WEBINAR

Multifunctional Amendments and Site Characterization Effectively Manage Back Diffusion from a Fractured Sandstone Aquifer

Matthew Burns
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- *LinkedIn*

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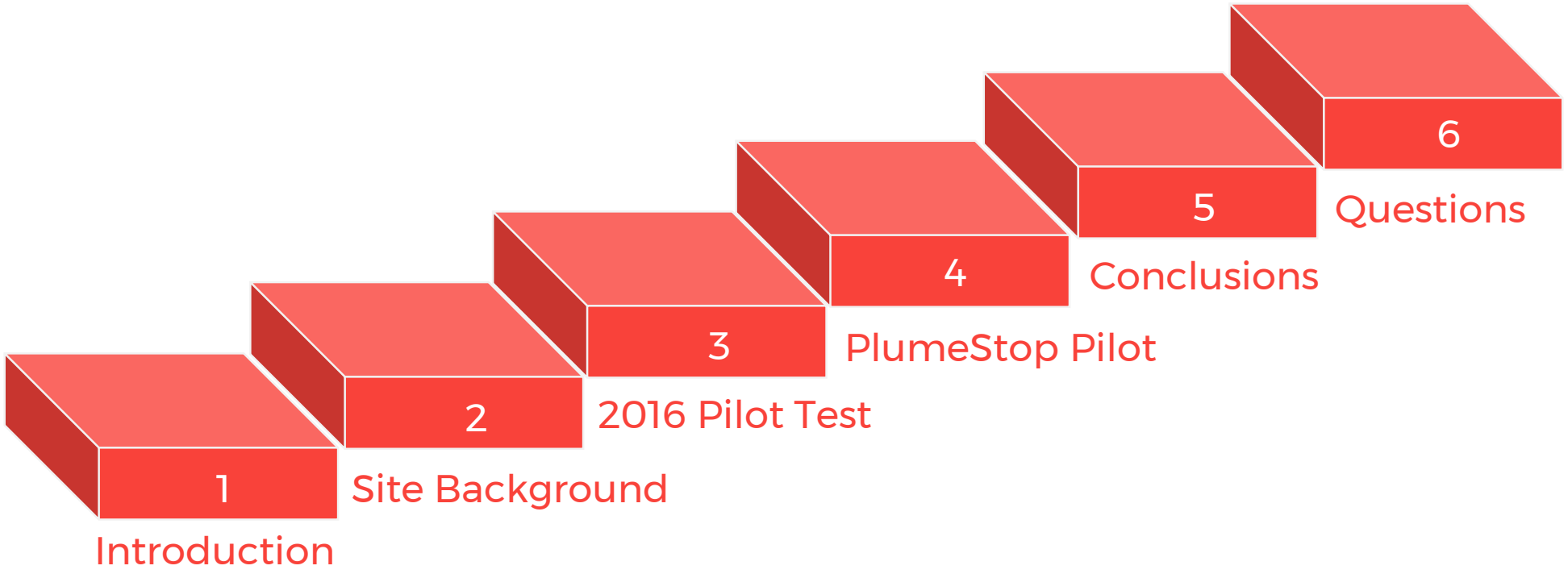
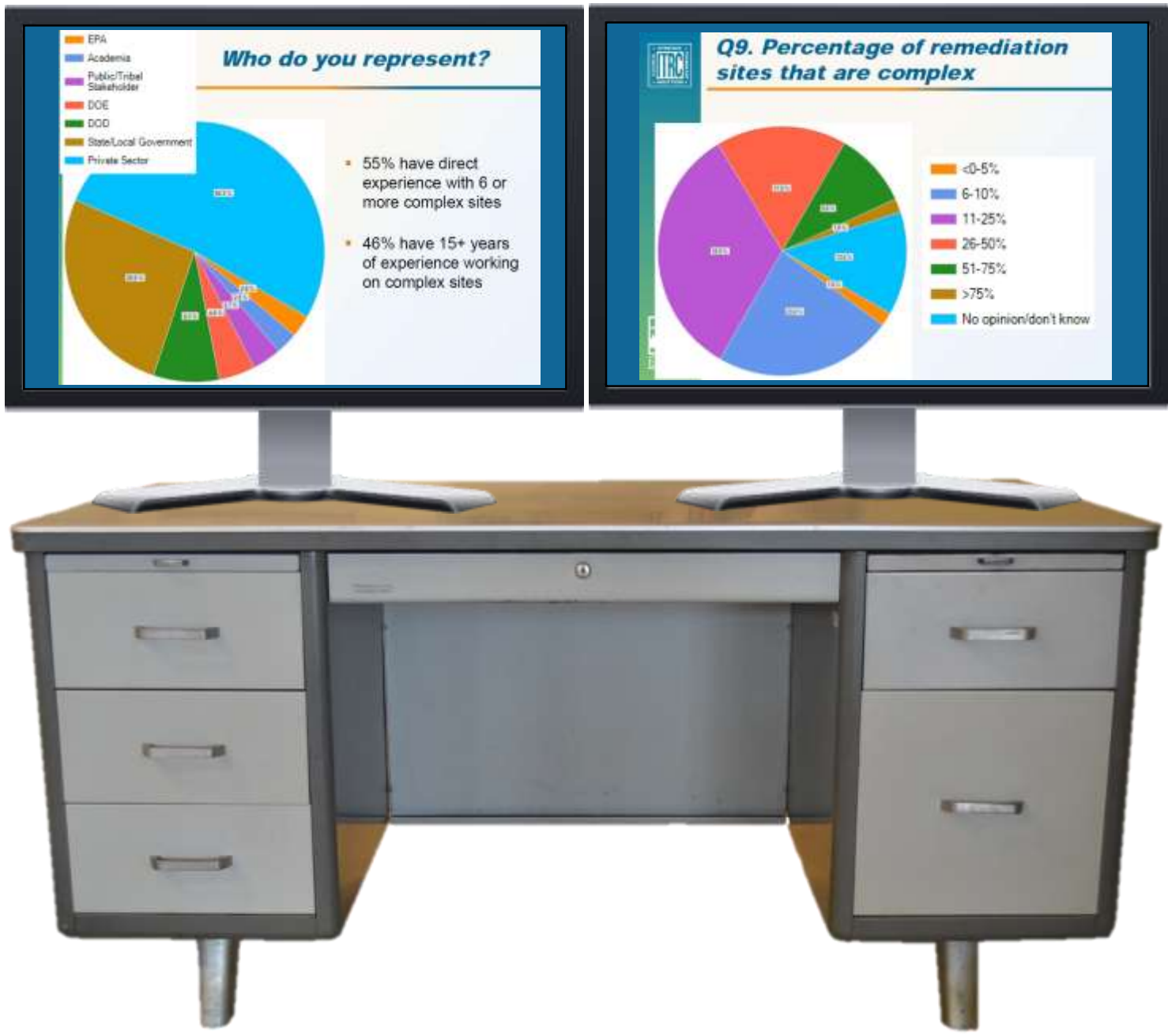
Outline


