CREATIVE THINKING
EXCEPTIONAL SOLUTIONS

Geosyntec consultants

# SUCCESSFUL BIOAUGMENTATION FOR DNAPL CARBON TETRACHLORIDE IN A KARST AQUIFER

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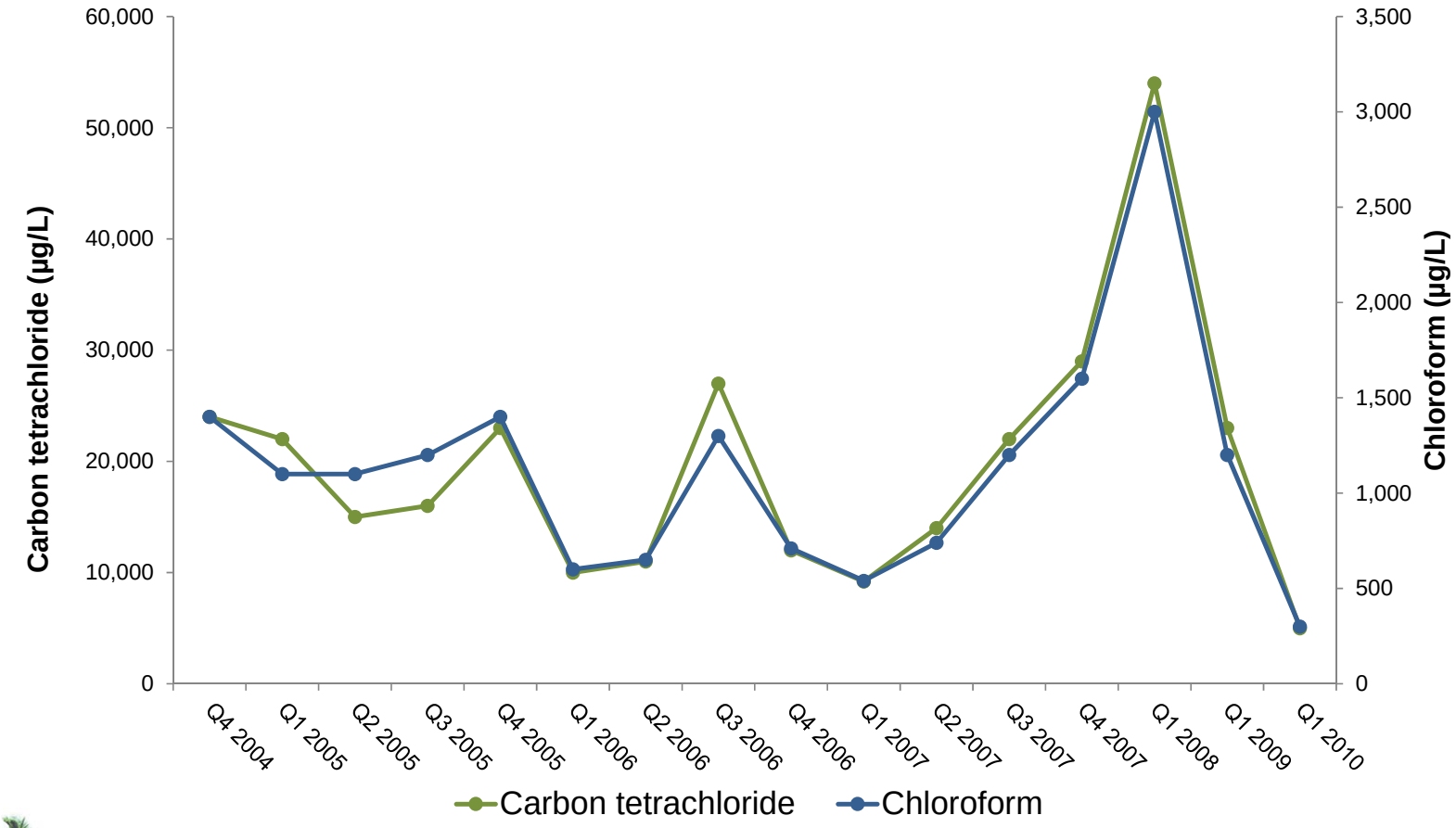
# Background

- Groundwater monitoring for a potential MNA remedy was being conducted at nine wells in three different SWMUs at a plant using many different chemicals in production operations
- Two wells in two separate SWMUs were found to have carbon tetrachloride concentrations indicative of DNAPL - MW-47D and HE-04
- Both screened approximately 55 to 65 ft bgs NOT connected hydraulically and additional wells could not be installed in the area
- Bench-scale treatability studies with KB-1® Plus *Chlorinated Methane Formulation* with emulsified vegetable oil as the electron donor indicated carbon tetrachloride could be degraded to innocuous end products
- A pull-push field pilot was initiated at MW-47D in 2010

# MW47-D Contaminant Concentrations in Groundwater vs. Time



# Pull-Push Amendment Injection

1. Extracted ~3,000 gals of water from MW-47D while adding lactate and performing step test & sampling for VOCs & field parameters
2. Amended extracted groundwater with emulsified vegetable oil & Vitamin B12. Bromide tracer also added.
3. Gravity fed amended groundwater & dechlorinating bacterial consortium
4. Reinstalled dedicated equipment & continued to monitor groundwater at MW-47D

# Pull-Push Amendment Injection

- Design Safety Review
- Field parameters monitored during extraction to control for surface water intrusion (close proximity to a river)
- During extraction of the 3,000 gallons of groundwater perform a step test to evaluate sustainable flow rates, WL effects in surrounding wells and estimate hydraulic conductivity
- Samples collected for baseline concentrations of bromide, TOC and VOCs
- Groundwater stored in PE tank (with volatiles control on outlet) amended with emulsified vegetable oil (electron donor) + bromide
- Gravity injection – 1/3 volume then ½ KB-1® Plus then another 1/3 then 2nd ½ KB-1 then final 1/3 volume followed by groundwater from MW-47S to flush amendments into the formation
- Install dedicated sampling equipment

