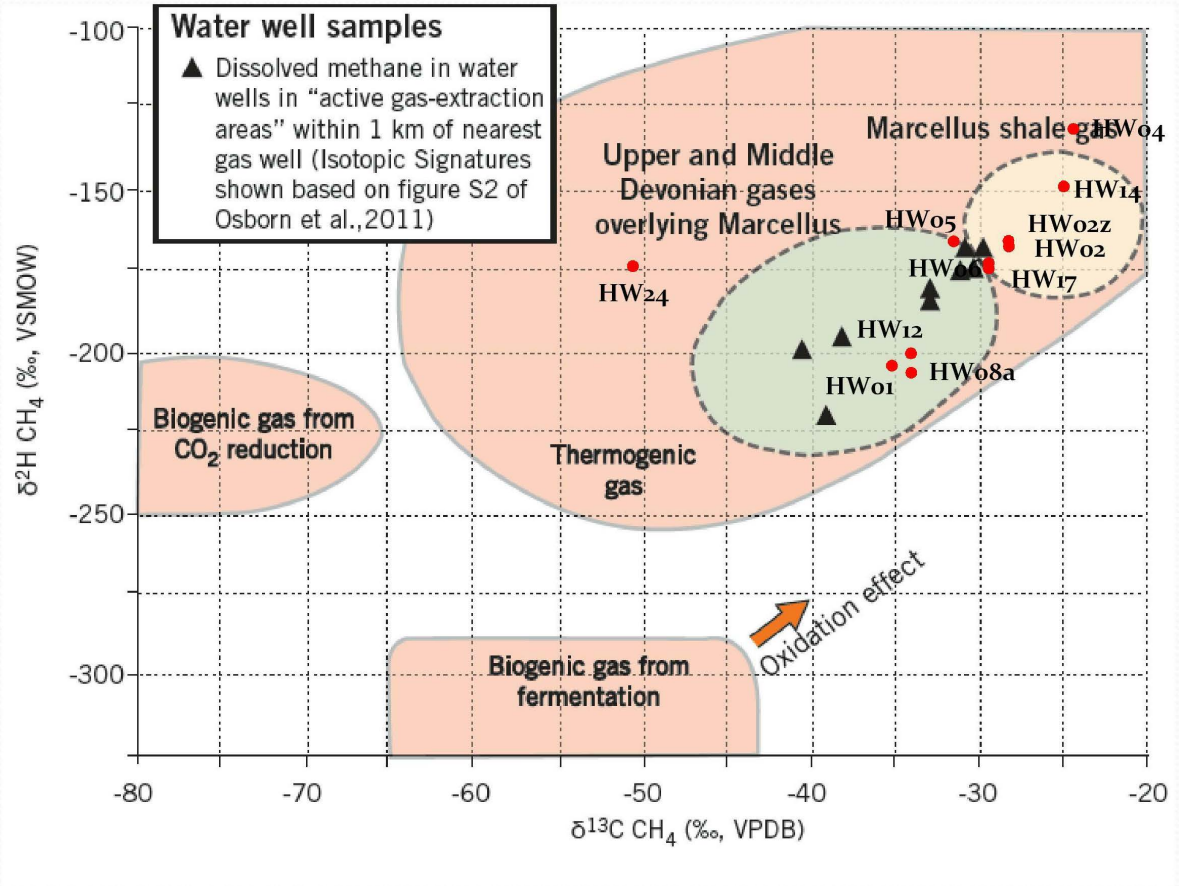
Component	Chemical mol. %	$\delta^{13}C$ ‰	δD ‰	$\delta^{18}O$ ‰
Carbon Monoxide	nd			
Hydrogen Sulfide	na			
Helium	0.0112			
Hydrogen	nd			
Argon	0.628			
Oxygen	0.80			
Nitrogen	40.72			
Carbon Dioxide	0.094			
Methane	57.06	-29.30	-160.6	
Ethane	0.687			
Ethylene	nd			
Propane	nd			
Propylene	0.0001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