1
Introduction
2
Site Background
3
2016 Pilot Test
4
PlumeStop Pilot
5
Conclusions
6
Questions

Complex Sites

Complex Sites



Back Diffusion

Back Diffusion

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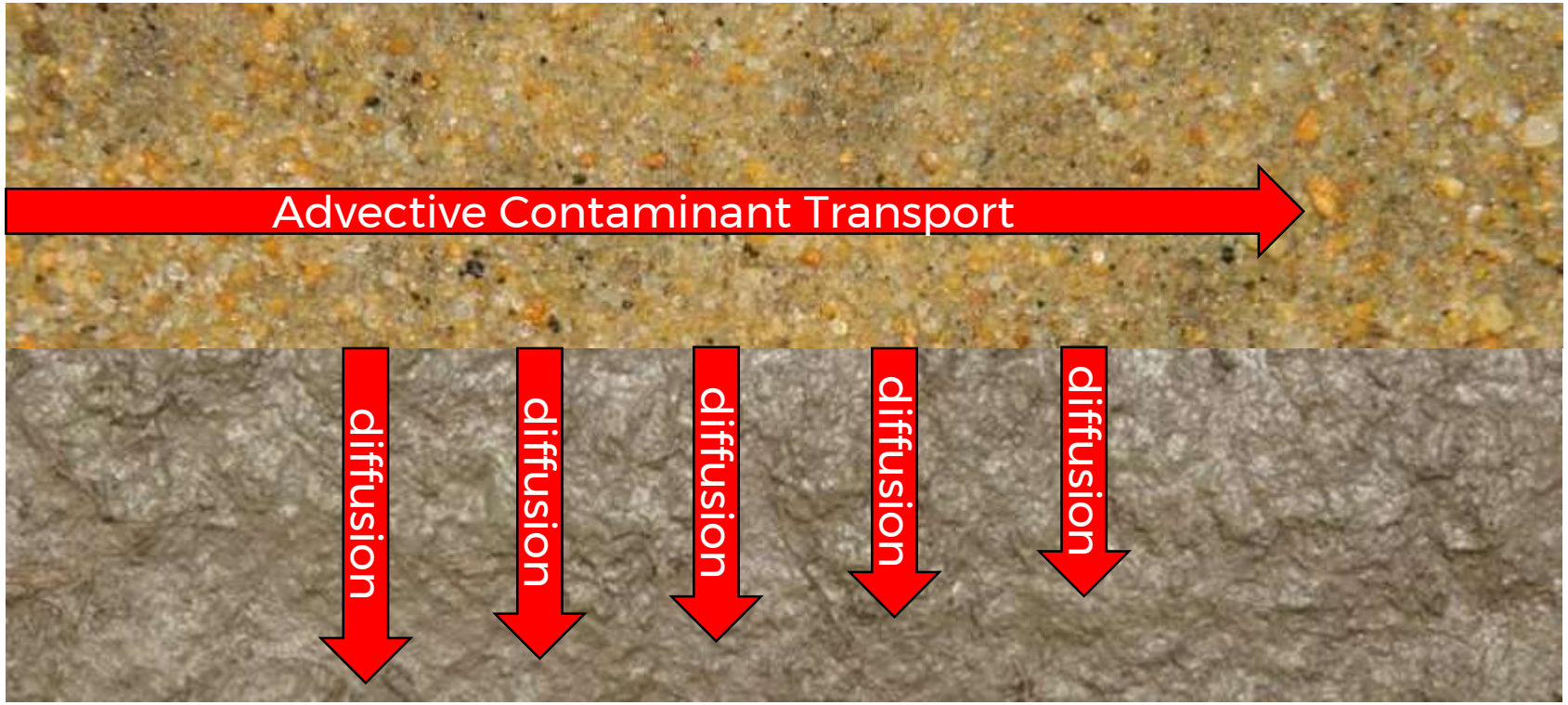
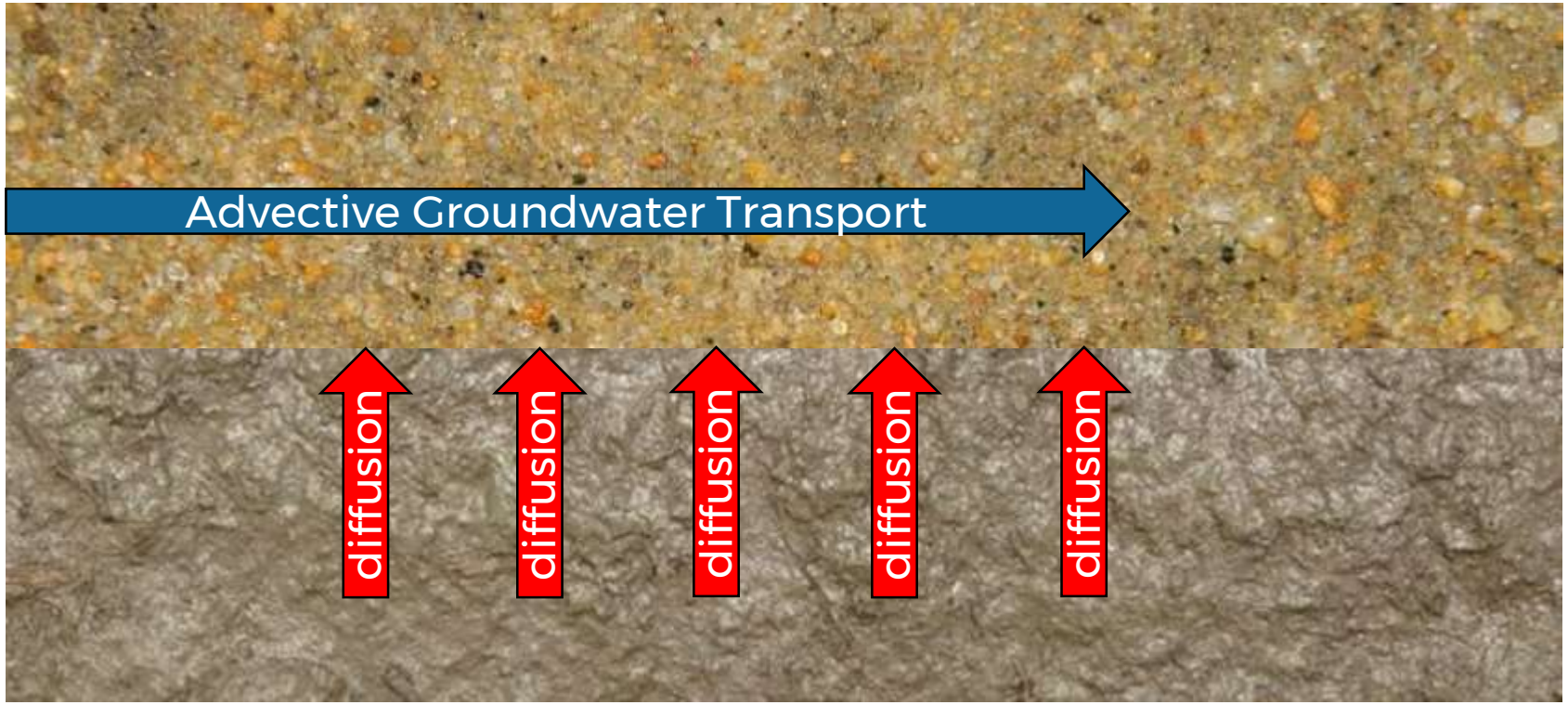
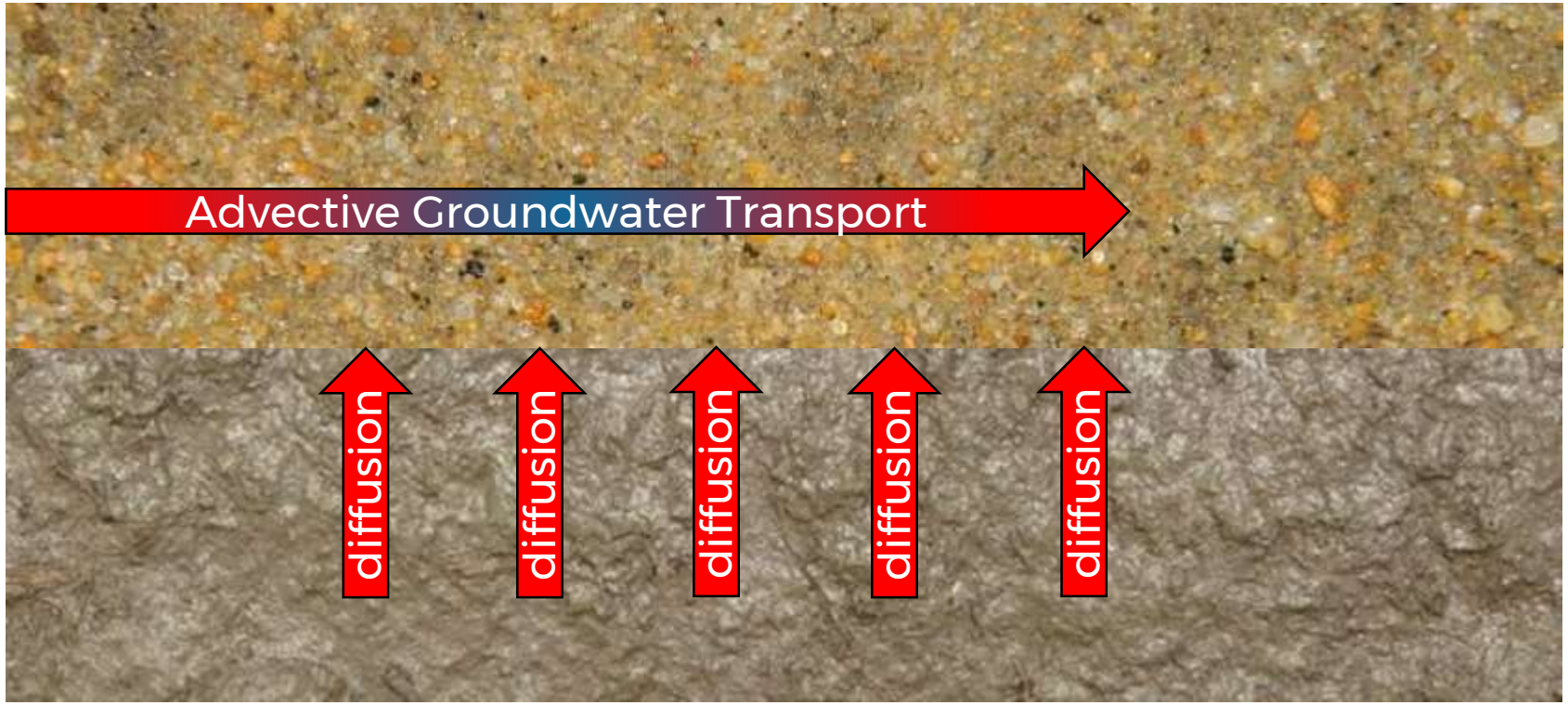