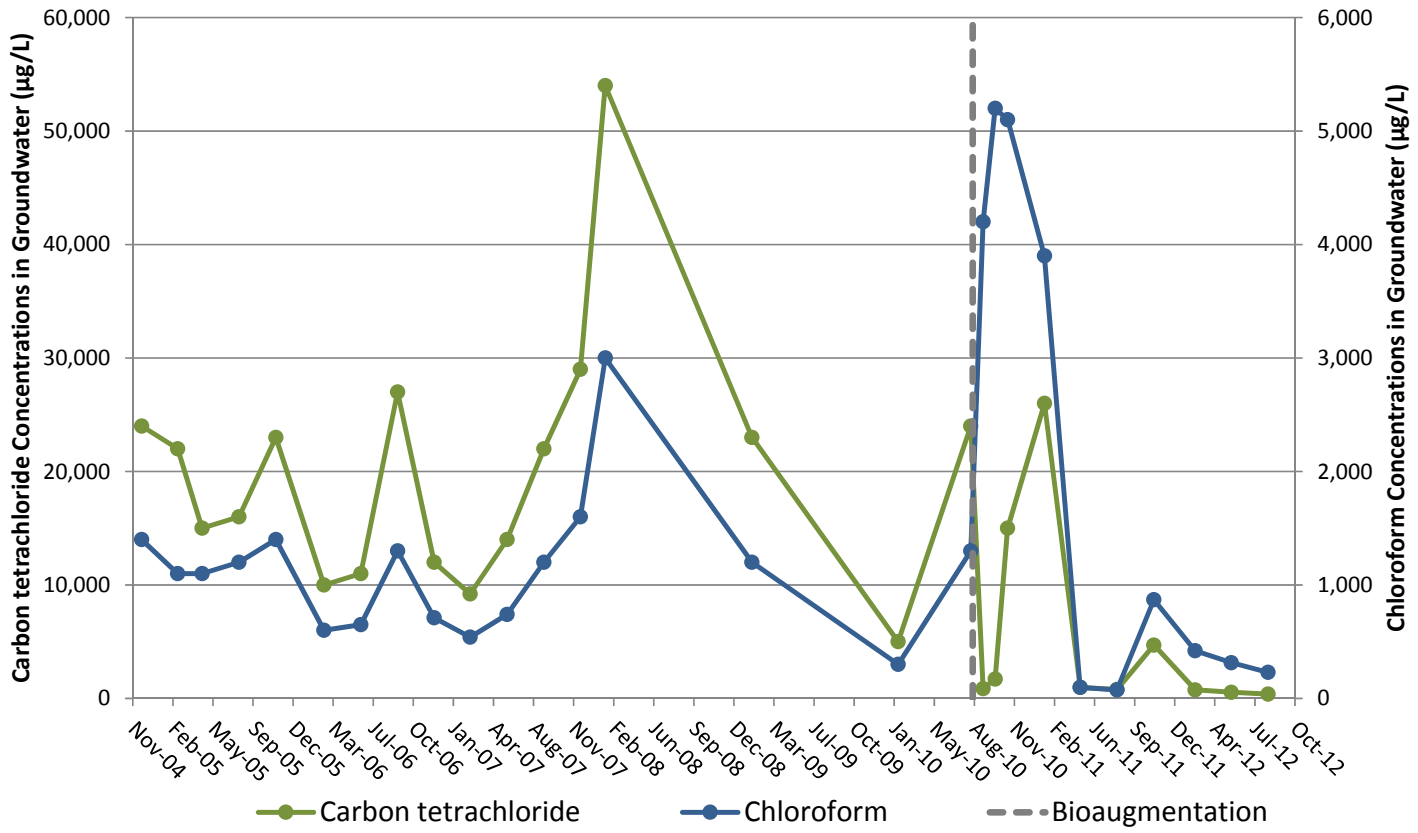
# Sampling Program for MW-47D

| | Baseline | 1st weekly | 2nd weekly | 3rd weekly | 1st monthly | 2nd monthly | 3rd monthly | 6 month | 9 month | 1 year |
|---|---|---|---|---|---|---|---|---|---|---|
| | 8/2-17/2010 | 8/24/2010 | 8/31/2010 | 9/7/2010 | 9/14/2010 | 10/12/2010 | 11/9/2010 | 2/9/2011 | 5/10/2011 | 8/9/2011 |
| Field Parameters[1] | X | | | | X | X | X | X | X | X |
| VOCs (EPA Method 8260B) | X | | | | X | X | X | X | X | X |
| TOC (Method SM 20 5310C) | X | | | | X | X | X | X | X | X |
| Bromide (EPA Method 300) | X | X | X | X | X | X | X | X | X | X |
| Nitrate /sulfate (EPA Method 300) | X | | | | X | X | X | X | X | X |
| Chloride & sulfide[2] (EPA Method 300 & SM20 4500 S2) | | | | | | | X | X | X | X |
| Carbon dioxide (Method SM20 4500 CO2) | X | | | | X | X | X | X | X | X |
| Ethene, ethane, methane) (Method SW-846 8015B modified) | X | | | | X | X | X | X | X | X |
| Alkalinity (SM20 2320 B) | X | | | | X | X | X | X | X | X |

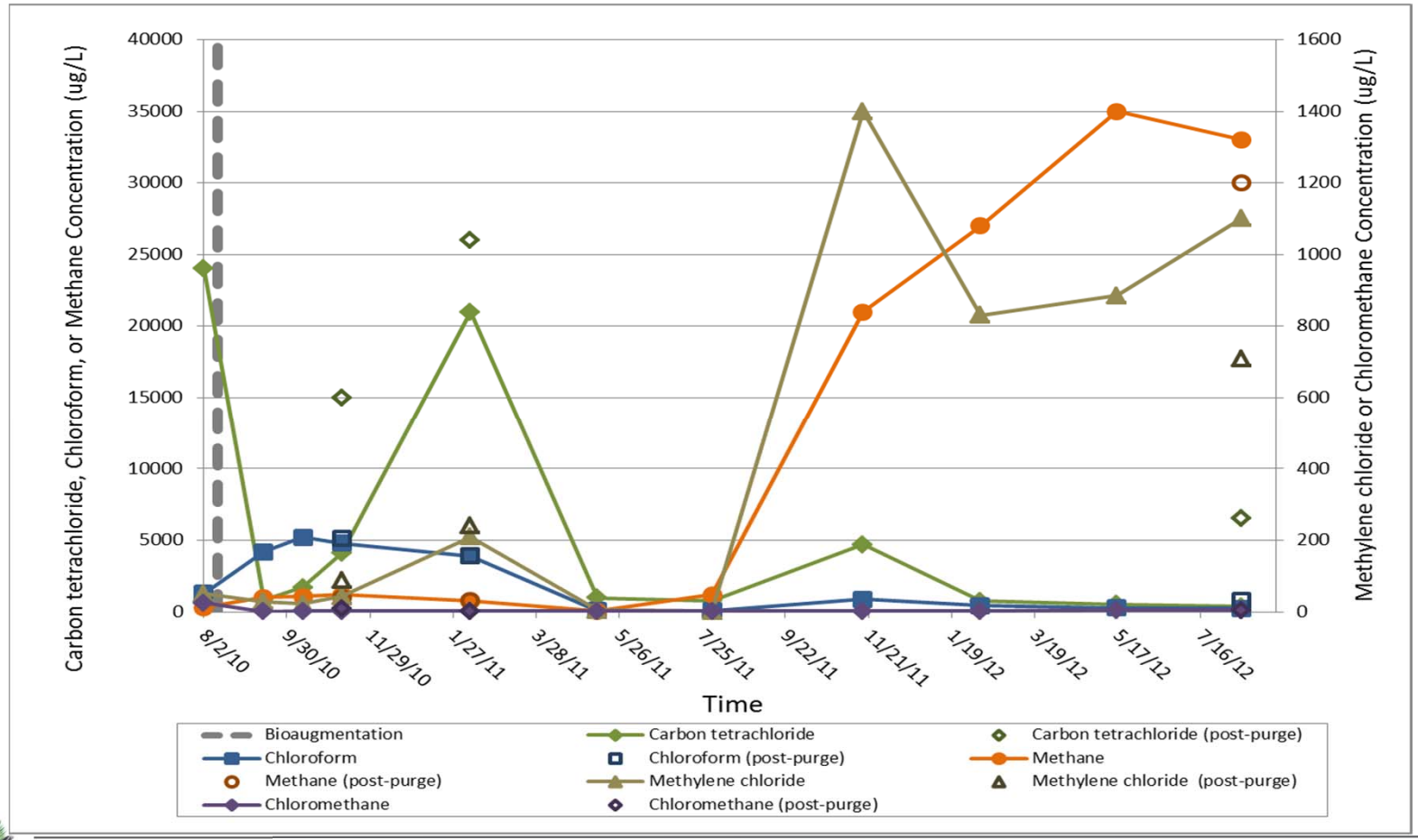
[1]Field parameters include DO, ORP, pH, conductivity, temperature, and turbidity measured by a multi-parameter probe in a flow-through cell during purging of the well.