-29

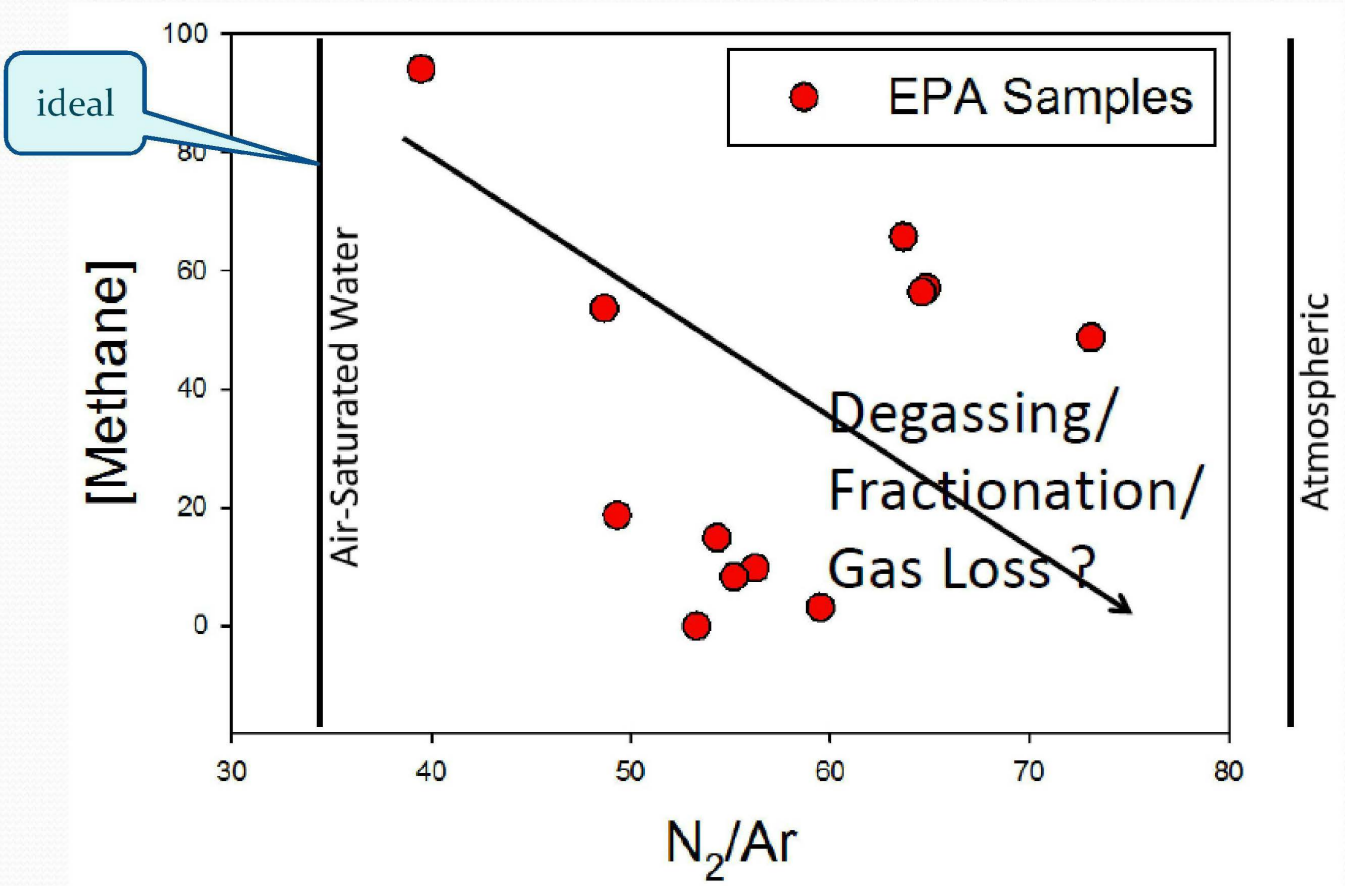
-160

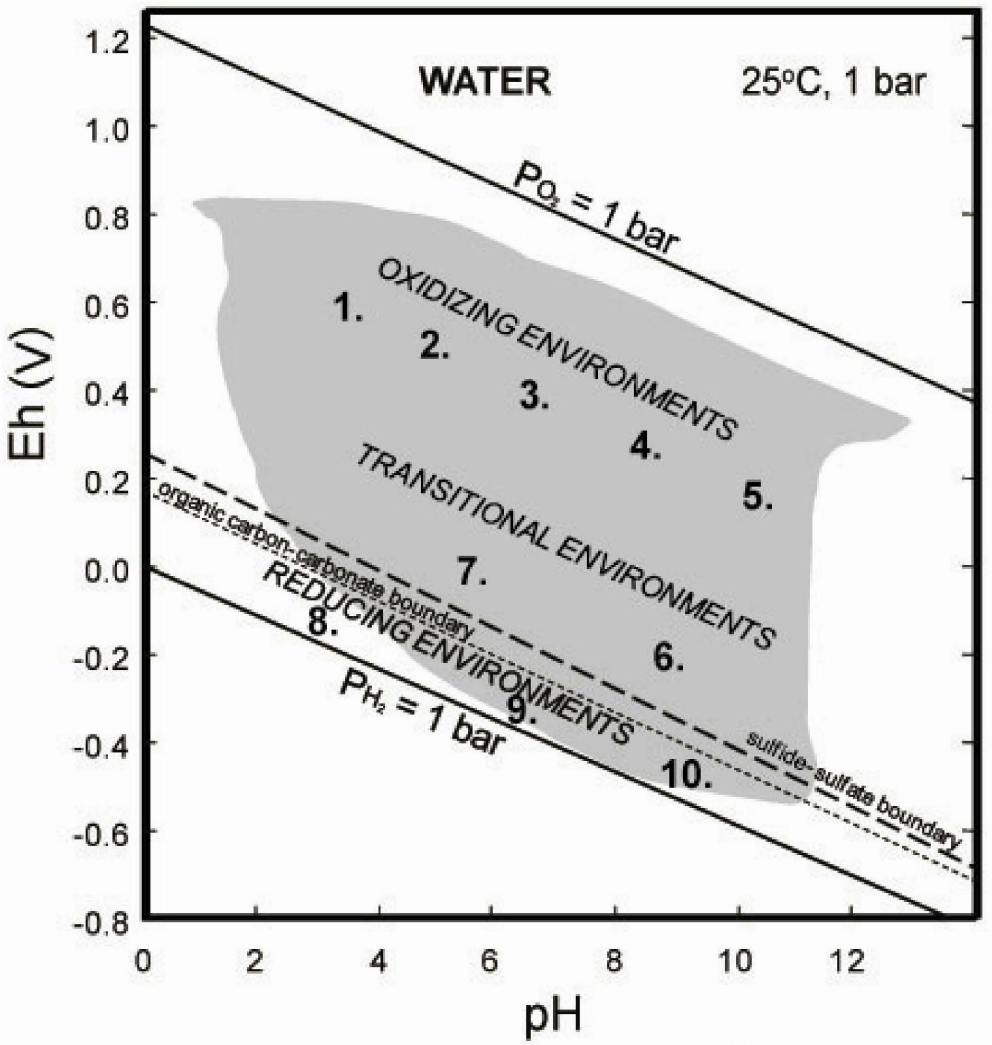
Total BTU/cu.ft. dry @ 60deg F & 14.7psia, calculated: 590

Specific gravity, calculated: 0.736


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
HW04
HW14
Upper and Middle Devonian gases overlying Marcellus
HW05
HW02z
HW02
HW17
HW24
HW12
HW01
HW08a
Biogenic gas from CO_2 reduction
Thermogenic gas
Oxidation effect
Biogenic gas from fermentation
-100
-150
-200
-250
-300
δ^2H CH_4 (‰, VSMOW)
-80
-70
-60
-50
-40
-30
-20
$\delta^{13}C$ CH_4 (‰, VPDB)

Sample Quality - degassing?