Back Diffusion

Remediate Transmissive Zones

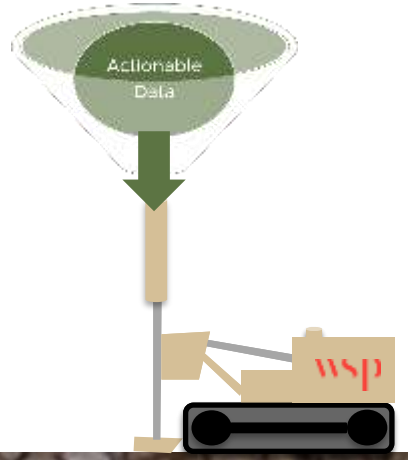


Back Diffusion



Managing Complex Sites

Managing Complex Sites



Initiate

Plan & Design

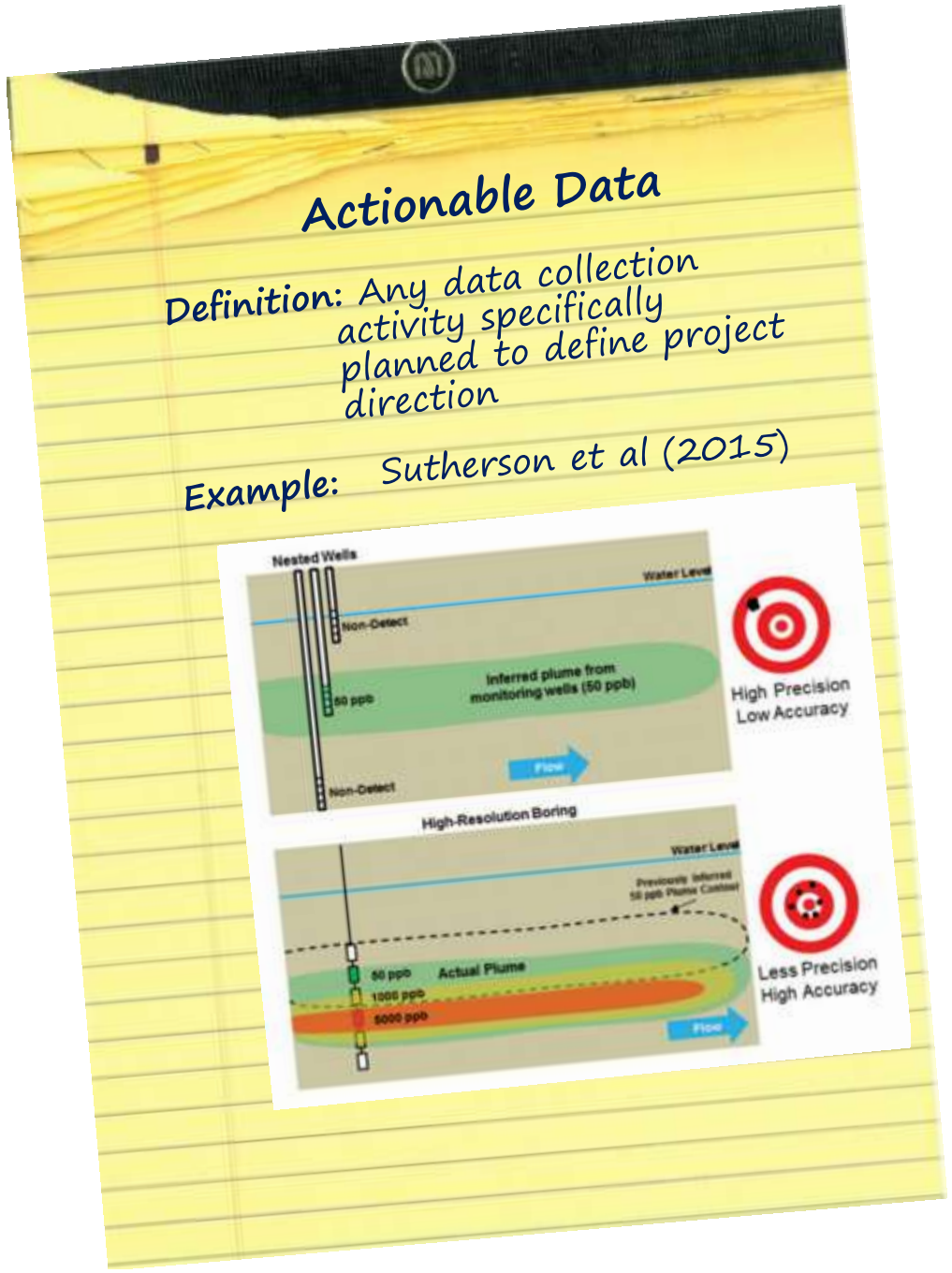
Execute

Monitor & Control

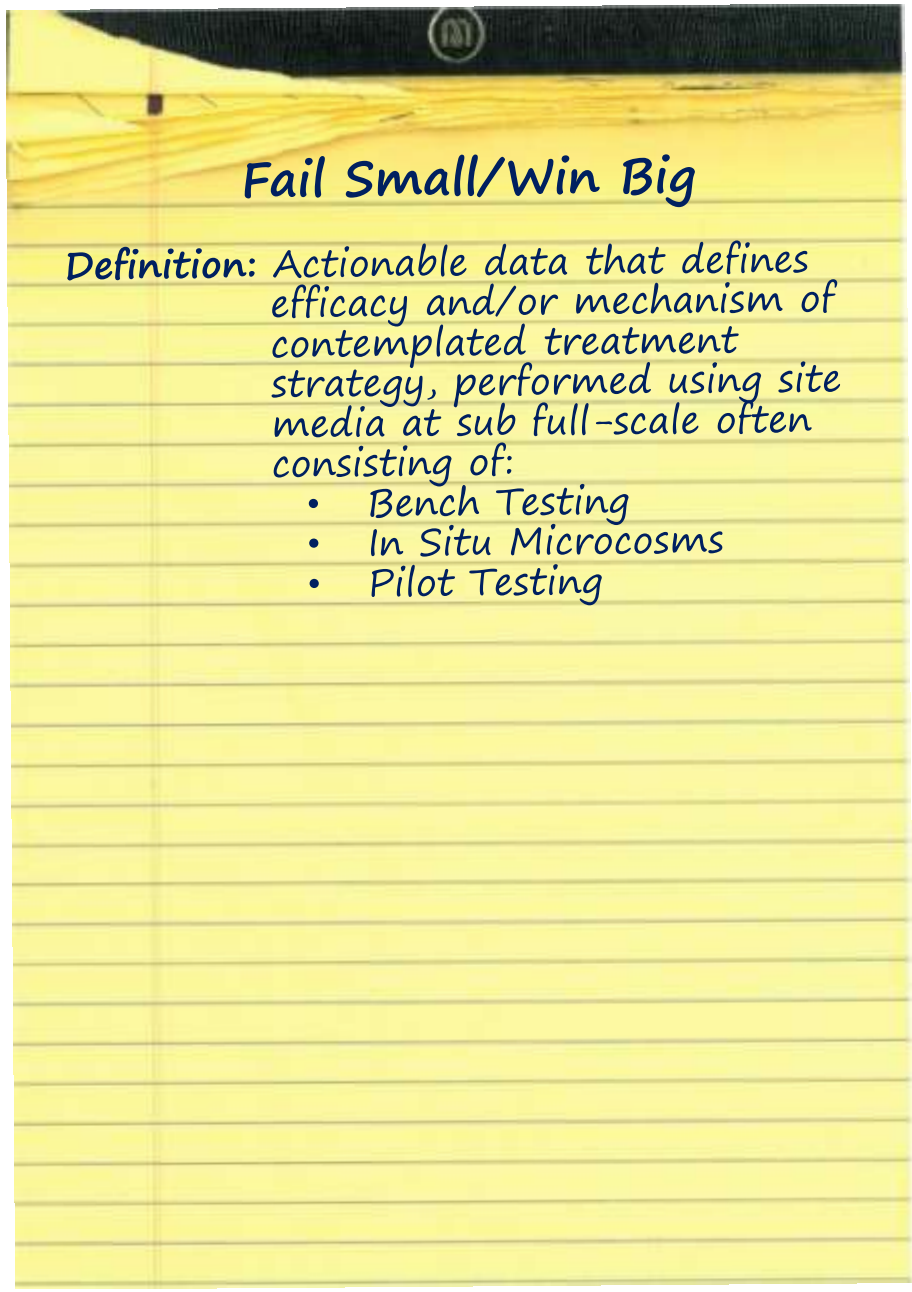
Close

wsp

Actionable Data



Actionable Data



Site Background

Site Background

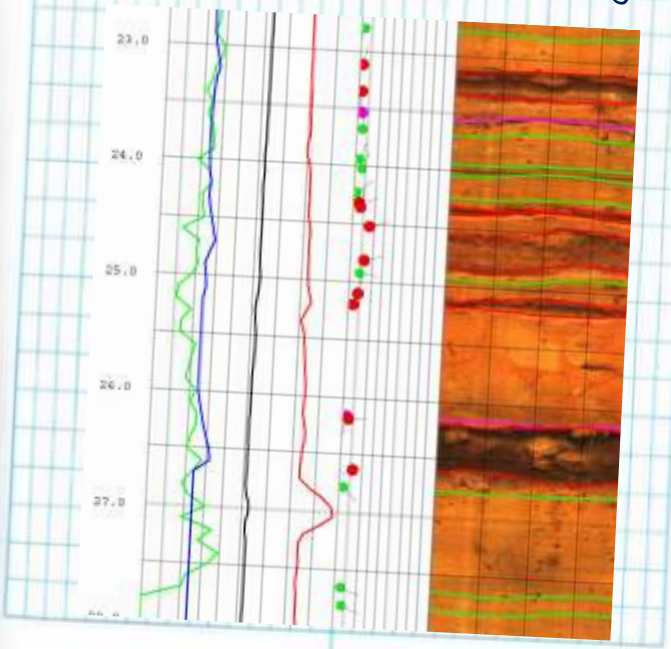
Manufacturing facility since 1961
- Gas values
- Metals processing – melt/re-melt, die casting, tapping
- Solvents, degreasers, cutting oils

Contaminants
- TCE (≥ 10,000 µg/l)
- 1,1,1-TCA (≥ 250 µg/l)
- Some daughters

Site Characteristics
- Source on top of hill
- Dissolved plume extends ≈ 1500 ft to a gaining stream

Remediation/Mitigation
- Vadose zone excavated
- VI intrusion mitigation

Fractured Sandstone Matrix
- Relatively high primary porosity
- High flow fractures (secondary porosity
- Back diffusion from primary matrix likely



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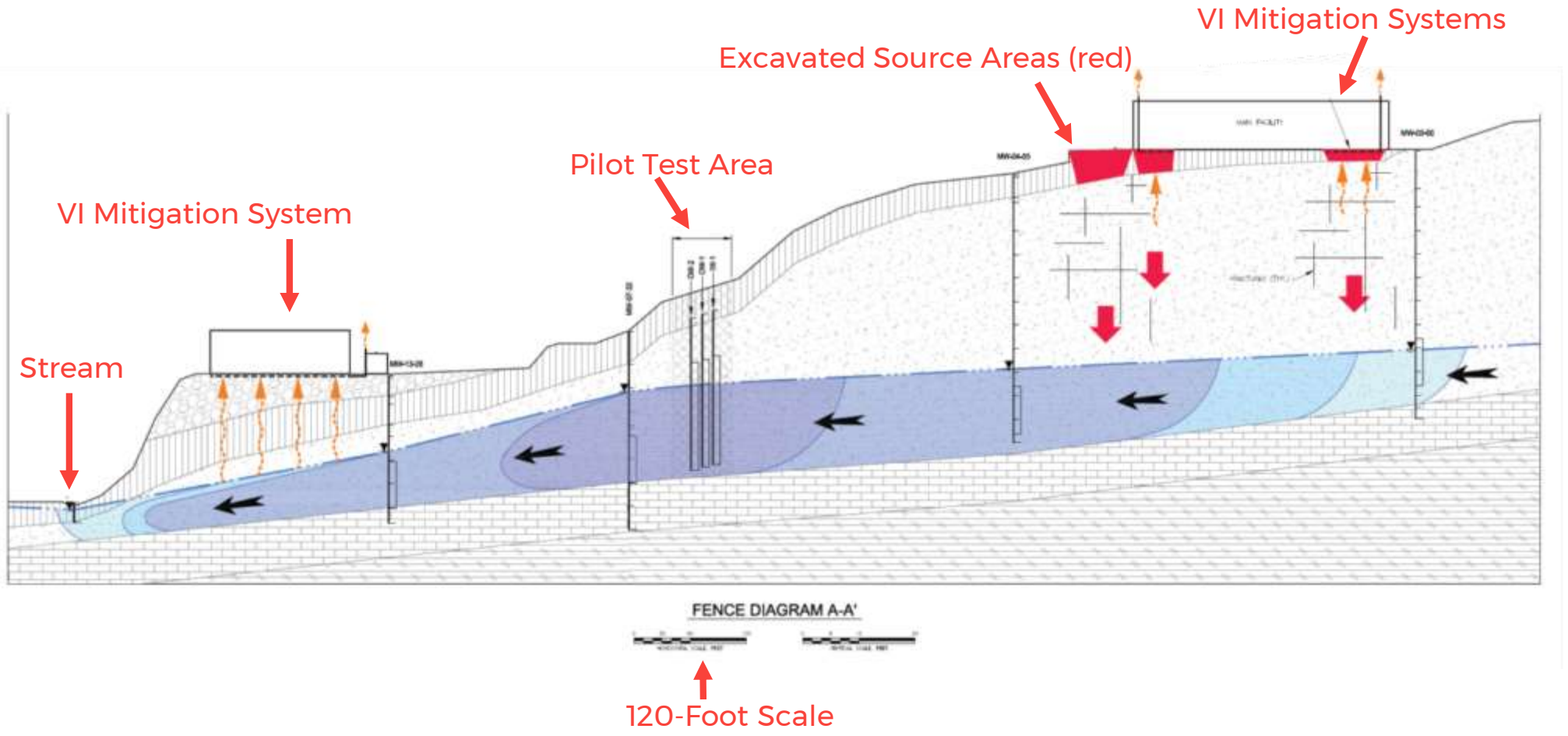