[2]Sulfide and chloride were added to the analyses list in November 2010. For the September 2010 and October 2010 sampling events, chloride analysis was performed past the holding time.

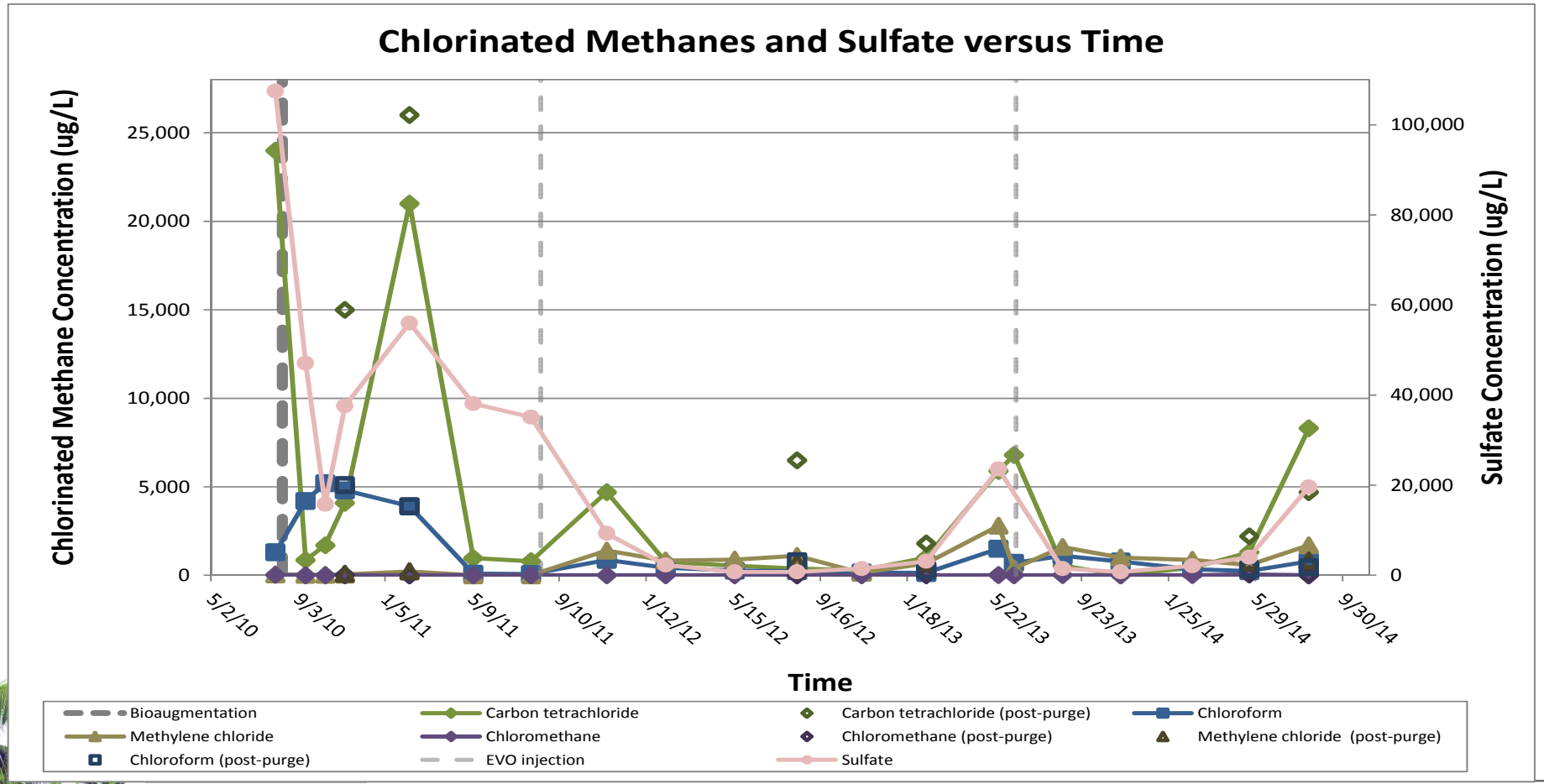
# MW-47D Historical Contaminant Concentrations in Groundwater



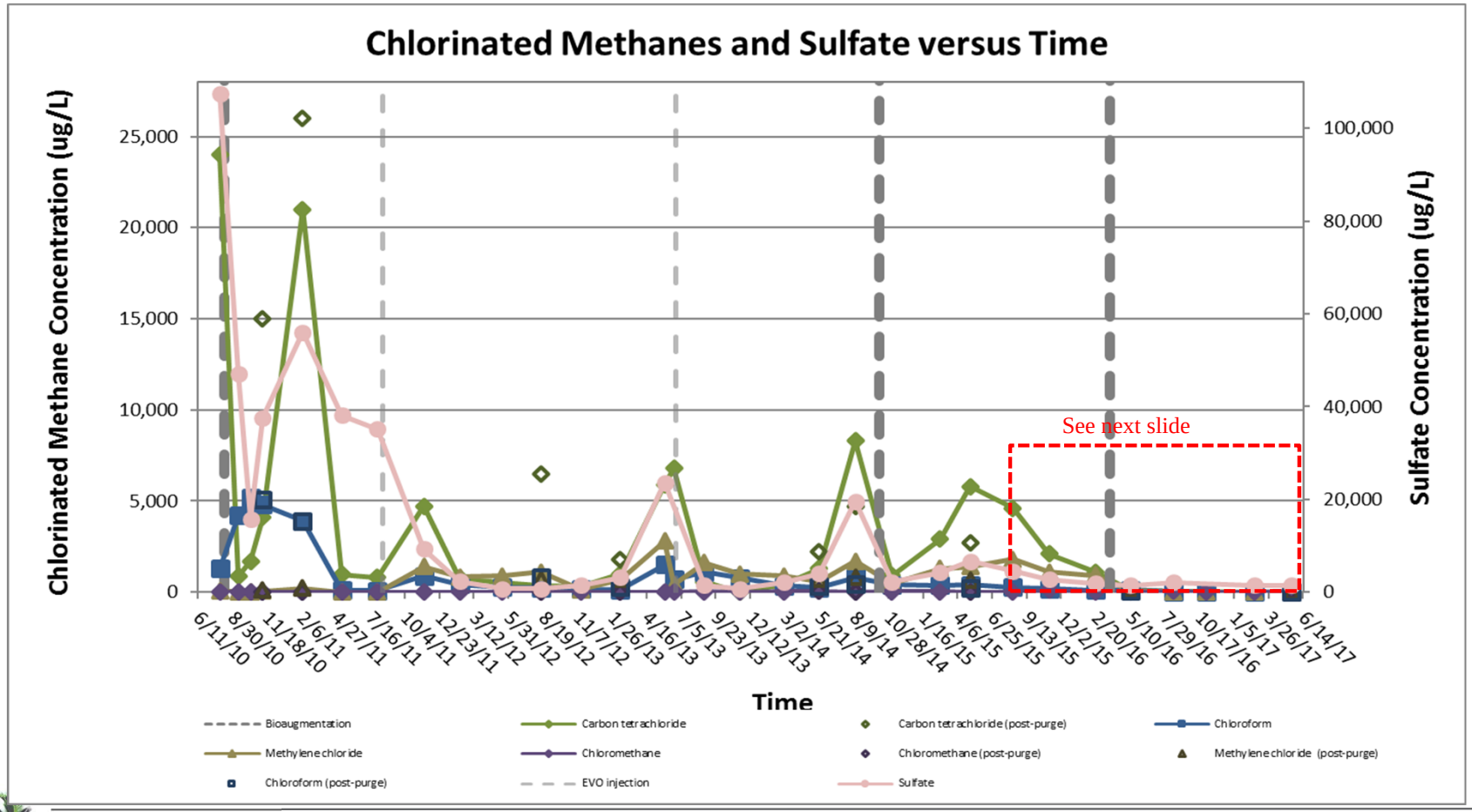
# Chlorinated Methanes versus Time – MW-47D