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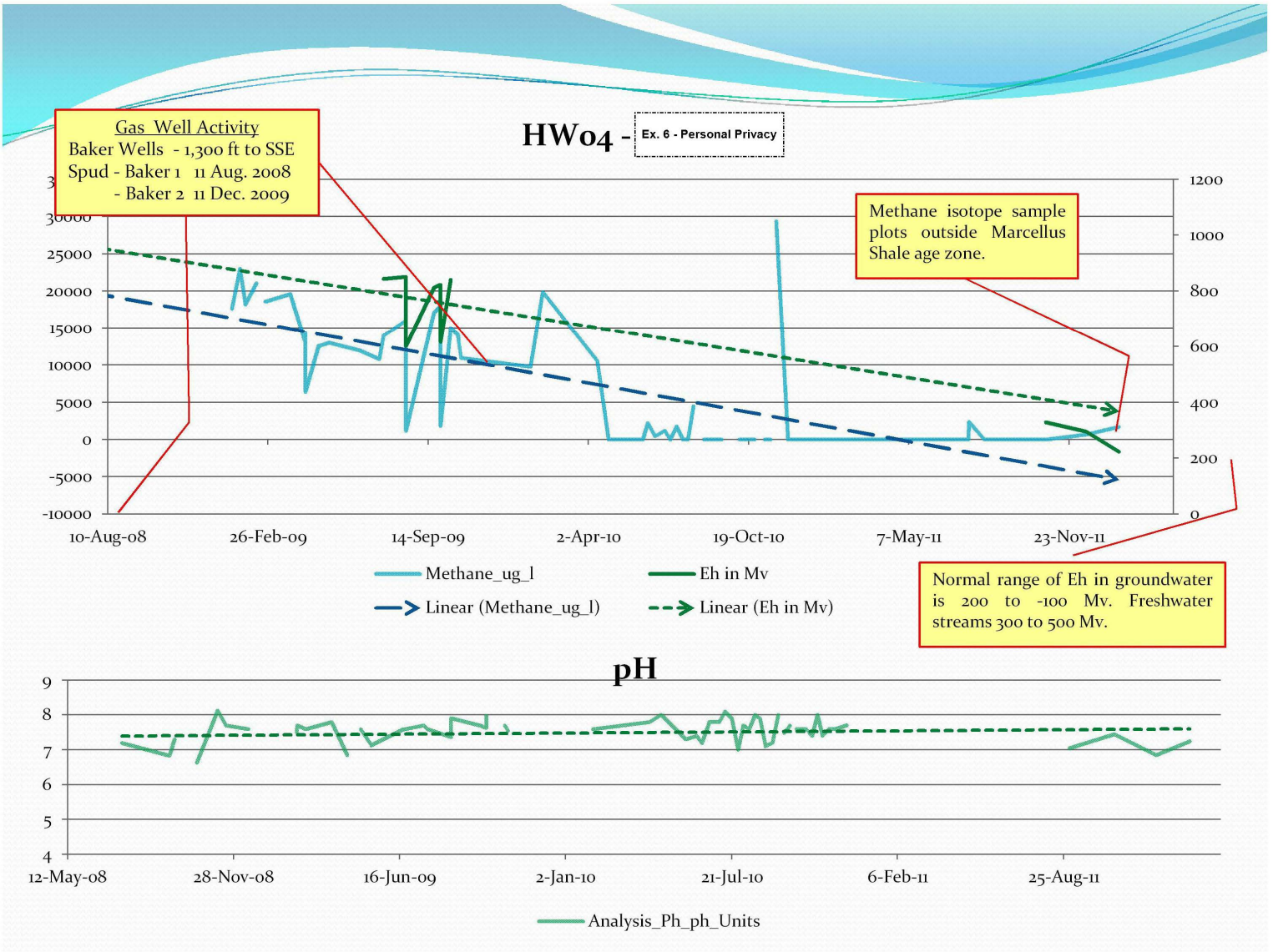
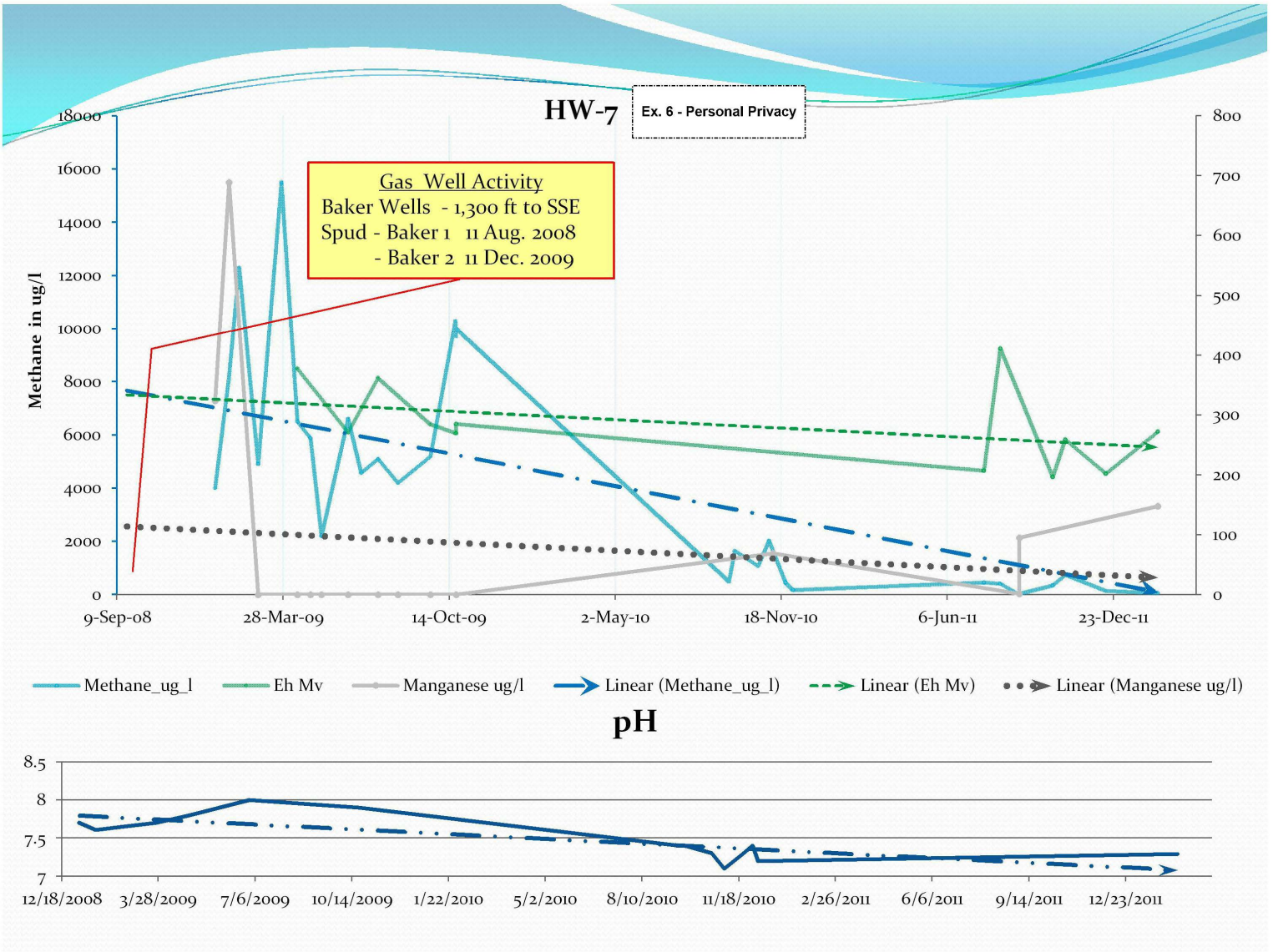
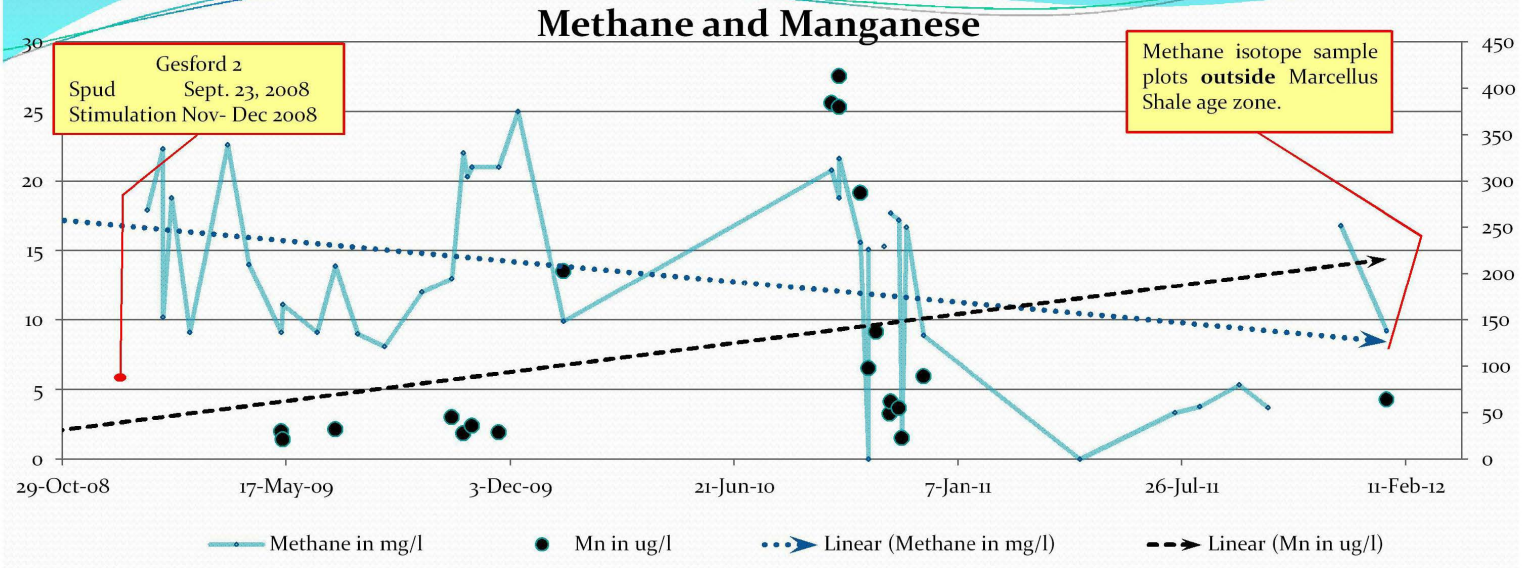