Pre-Design Studies

MEMO

TO: Arkansas Project Team

FROM: Michael Brown, Ph.D.

SUBJECT: Pre-Design Studies

DATE: January 10, 2016

The scope of work (SOW) for the Arkansas project predesign study includes installing a series of bedrock monitoring wells to support the following investigation components:

- Geophysical logging (natural gamma radiation, optical televiewer, and three-arm caliper)
- Pumping tests (step drawdown, constant rate, and recovery)
- Pilot test: bioremediation plus biogeochemical reductive transformation
- Dye tracer test (to be conducted with pilot test)
- Performance monitoring for a period of one year to include advanced diagnostics to assess contaminant degradation and degradation mechanism

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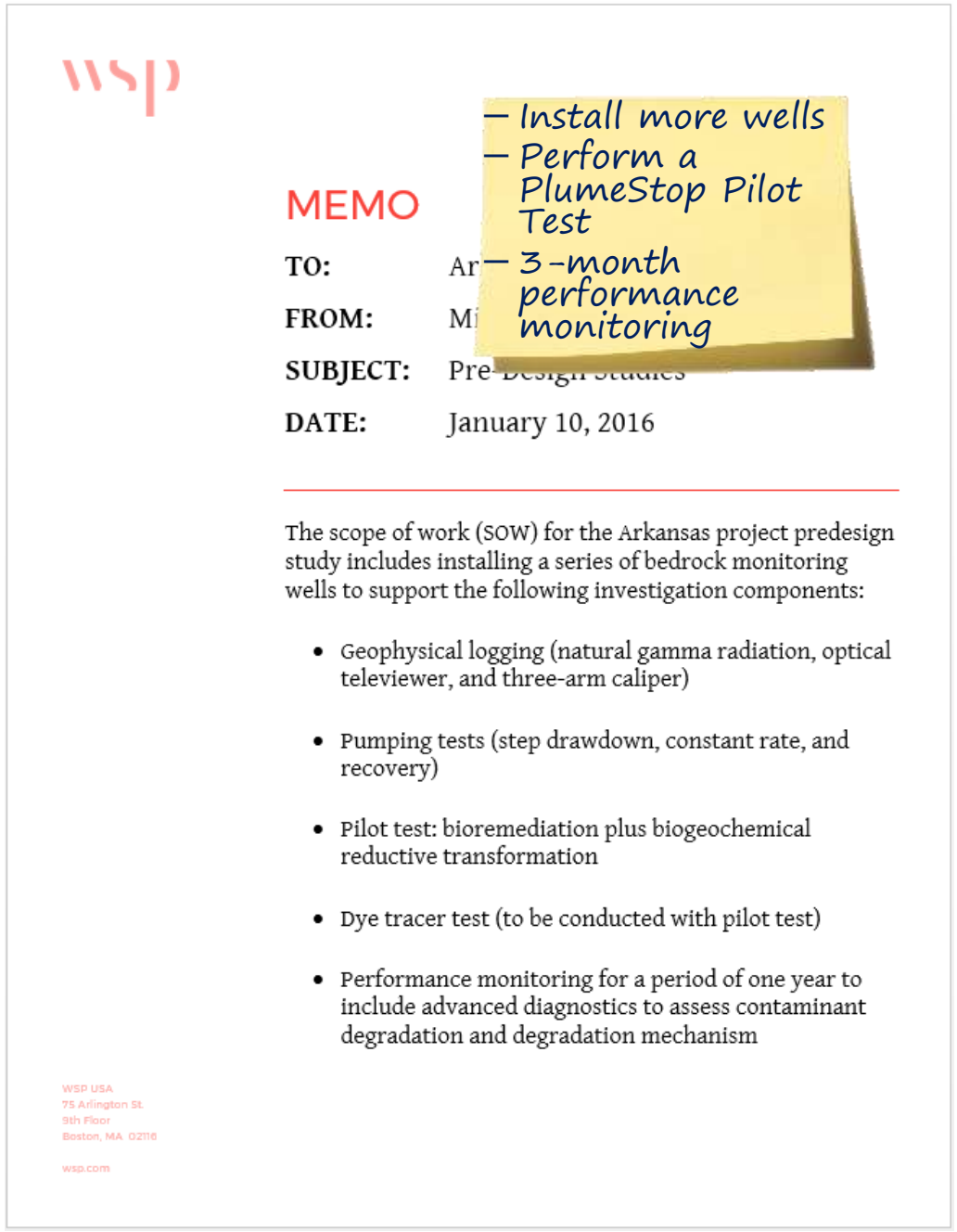
Pre-Design Studies



MEMO

TO: Ar

FROM: Mi

SUBJECT: Pre-Design Studies

DATE: January 10, 2016

– Install more wells
– Perform a PlumeStop Pilot Test
– 3-month performance monitoring