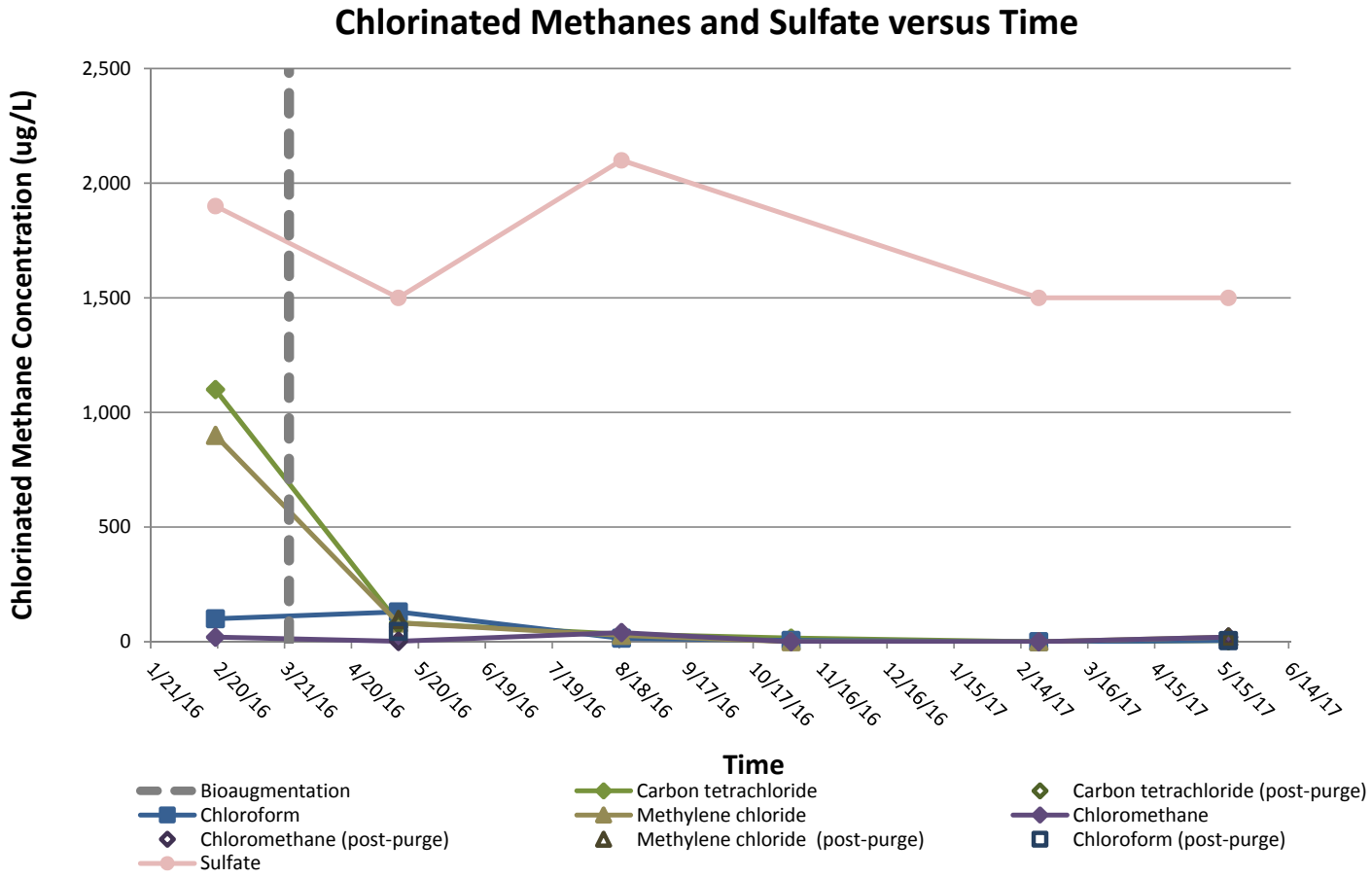
# MW-47D


Chlorinated Methanes and Sulfate versus Time
Chlorinated Methane Concentration (ug/L)
Sulfate Concentration (ug/L)
25,000
20,000
15,000
10,000
5,000
0
100,000
80,000
60,000
40,000
20,000
0
5/2/10
9/3/10
1/5/11
5/9/11
9/10/11
1/12/12
5/15/12
9/16/12
1/18/13
5/22/13
9/23/13
1/25/14
5/29/14
9/30/14
Time
Bioaugmentation
Carbon tetrachloride
Carbon tetrachloride (post-purge)
Chloroform
Methylene chloride
Chloromethane
Chloromethane (post-purge)
Methylene chloride (post-purge)
Chloroform (post-purge)
EVO injection
Sulfate