HW04 - Ex. 6 - Personal Privacy
Gas Well Activity
Baker Wells - 1,300 ft to SSE
Spud - Baker 1 11 Aug. 2008
- Baker 2 11 Dec. 2009
Methane isotope sample plots outside Marcellus Shale age zone.
Normal range of Eh in groundwater is 200 to -100 Mv. Freshwater streams 300 to 500 Mv.
30000
25000
20000
15000
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)
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
Ex. 6 - Personal Privacy
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

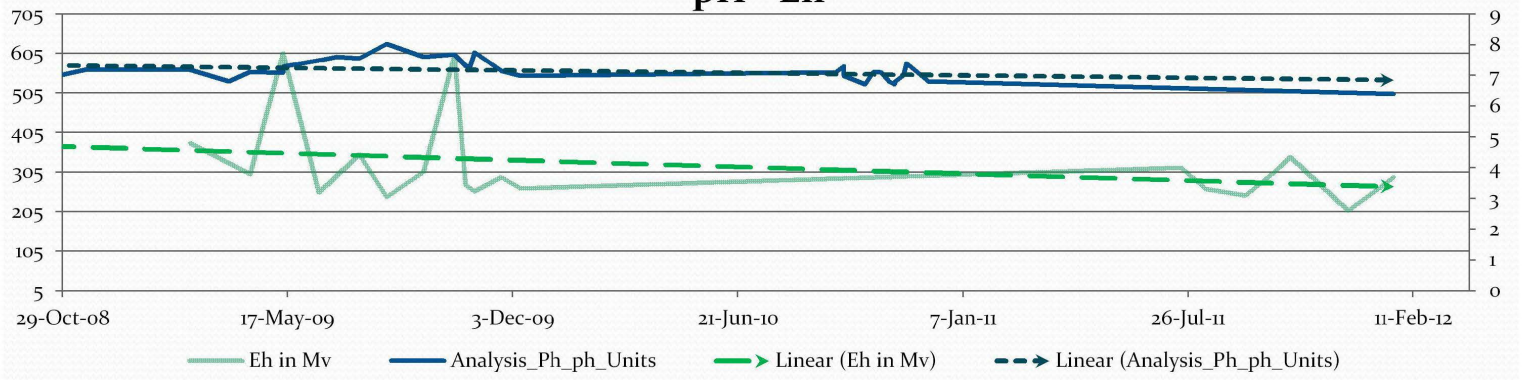
HW8

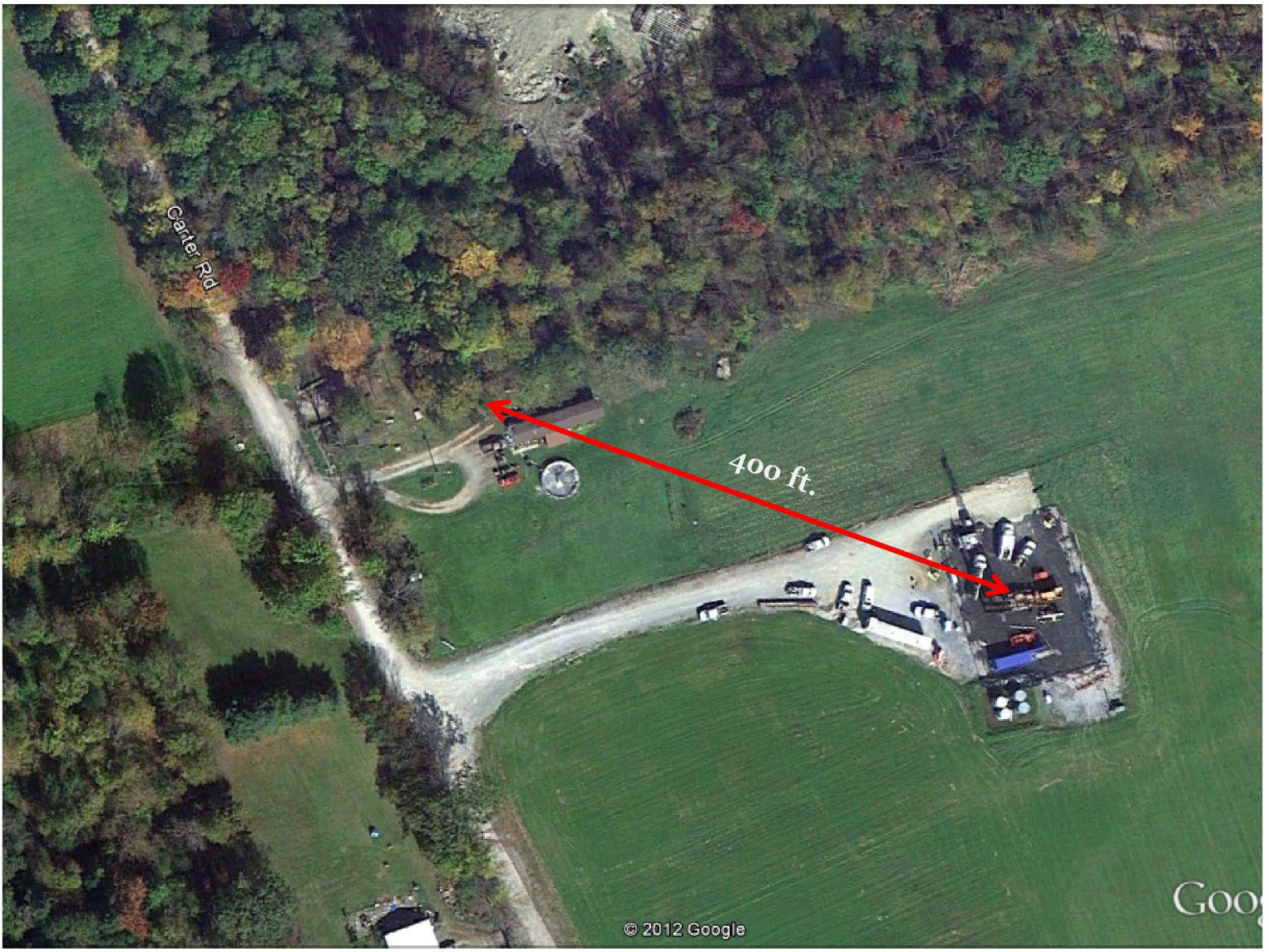
Ex. 6 - Personal Privacy

Methane and Manganese



pH - Eh




Carter Rd
400 ft.
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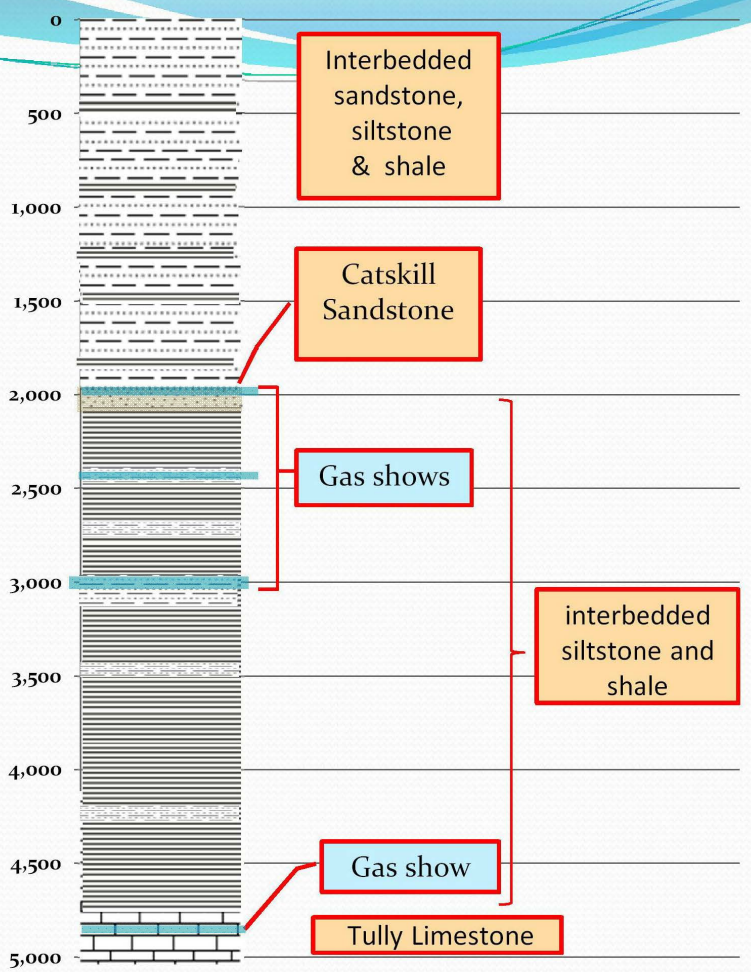
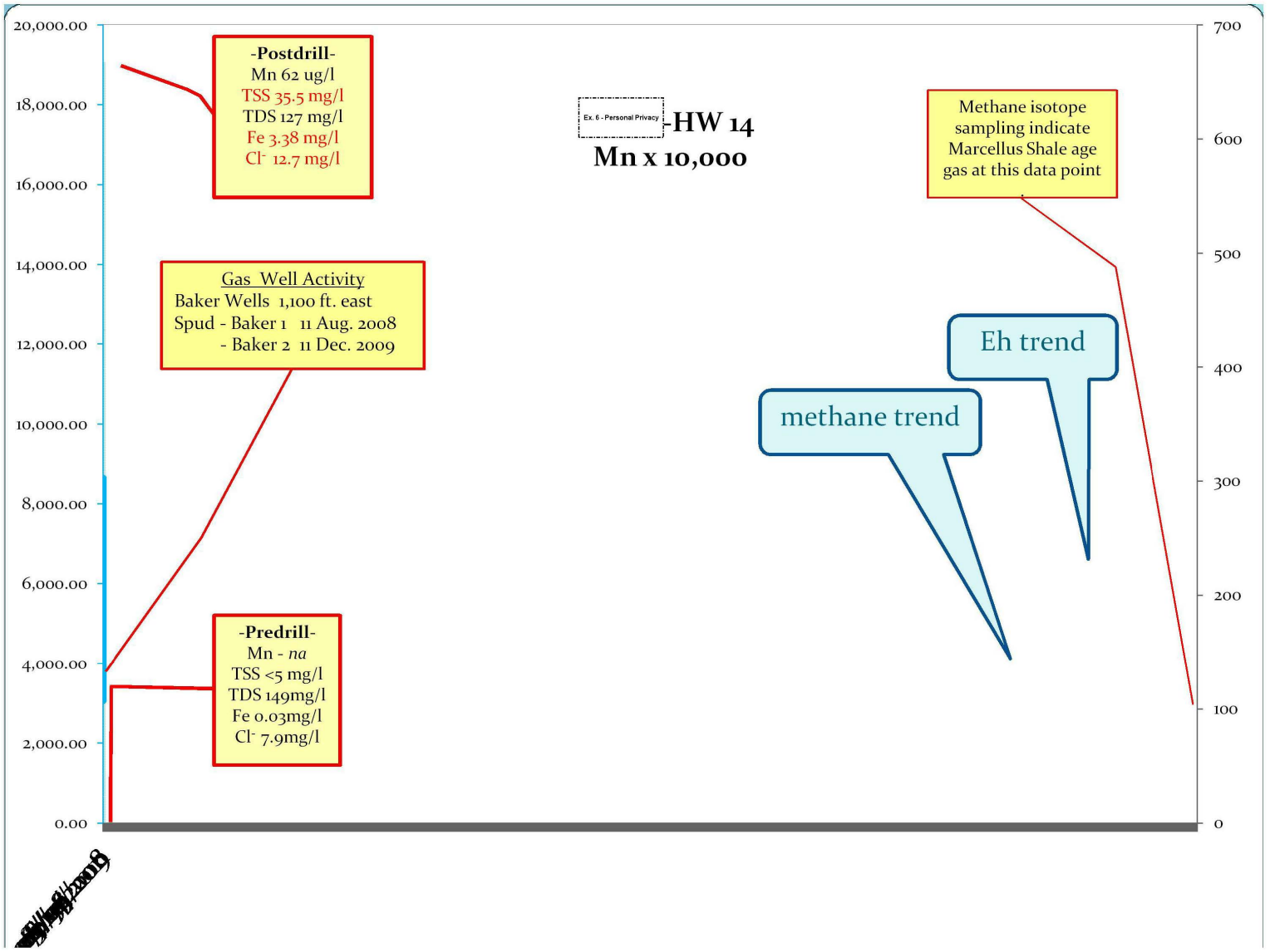
Gas is Gas

- 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 H2S which can have a greater impact on groundwater.
- This gas disrupts groundwater quality