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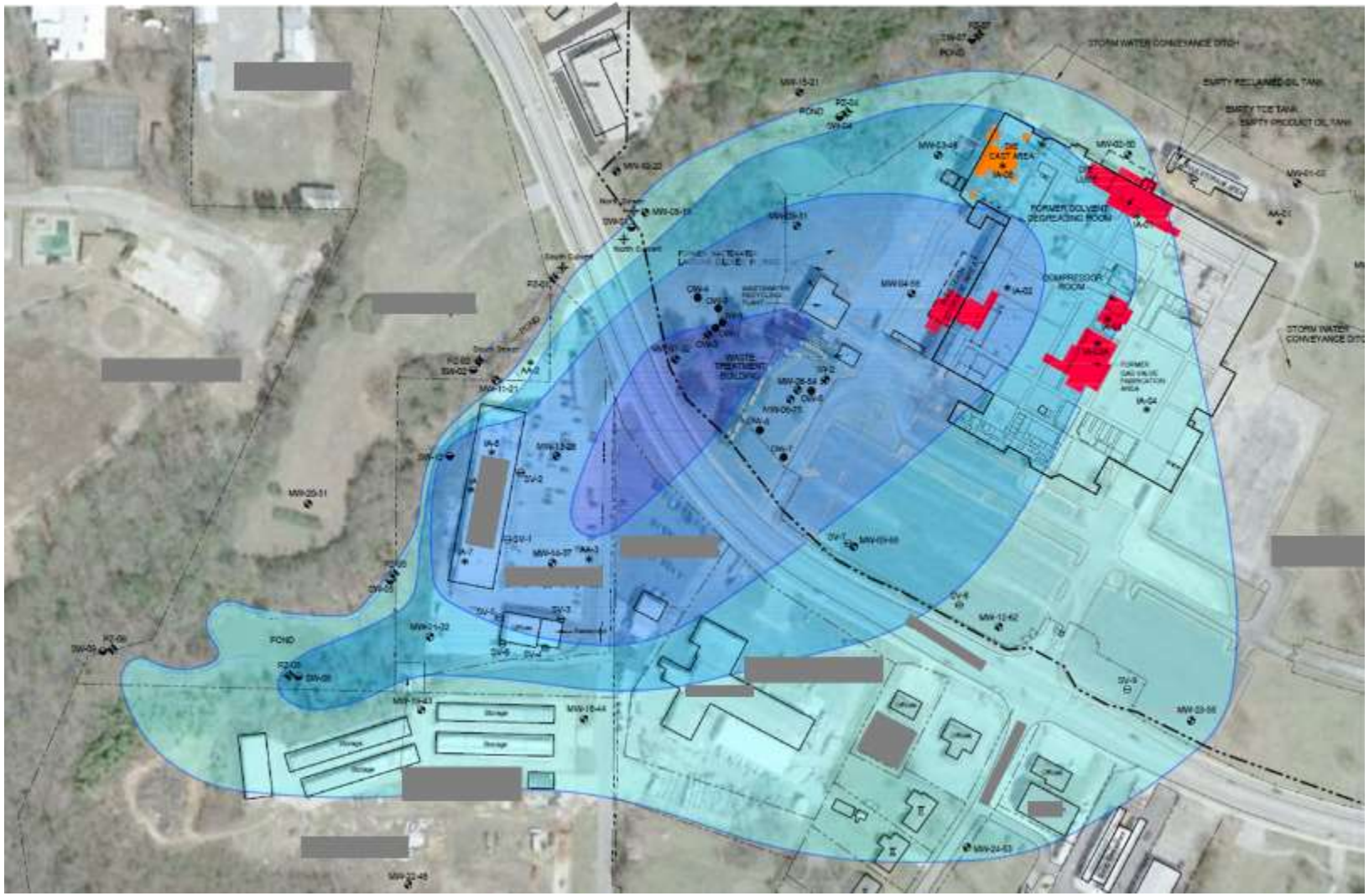
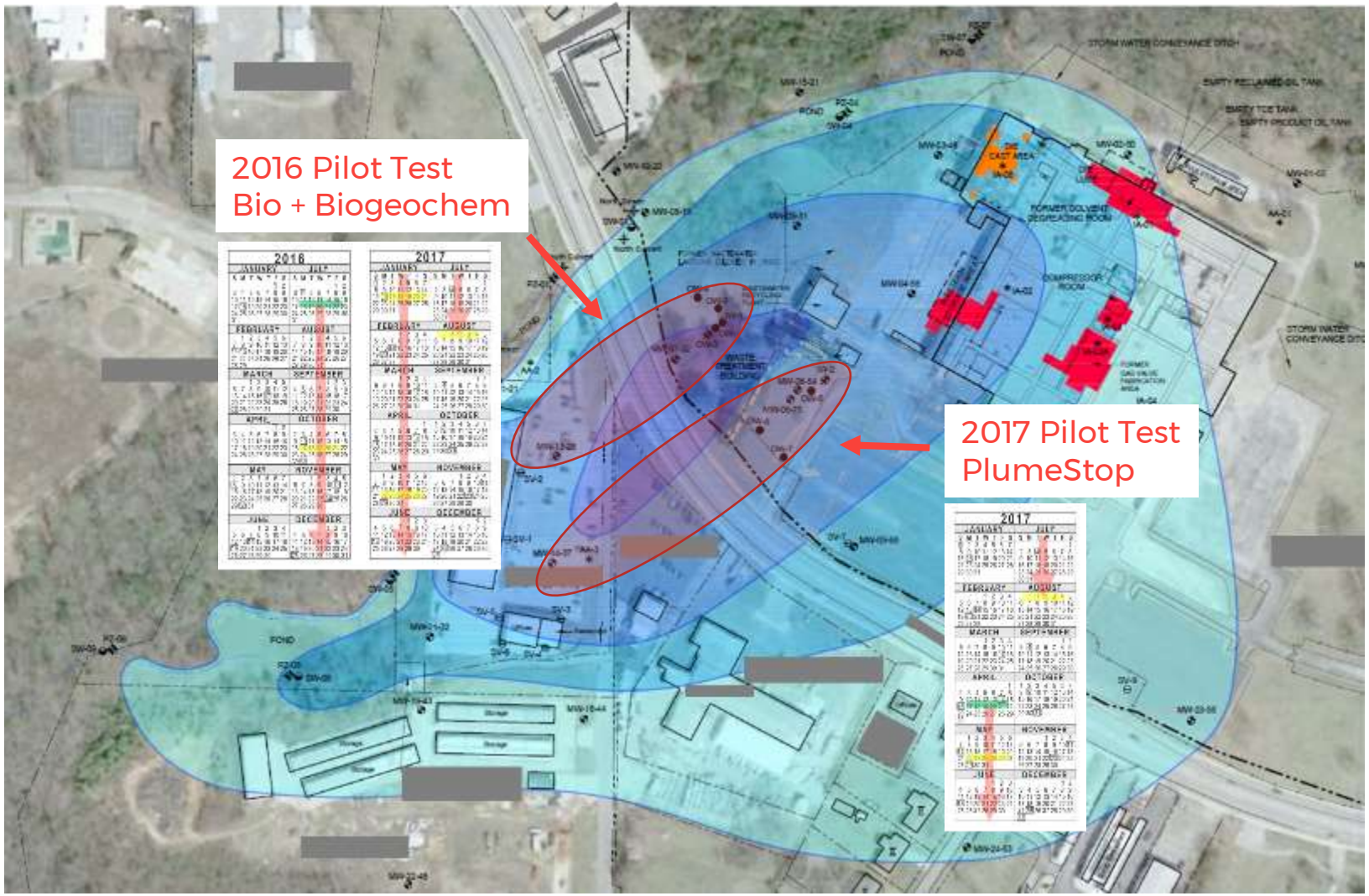
Site Layout

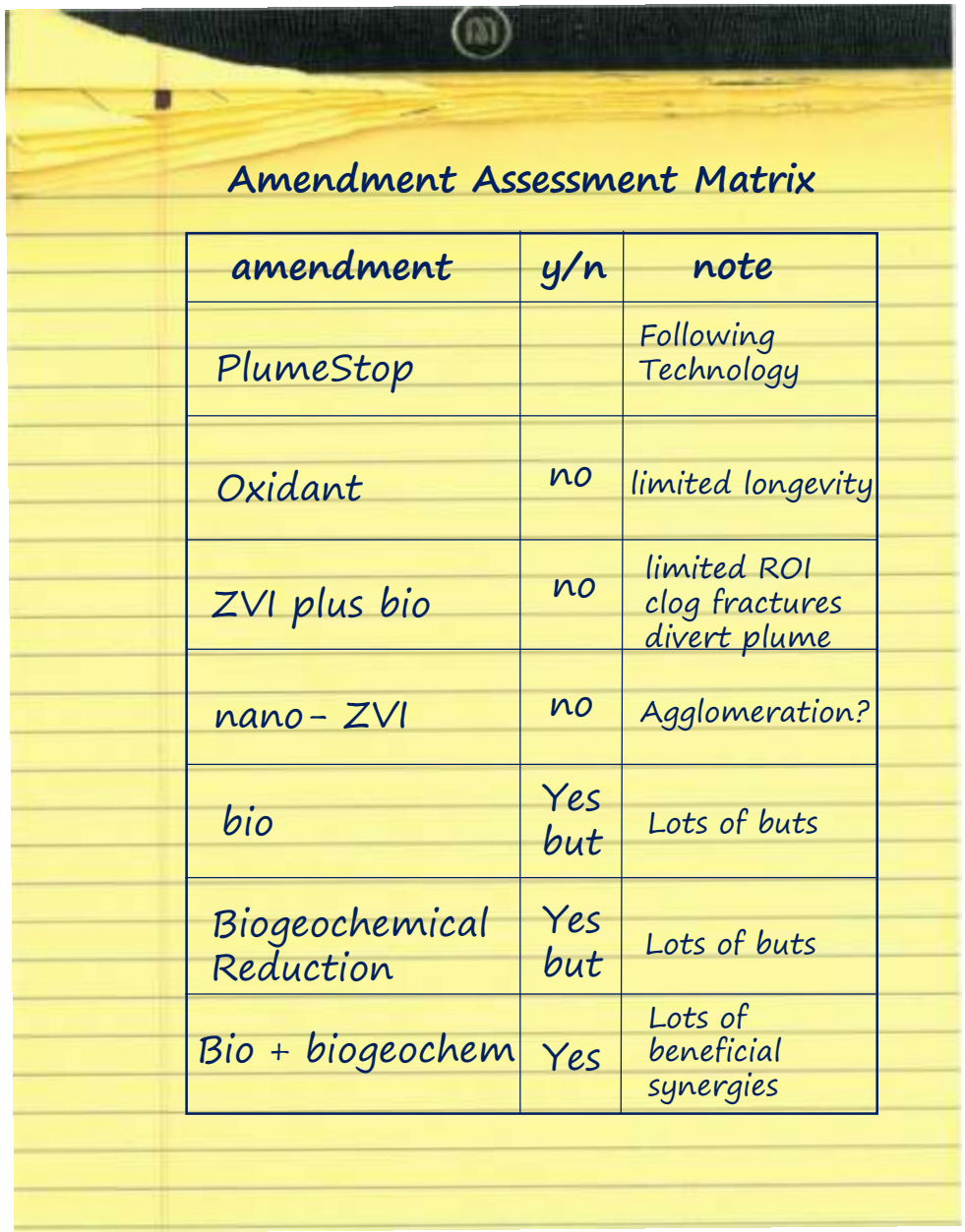

STORM WATER CONVEYANCE DITCH
EMPTY RECLAIMED OIL TANK
EMPTY TCE TANK
EMPTY PRODUCT OIL TANK
POND
FORMER DEGREASING ROOM
COMPRESSOR ROOM
WASTE TREATMENT BUILDING
FORMER GAS VALVE FABRICATION AREA
STORM WATER CONVEYANCE DITCH