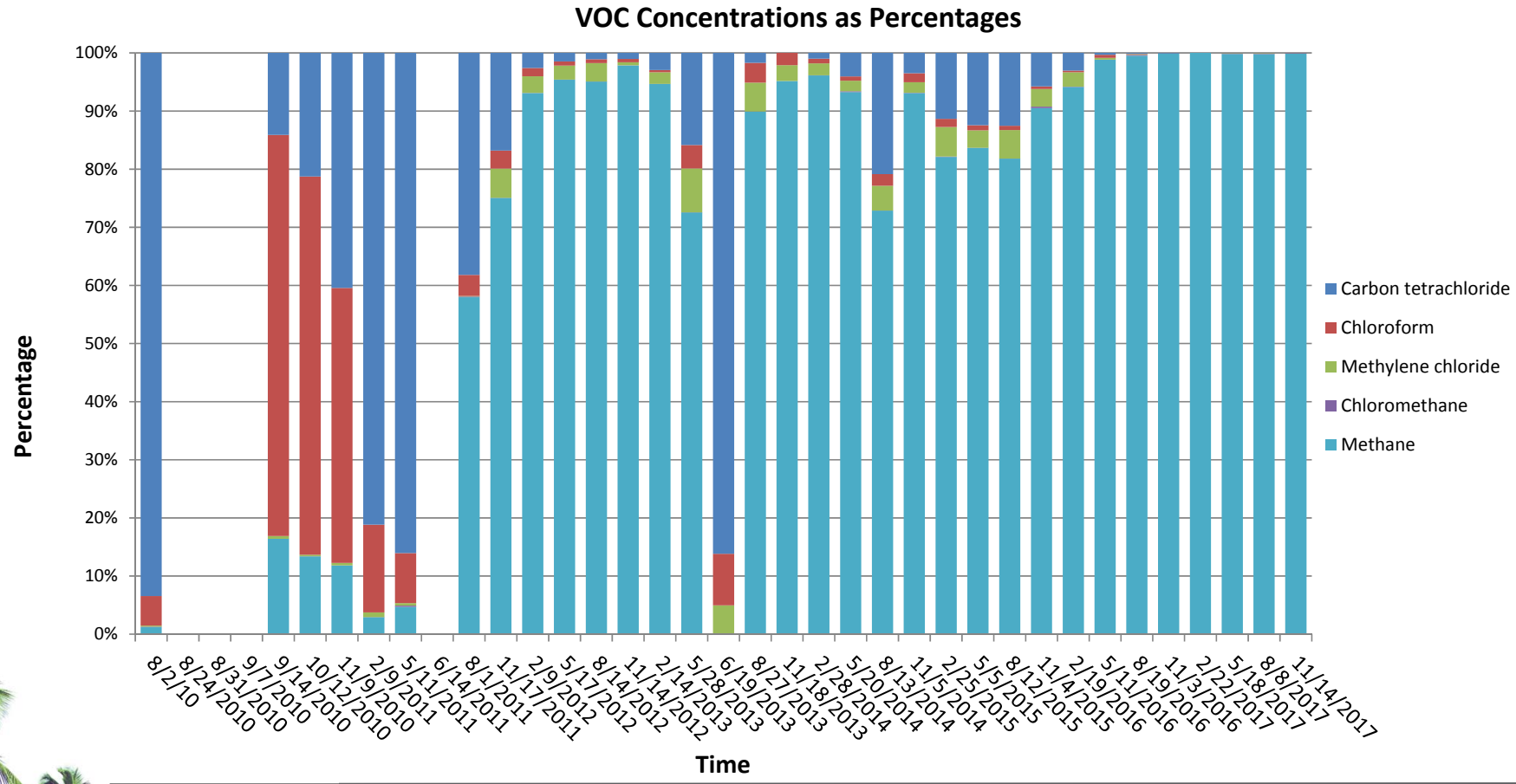
# MW-47D


Chlorinated Methanes and Sulfate versus Time
Chlorinated Methane Concentration (ug/L)
Sulfate Concentration (ug/L)
25,000
20,000
15,000
10,000
5,000
0
100,000
80,000
60,000
40,000
20,000
0
See next slide
6/11/10
8/30/10
11/18/10
2/6/11
4/27/11
7/16/11
10/4/11
12/23/11
3/12/12
5/31/12
8/19/12
11/7/12
1/26/13
4/16/13
7/5/13
9/23/13
12/12/13
3/2/14
5/21/14
8/9/14
10/28/14
1/16/15
4/6/15
6/25/15
9/13/15
12/2/15
2/20/16
5/10/16
7/29/16
10/17/16
1/5/17
3/26/17
6/14/17
Time
Bioaugmentation
Carbon tetrachloride
Carbon tetrachloride (post-purge)
Chloroform
Methylene chloride
Chloromethane
Chloromethane (post-purge)
Methylene chloride (post-purge)
Chloroform (post-purge)
EVO injection
Sulfate