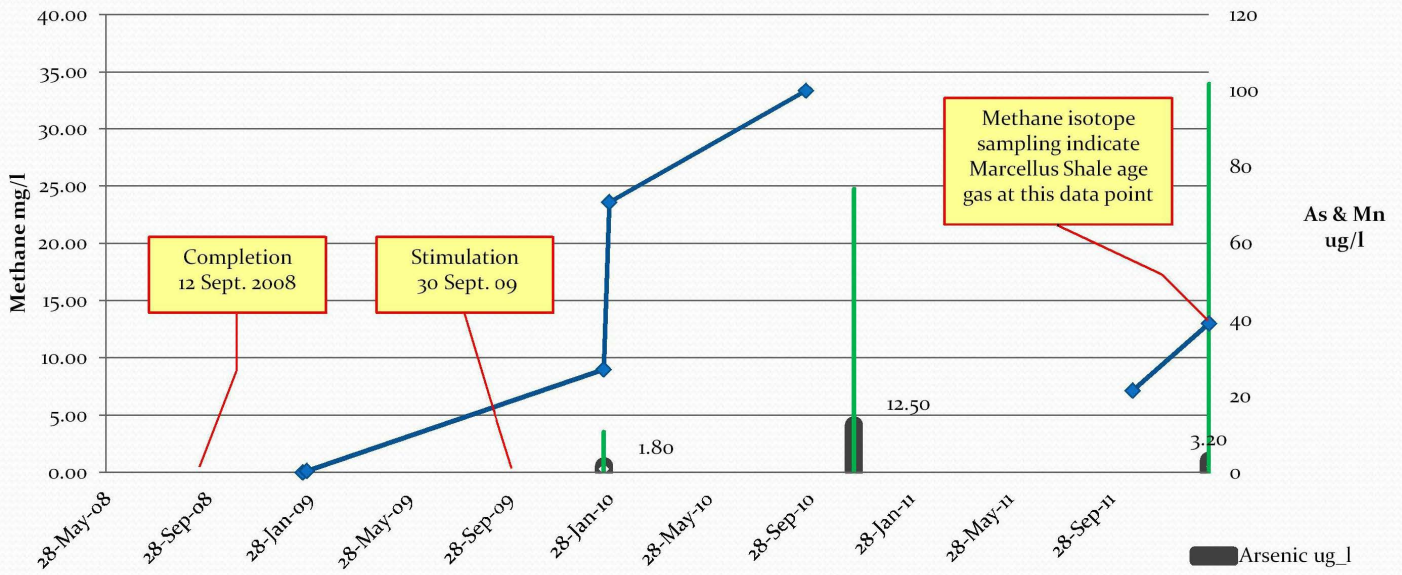


From Gesford 2 Well Record and Completion Report


Ex. 6 - Personal Privacy -HW 14
Mn x 10,000
-Postdrill-
Mn 62 ug/l
TSS 35.5 mg/l
TDS 127 mg/l
Fe 3.38 mg/l
Cl⁻ 12.7 mg/l
Gas Well Activity
Baker Wells 1,100 ft. east
Spud - Baker 1 11 Aug. 2008
- Baker 2 11 Dec. 2009
-Predrill-
Mn - na
TSS <5 mg/l
TDS 149mg/l
Fe 0.03mg/l
Cl⁻ 7.9mg/l
Methane isotope sampling indicate Marcellus Shale age gas at this data point
Eh trend
methane trend
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