Site Layout


2016 Pilot Test
Bio + Biogeochem
2016
2017
2017 Pilot Test
PlumeStop
2017

2016 Pilot Test Goals

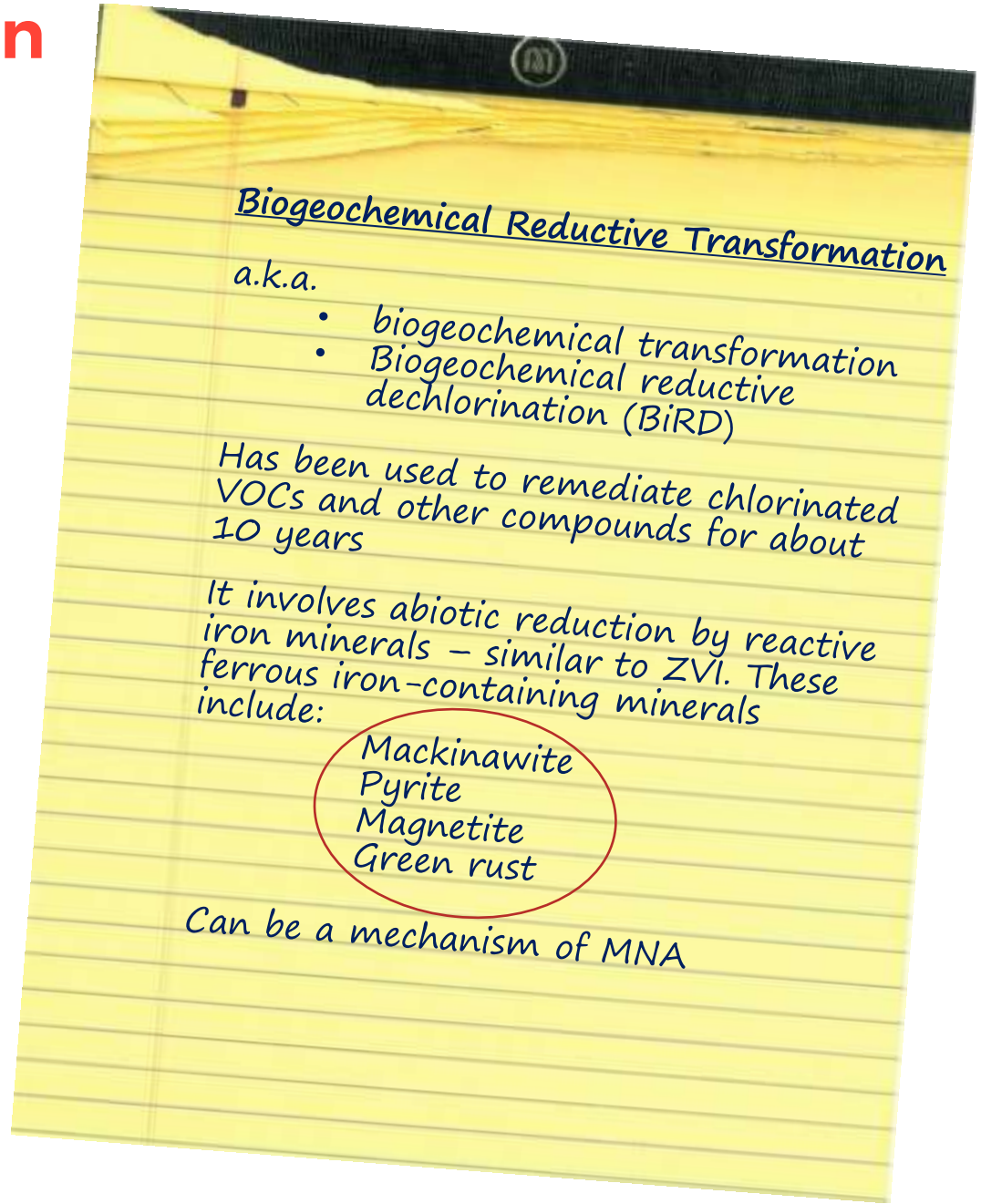
2016 Pilot Test Goals



Amendment Assessment Matrix

amendment	y/n	note
PlumeStop		Following Technology
Oxidant	no	limited longevity
ZVI plus bio	no	limited ROI clog fractures divert plume
nano- ZVI	no	Agglomeration?
bio	Yes but	Lots of buts
Biogeochemical Reduction	Yes but	Lots of buts
Bio + biogeochem	Yes	Lots of beneficial synergies

Biogeochemical Reduction



Biogeochemical Reduction

Engineering Biogenic Iron Sulfide

(1) Iron Reduction

Fe^{3+} + organic matter → Fe^{2+} + H_2O + CO_2

(2) Sulfate Reduction

SO_4^{2-} + organic matter → S^{2-} + H_2O + CO_2

(3) Iron Sulfide Precipitation

HS^- + Fe^{2+} → FeS + H^+

Addition of sulfate to form FeS to treat chlorinated VOCs is a Patented Process:

- Kennedy - US Patent Off. #6,884,352 B1
- Contact Jim Studer of InfraSur
  - jstuder@InfraSUR-LLC.com
  - 505-858-3136

Synergies

Biotic and Fe-based Abiotic Reductive Pathways are Compatible & Complementary

- Ferric iron inhibition disproven
  - Wei and Finneran Sci. Technol., 2011, 45 (17)
- Fe Reduces Dehalococcoides (DHC) inhibition
  - Sulfide (precipitates with ferrous iron)
  - Abiotic treatment of 1,1,1trichlorethane
  - Iron reducers supply vitamin B12
- Some reduced minerals are not very reactive with dichloroethene – biodegradation can manage
- Generally, fermentable donors have a higher delivery efficiency than zero valent iron (ZVI) which results in a greater radius of influence (ROI)
- Lower redox potentials
- Minimize surface pacification
- Extend treatment longevity and manage rebound

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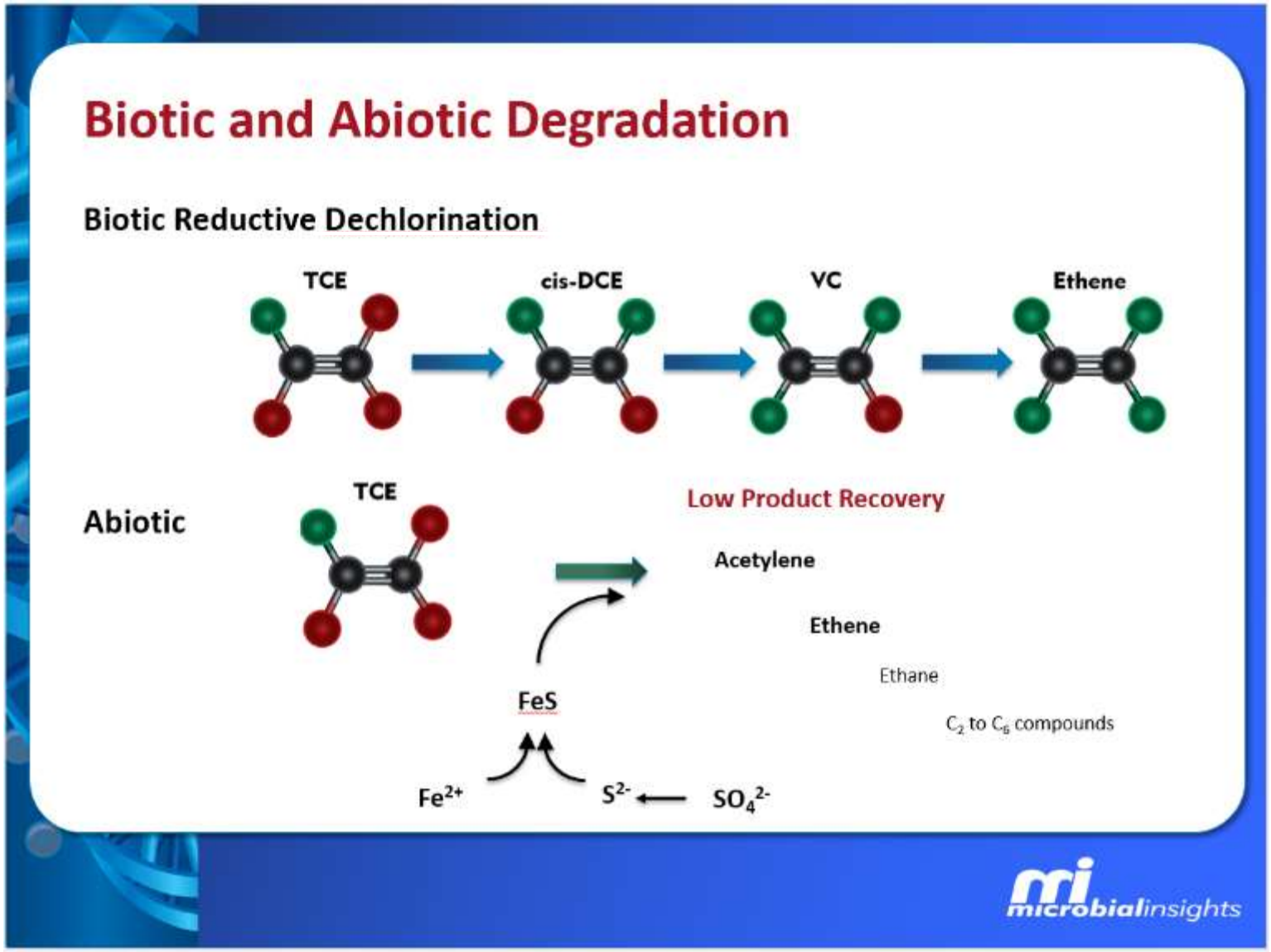
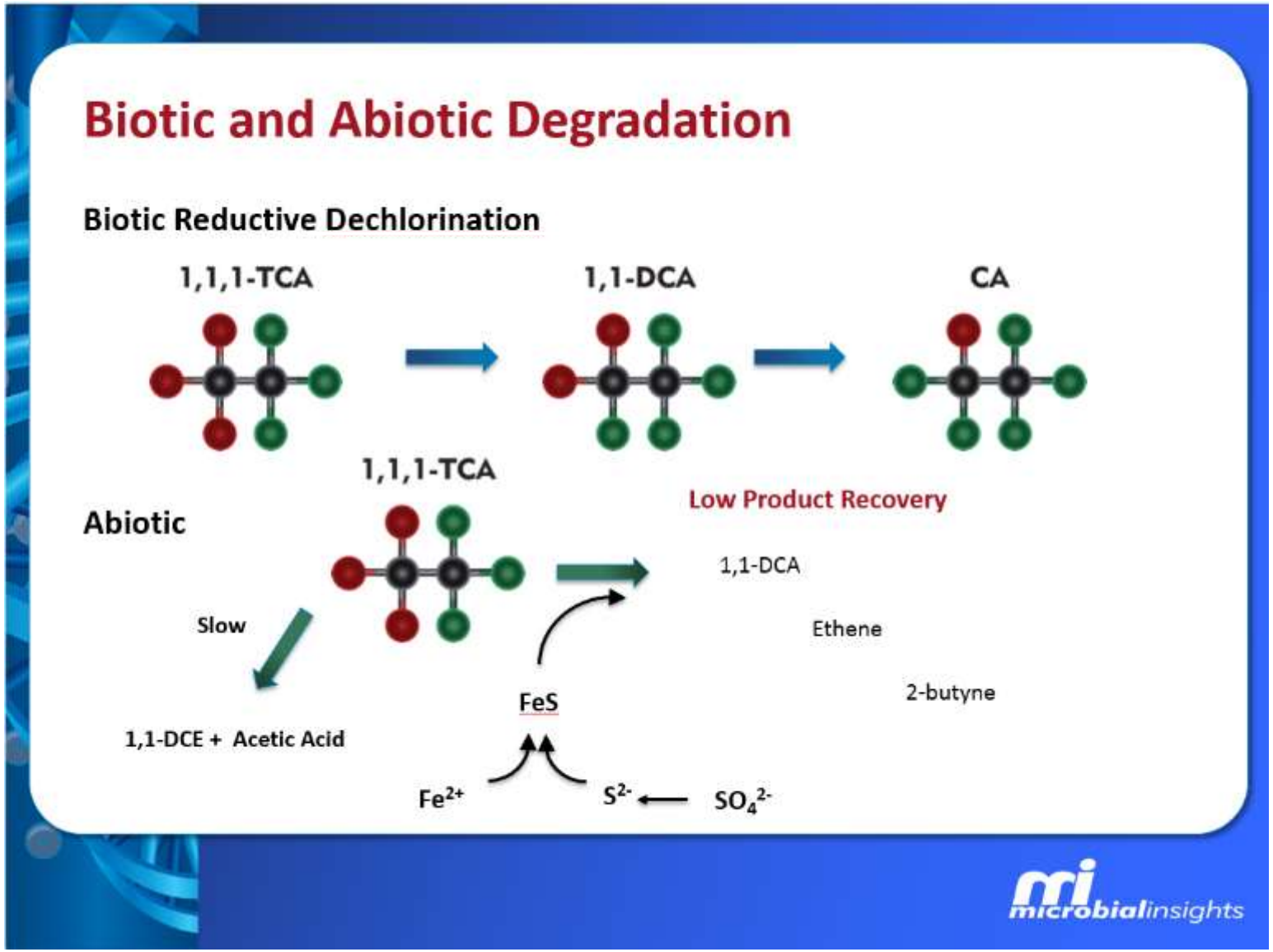
TCE Degradation Pathways