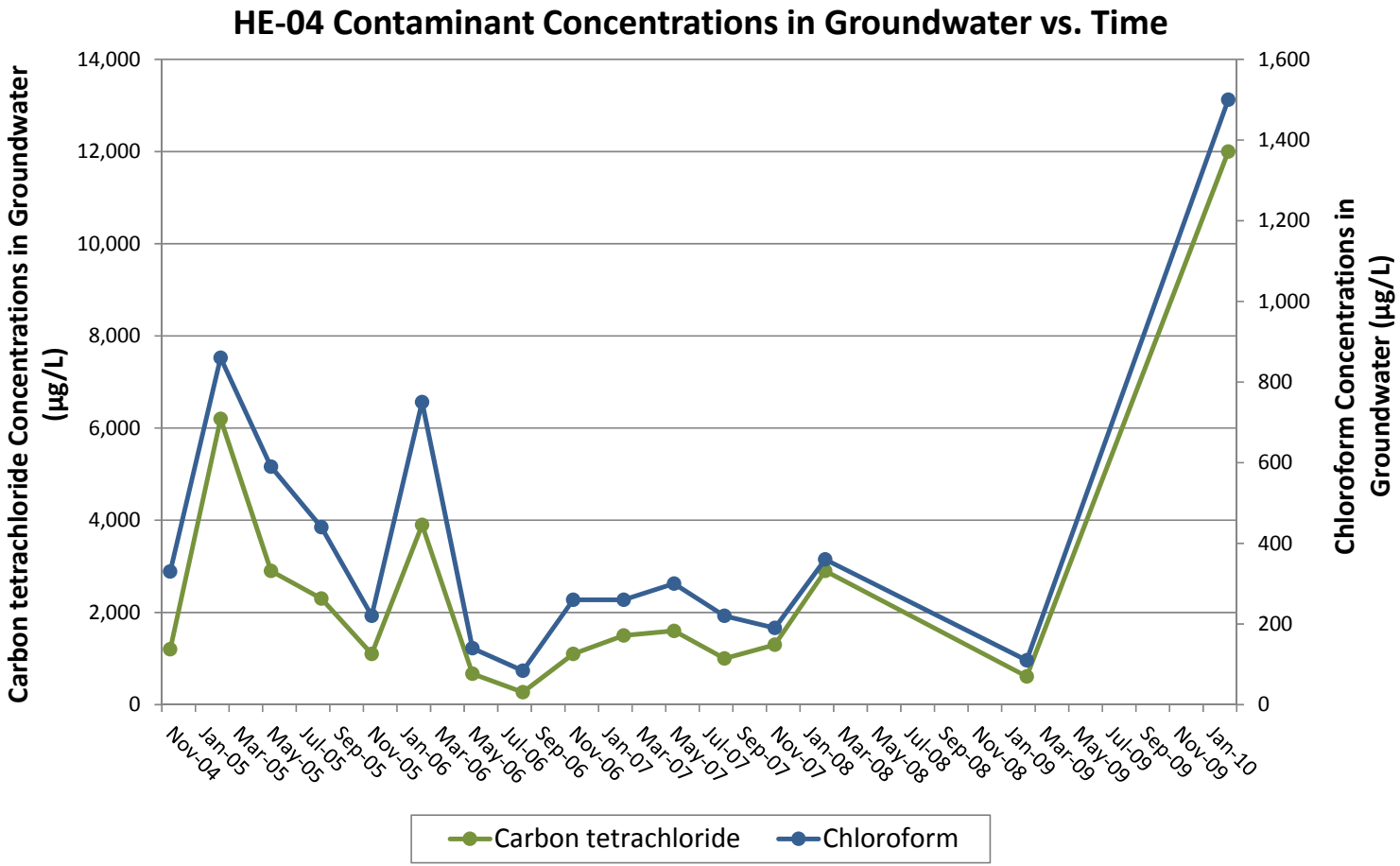
# MW-47D Recent Results



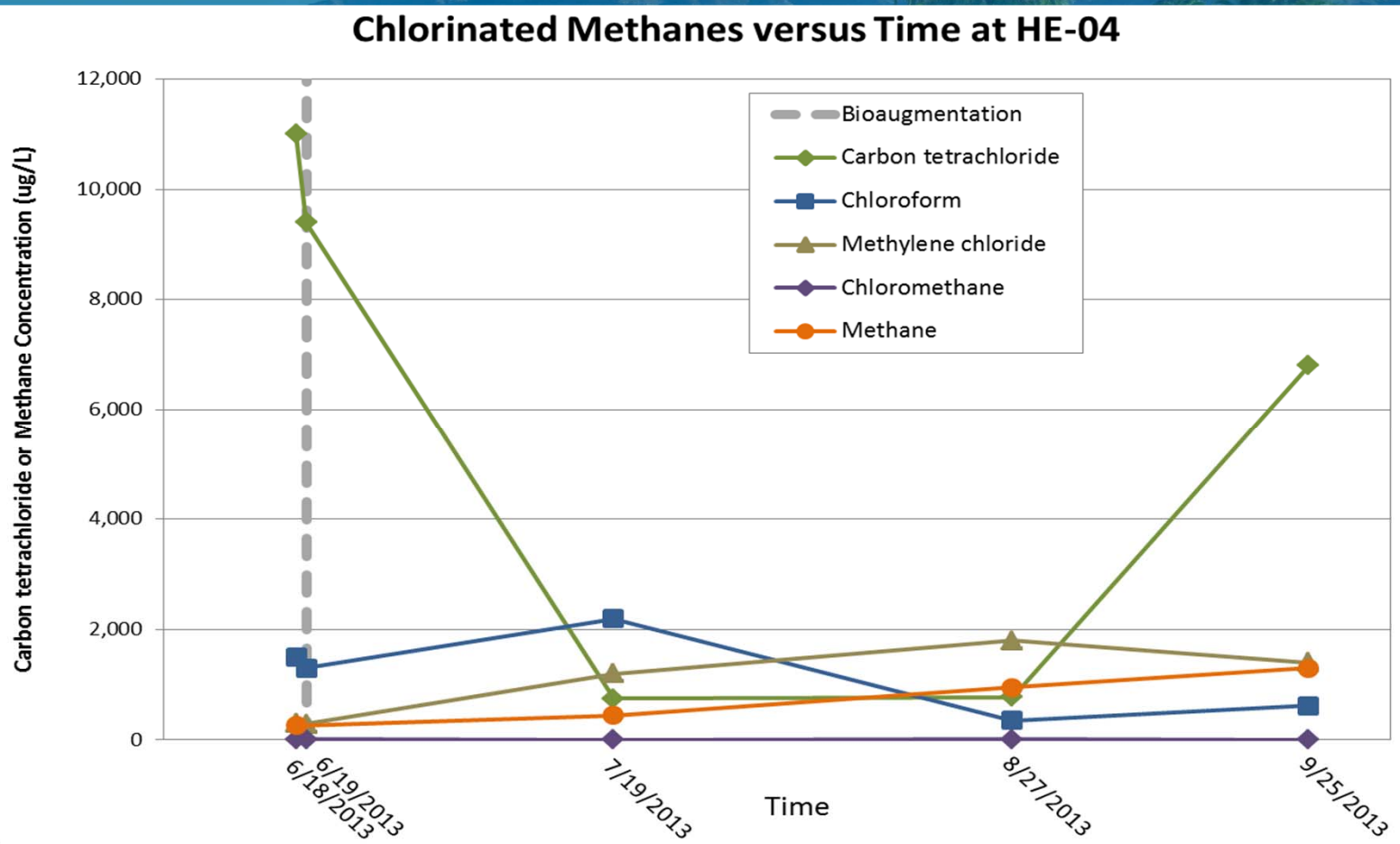
# MW-47D VOC Concentrations as % of Total



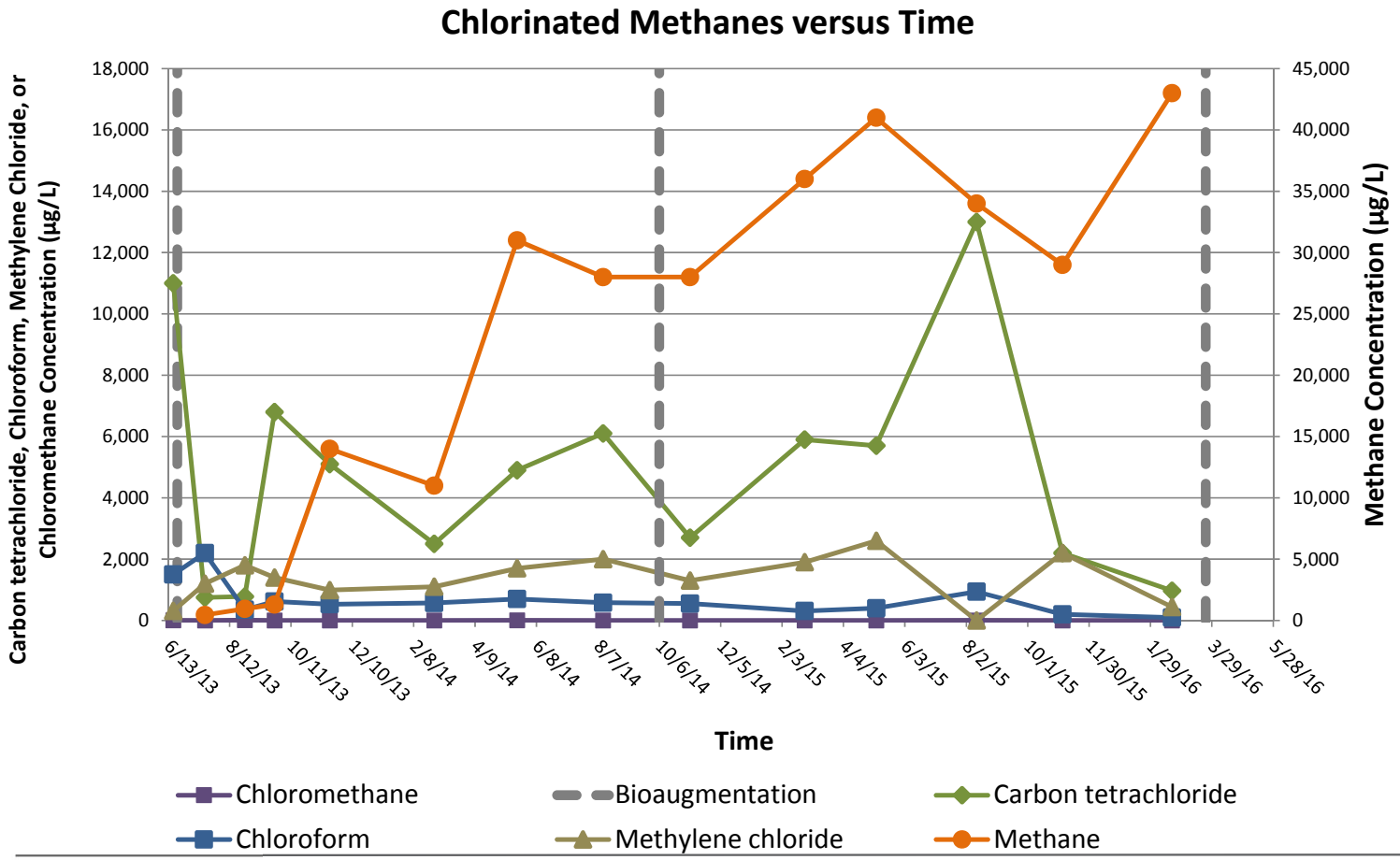
# HE-04


HE-04 Contaminant Concentrations in Groundwater vs. Time
Carbon tetrachloride Concentrations in Groundwater (µg/L)
Chloroform Concentrations in Groundwater (µg/L)
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1,600
1,400
1,200
1,000
800
600
400
200
0
Nov-04
Jan-05
Mar-05
May-05
Jul-05
Sep-05
Nov-05
Jan-06
Mar-06
May-06
Jul-06
Sep-06
Nov-06
Jan-07
Mar-07
May-07
Jul-07
Sep-07
Nov-07
Jan-08
Mar-08
May-08
Jul-08
Sep-08
Nov-08
Jan-09
Mar-09
May-09
Jul-09
Sep-09
Nov-09
Jan-10
Carbon tetrachloride
Chloroform