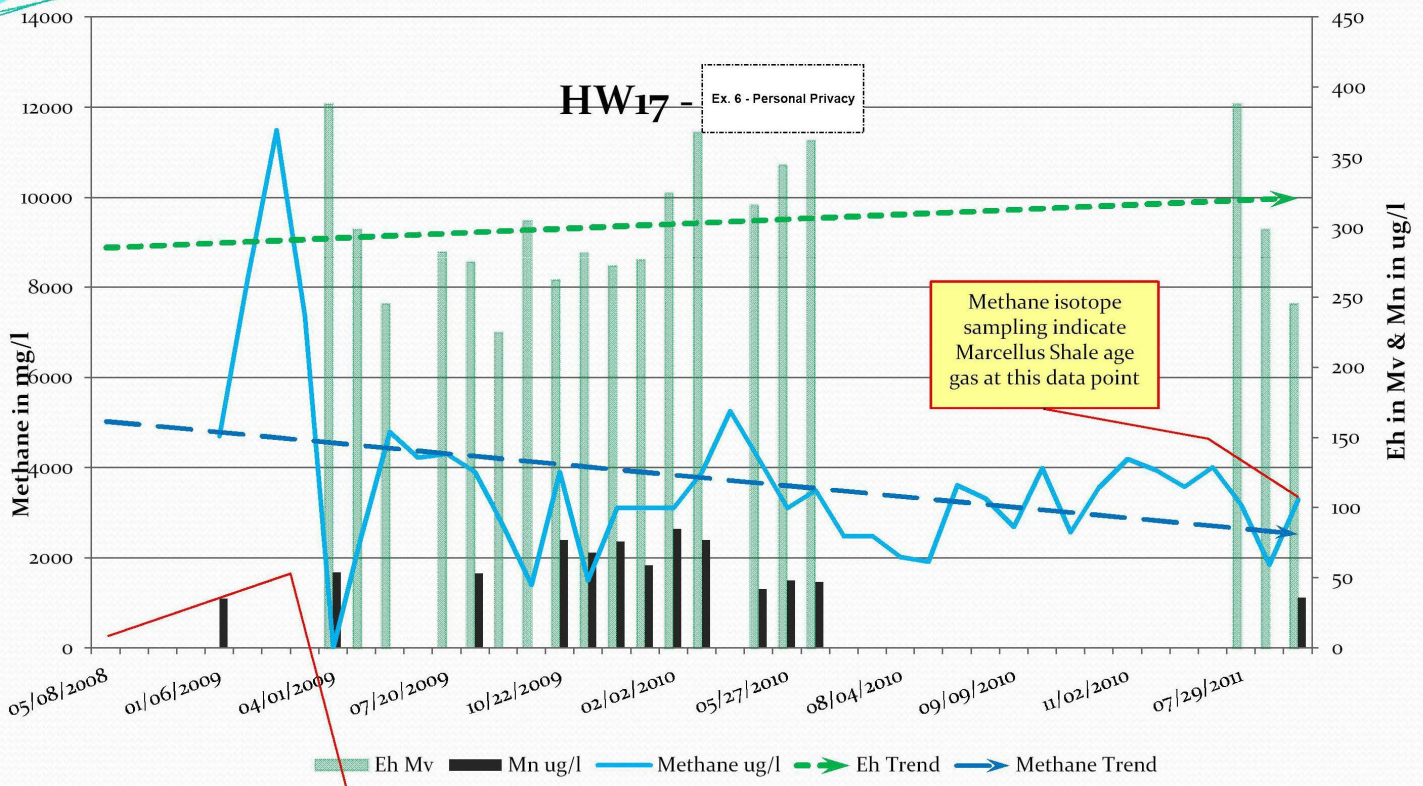
HW-2

Ex. 6 - Personal Privacy



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

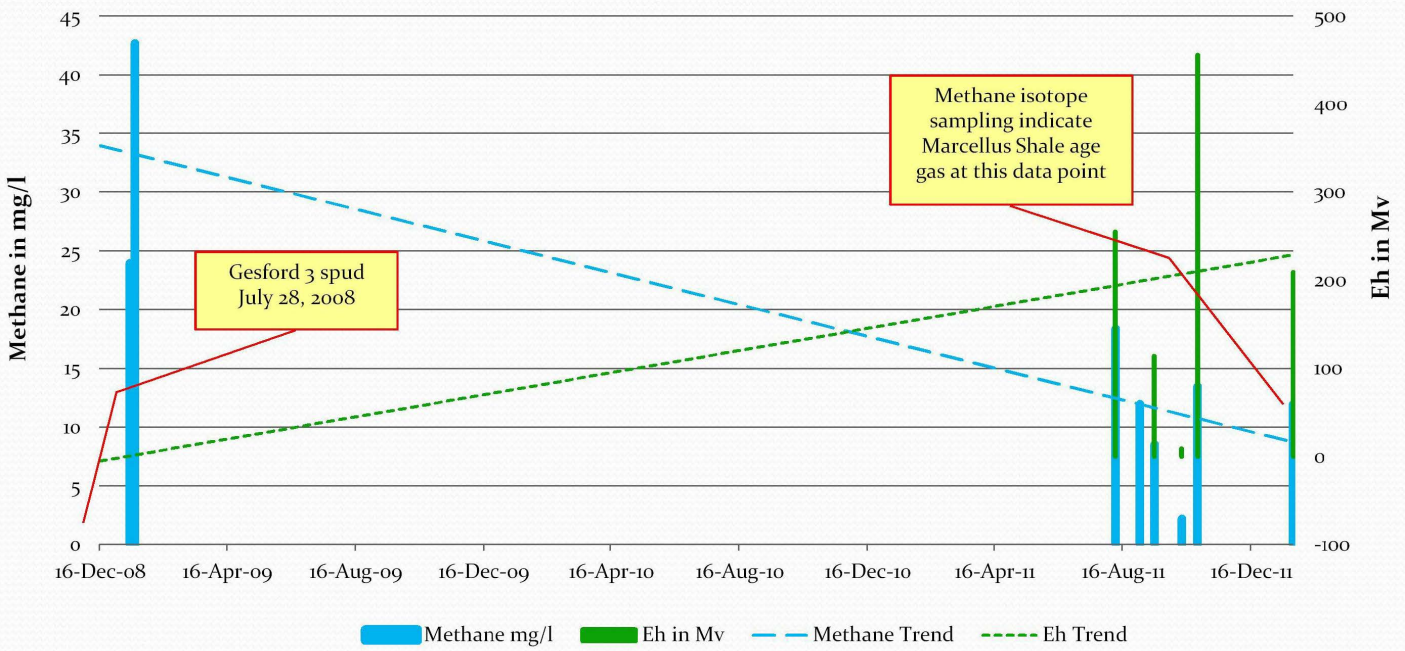
Note incomplete data set



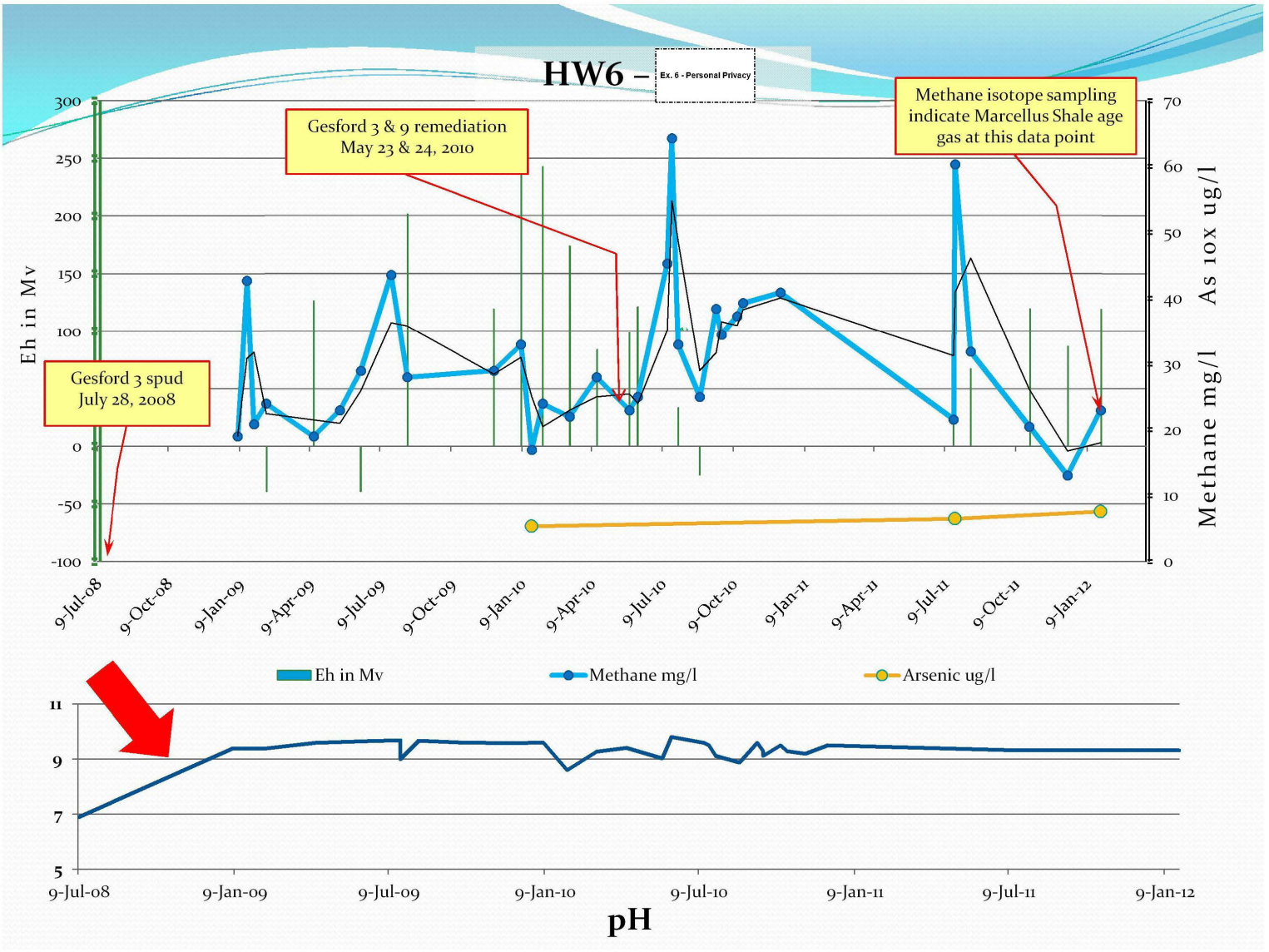
Gas Well	Date Spud	Distance to HW17
Lewis	5/28/2008	670 ft.
Ely 4H & 6H	3/27/2008	1,360 ft.
Costello 1	7/16/2008	1,350 ft.