TCA Degradation Pathways



Degradation Mechanism Identification

$$f_{abiotic} = \frac{\Sigma VOC_{t0} - \Sigma VOC_{t1}}{\Sigma VOC_{t0}}$$

where ΣVOC_t = TCE + DCE + VC + Ethene + Ethane

Biotic

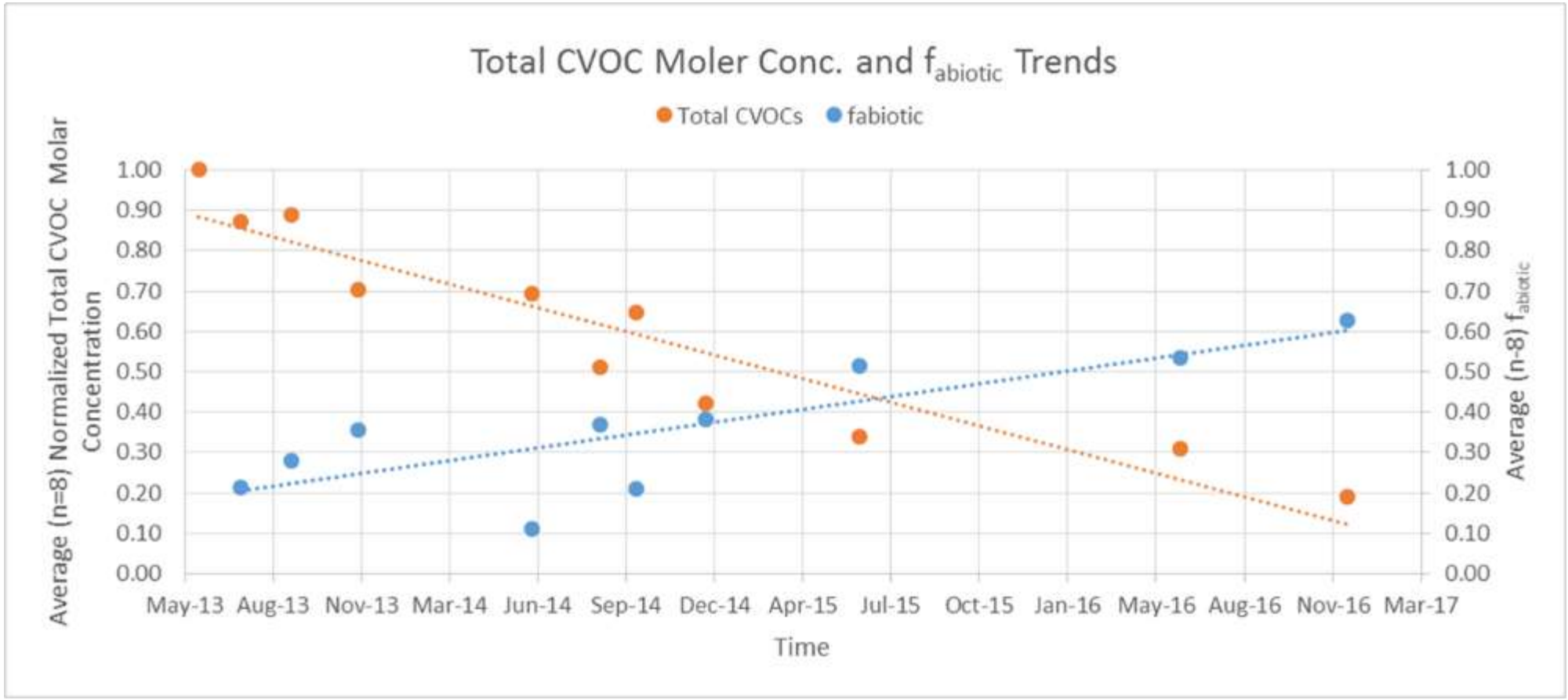
$f_{abiotic} \approx 0$

Abiotic

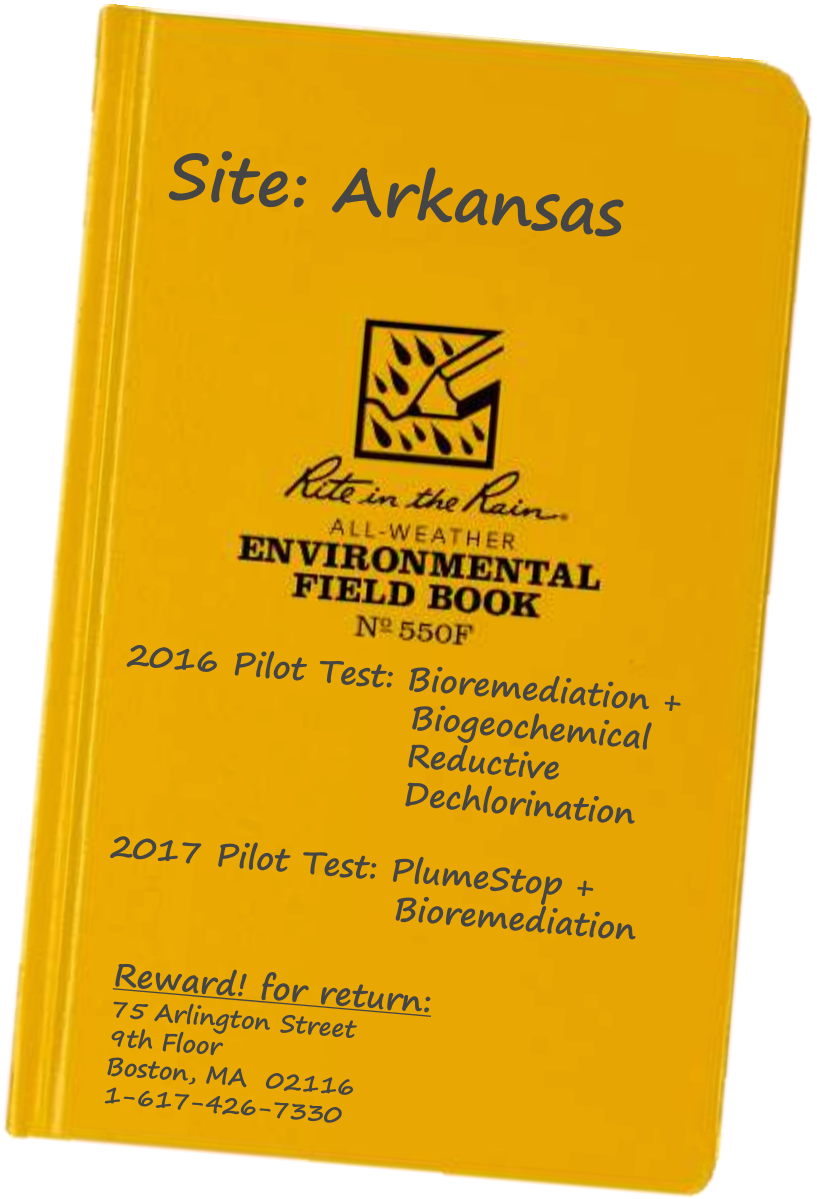
$f_{abiotic} \approx 1$

Degradation Mechanism Identification

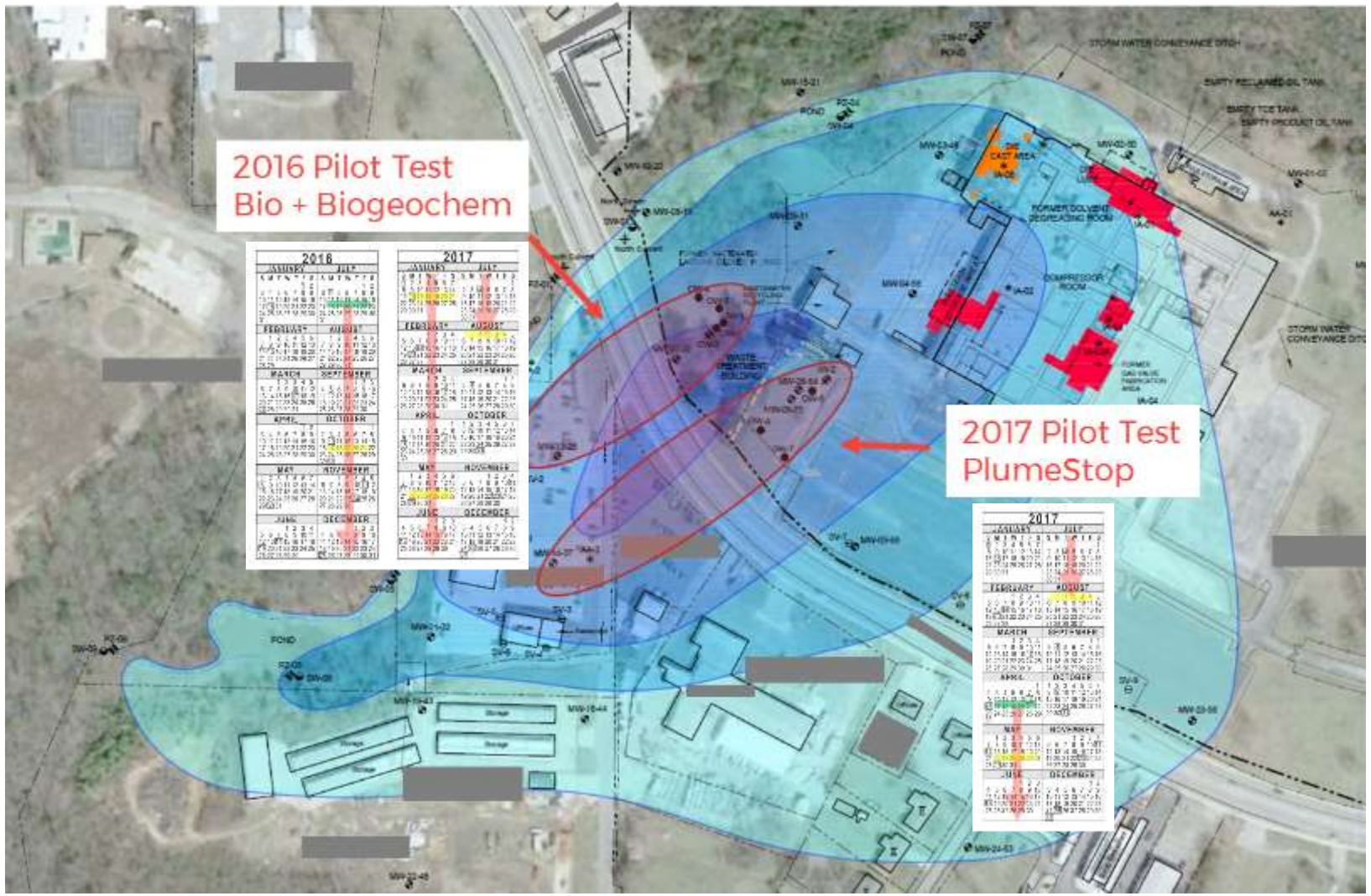
(3.5 years of data from a Bedrock Treatment Site in Missouri)