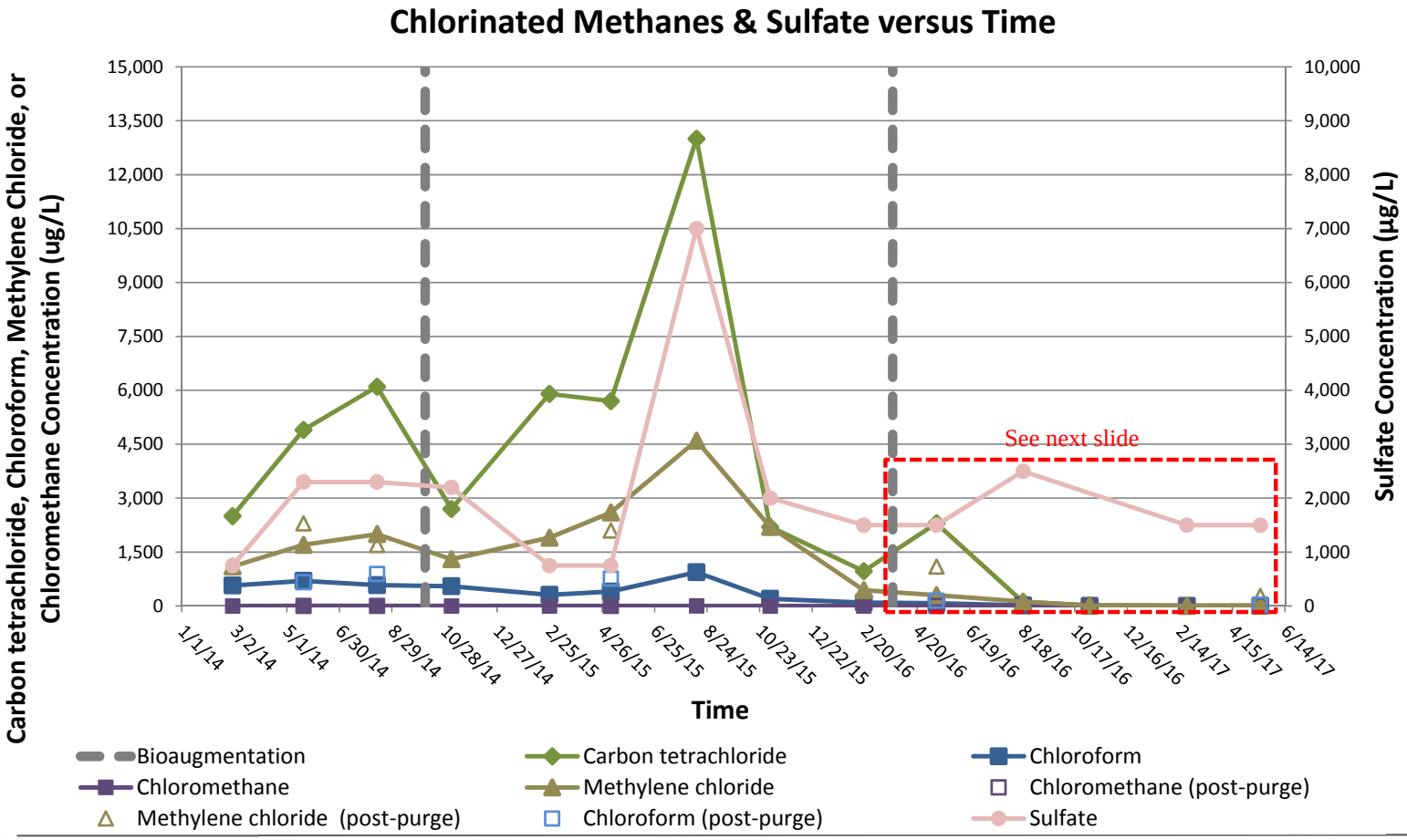
# CHLORINATED METHANES –HE-04



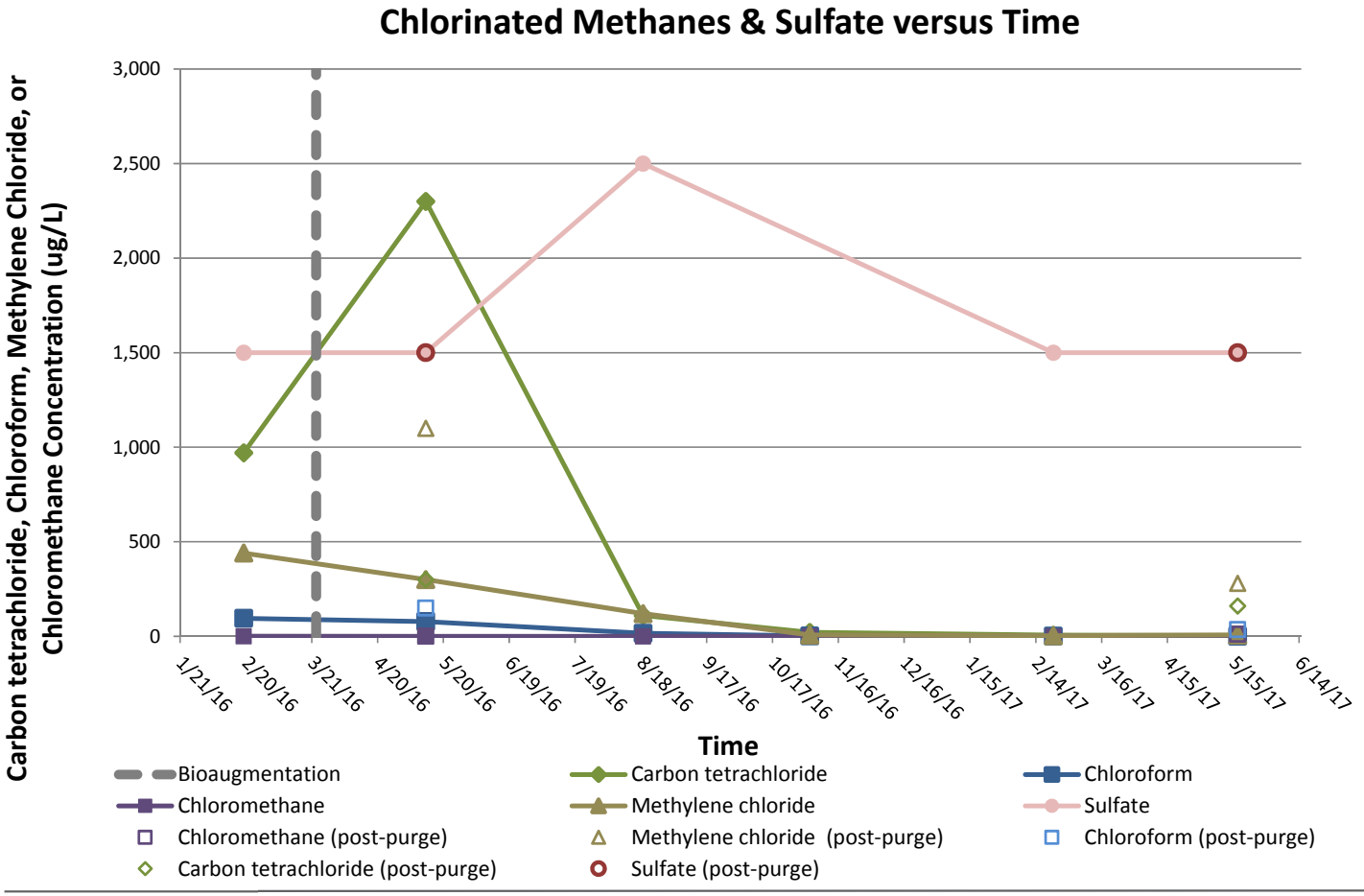
# HE-04


Chlorinated Methanes versus Time
Carbon tetrachloride, Chloroform, Methylene Chloride, or Chloromethane Concentration (µg/L)
Methane Concentration (µg/L)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
45,000
40,000
35,000
30,000
25,000
20,000
15,000
10,000
5,000
0
6/13/13
8/12/13
10/11/13
12/10/13
2/8/14
4/9/14
6/8/14
8/7/14
10/6/14
12/5/14
2/3/15
4/4/15
6/3/15
8/2/15
10/1/15
11/30/15
1/29/16
3/29/16
5/28/16
Time
Chloromethane
Bioaugmentation
Carbon tetrachloride
Chloroform
Methylene chloride
Methane

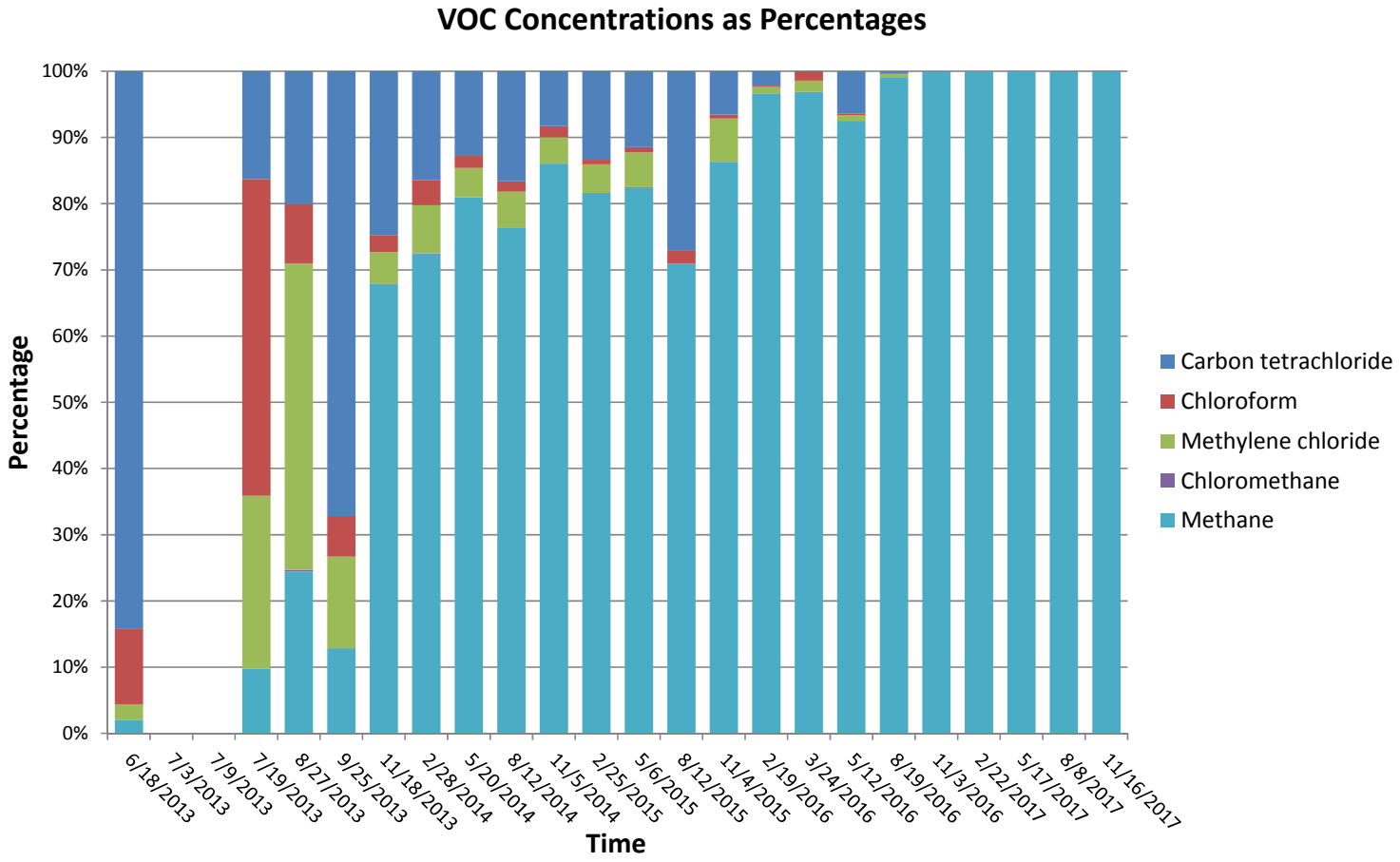
# HE-04 Recent Results



# HE-04


Chlorinated Methanes & Sulfate versus Time
Carbon tetrachloride, Chloroform, Methylene Chloride, or Chloromethane Concentration (ug/L)
3,000
2,500
2,000
1,500
1,000
500
0
1/21/16
2/20/16
3/21/16
4/20/16
5/20/16
6/19/16
7/19/16
8/18/16
9/17/16
10/17/16
11/16/16
12/16/16
1/15/17
2/14/17
3/16/17
4/15/17
5/15/17
6/14/17
Time
Bioaugmentation
Carbon tetrachloride
Chloroform
Chloromethane
Methylene chloride
Sulfate
Chloromethane (post-purge)
Methylene chloride (post-purge)
Chloroform (post-purge)
Carbon tetrachloride (post-purge)
Sulfate (post-purge)

# HE-04


VOC Concentrations as Percentages
Percentage
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
6/18/2013
7/3/2013
7/9/2013
7/19/2013
8/27/2013
9/25/2013
11/18/2013
2/28/2014
5/20/2014
8/12/2014
11/5/2014
2/25/2015
5/6/2015
8/12/2015
11/4/2015
2/19/2016
3/24/2016
5/12/2016
8/19/2016
11/3/2016
2/22/2017
5/17/2017
8/8/2017
11/16/2017
Time
Carbon tetrachloride
Chloroform
Methylene chloride
Chloromethane
Methane

# Summary/Lessons Learned

- CVOC sources existed upgradient of the biologically active zones (BAZ) and these periodically caused high concentrations of parent CVOCs
- Use of a bromide tracer showed that the initial decrease in CVOCs was primarily due to biodegradation, not dilution
- Sulfate proved to be a valuable tracer of upgradient groundwater entering the BAZ
- Initially low levels of methane increased as concentrations of the CVOCs decreased
- Bioaugmentation was conducted more often than typical reflecting karst geology
- Do not underestimate the value of degrading mass even if the source area is not well defined

Thank you

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QUESTIONS?

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