Note incomplete data set

HW1 - Ex. 6 - Personal Privacy

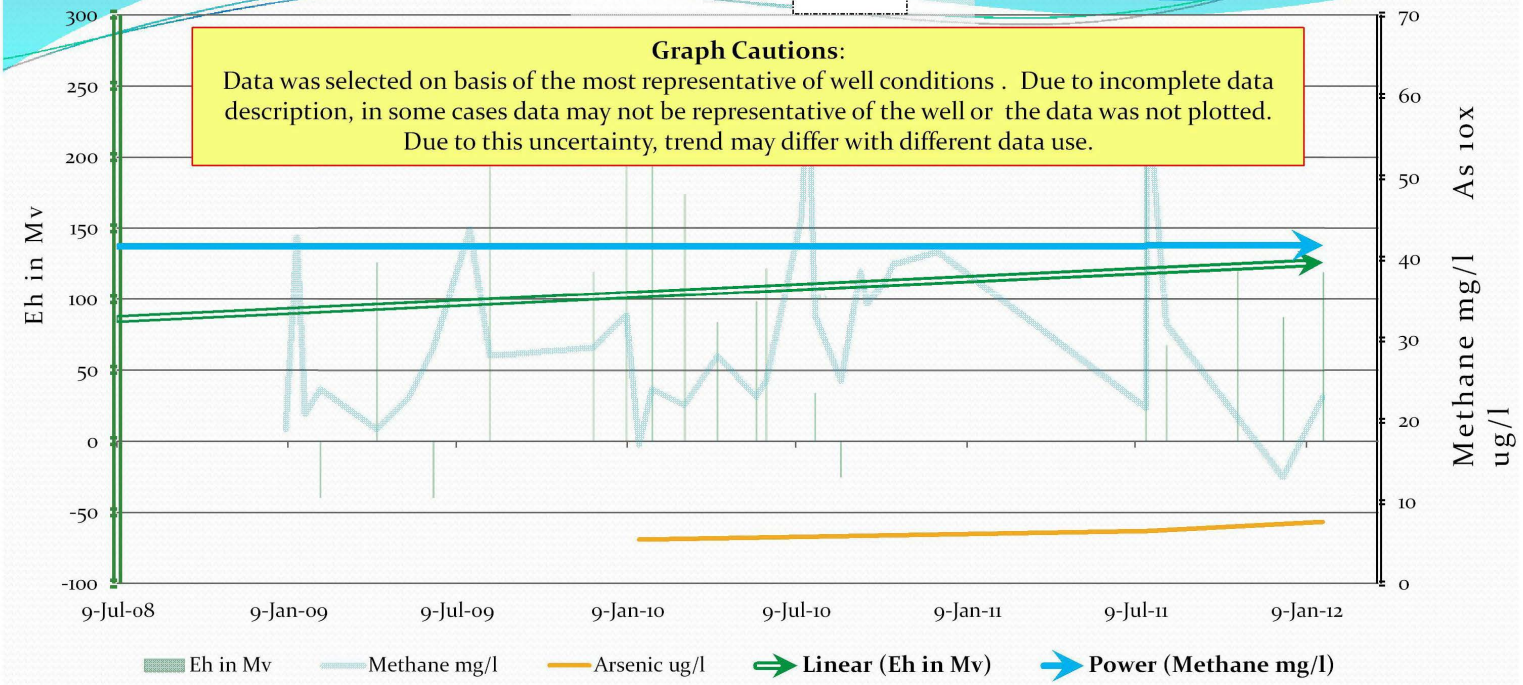


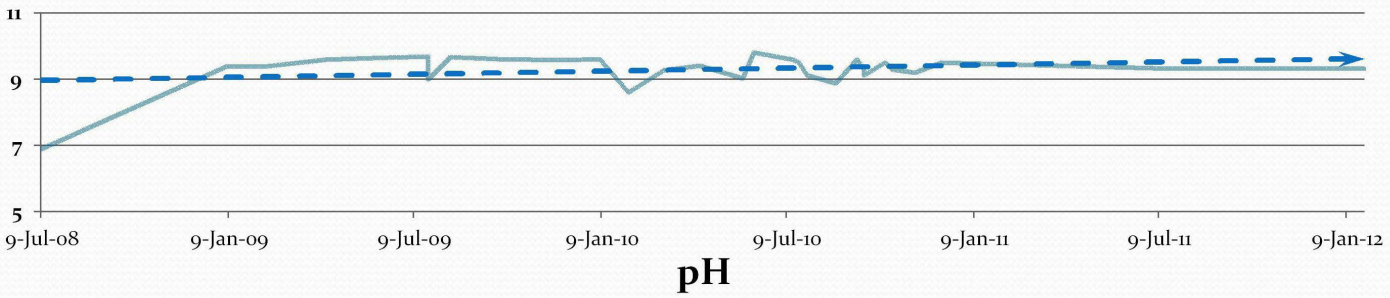
HW1 lacked data for nearly all constituents, particularly for the years 2009-2010

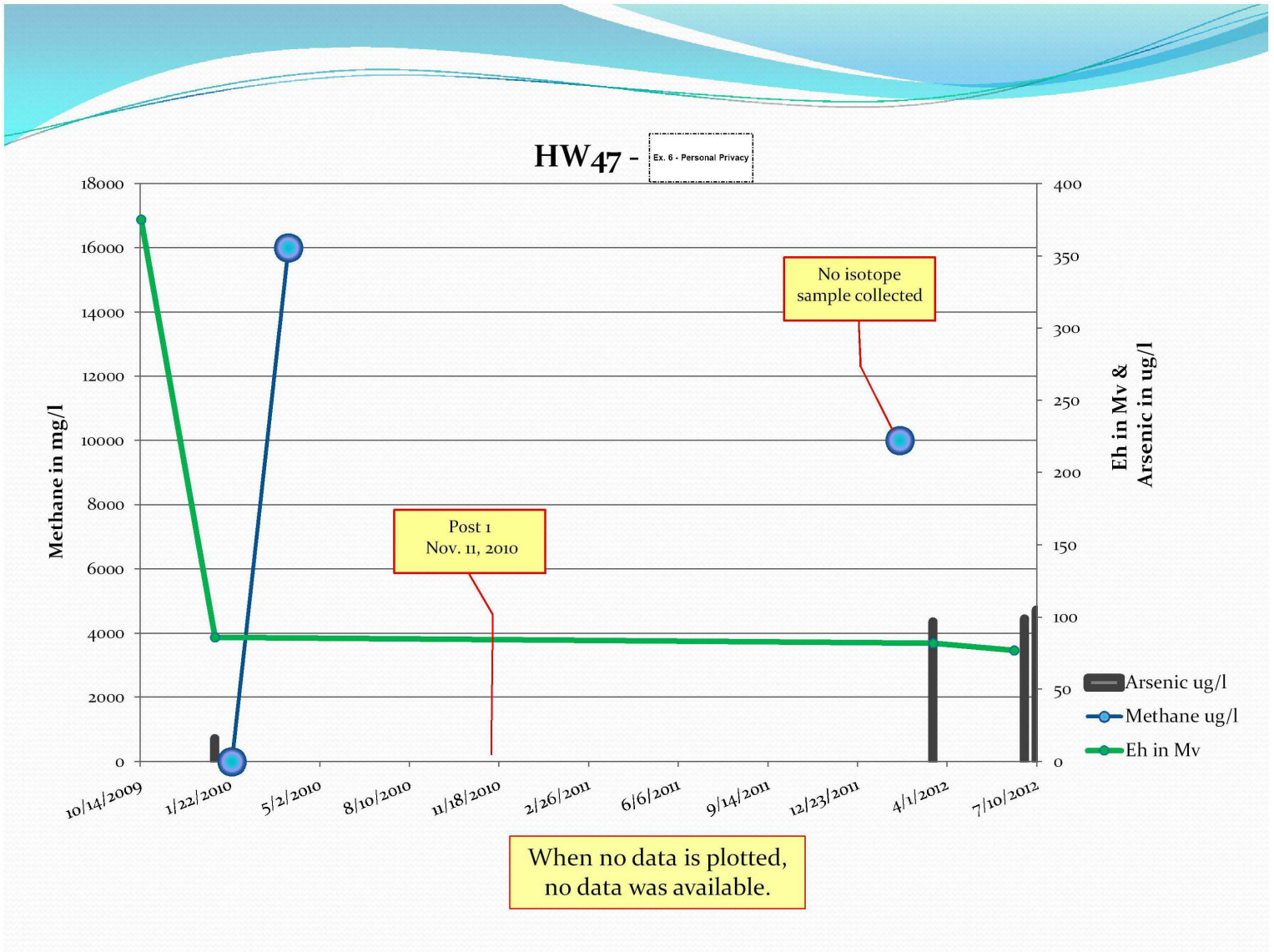

HW6 – Ex. 6 - Personal Privacy
Gesford 3 & 9 remediation
May 23 & 24, 2010
Methane isotope sampling indicate Marcellus Shale age gas at this data point
Gesford 3 spud
July 28, 2008
Eh in Mv
Methane mg/l
As 10x ug/l
300
250
200
150
100
0
-50
-100
70
60
50
40
30
20
10
0
9-Jul-08
9-Oct-08
9-Jan-09
9-Apr-09
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 – Ex. 6 - Personal Privacy

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.






HW47 - Ex. 6 - Personal Privacy
Methane in mg/l
Eh in Mv & Arsenic in ug/l
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
400
350
300
250
200
150
100
50
0
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
4/1/2012
7/10/2012
No isotope sample collected
Post 1 Nov. 11, 2010
Arsenic ug/l
Methane ug/l
Eh in Mv
When no data is plotted, no data was available.