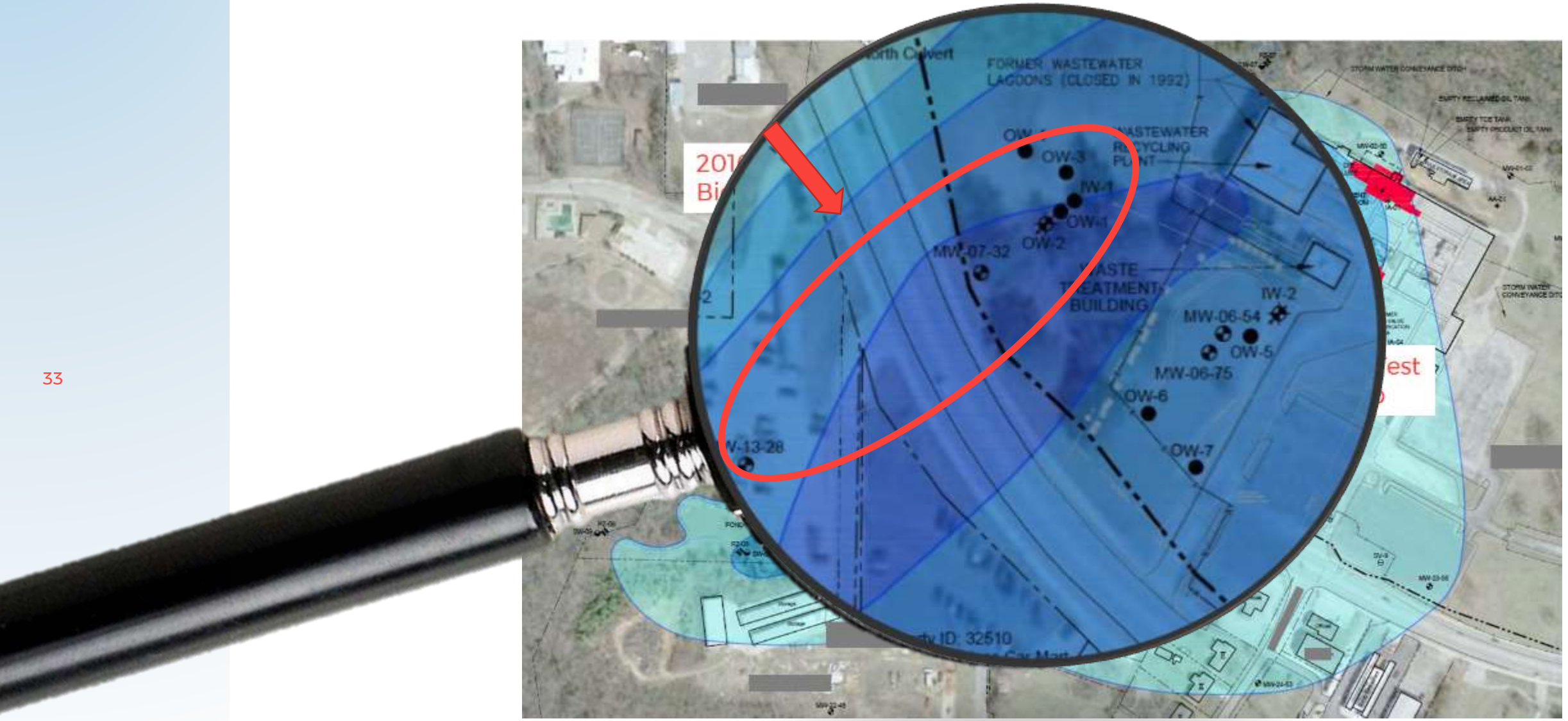
2016 Pilot Test



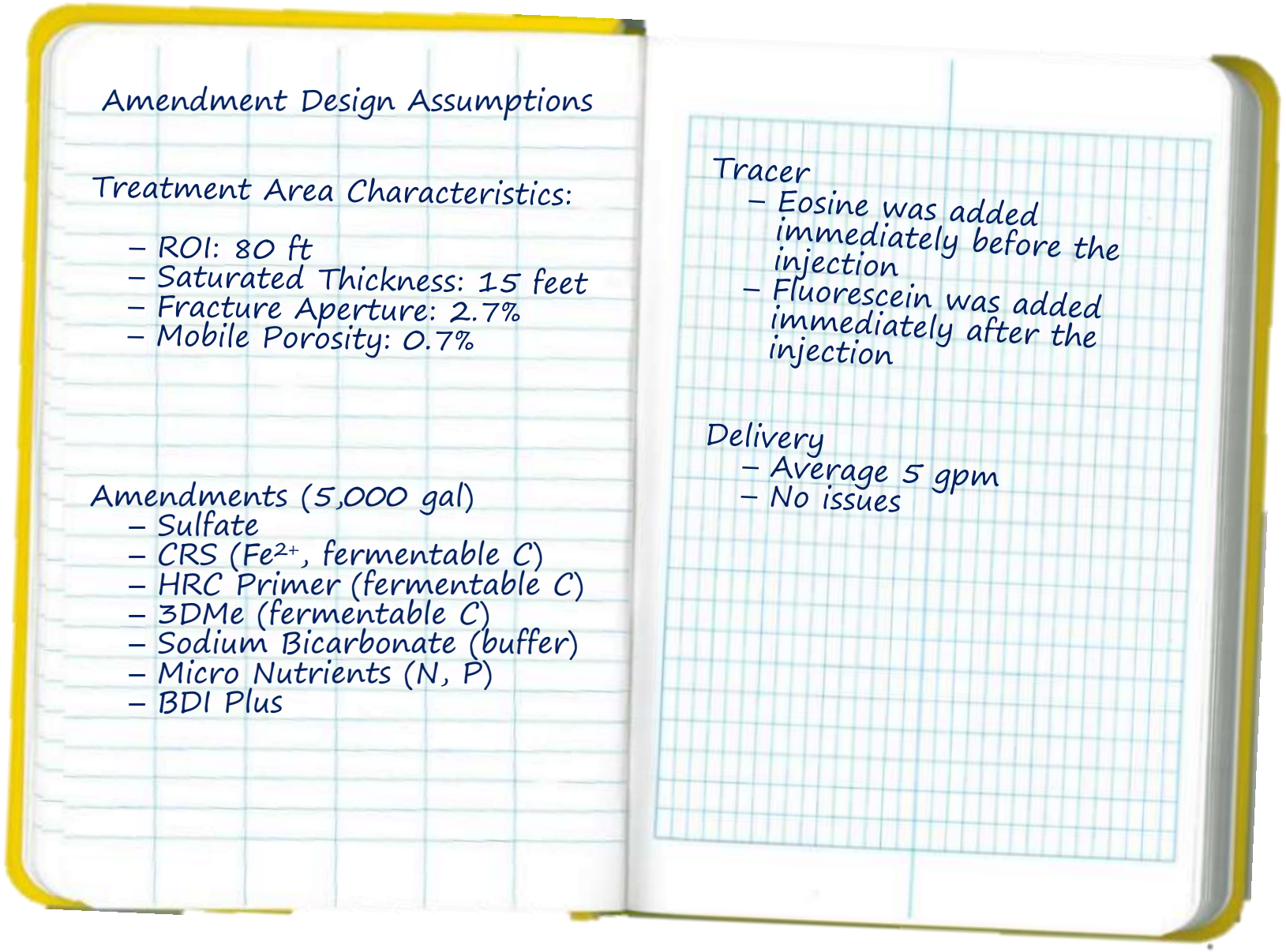
2016 Pilot Test Layout



2016 Pilot Test Layout



2016 Pilot Test Amendment



Performance Monitoring Plan
(baseline plus four quarterly sampling events)

Chemical

- VOCs
  - Parents
  - Daughters
- Dissolved Gases
  - Ethene
  - Acetylene
- DOC
- Tracer dyes

Geochemical

- Field Measurements
  - ORP, DO
  - pH
  - Etc.
- Nitrate
- Ferrous Iron
- Manganese
- Sulfate & Sulfide
- Methane
- Alkalinity

MBTs

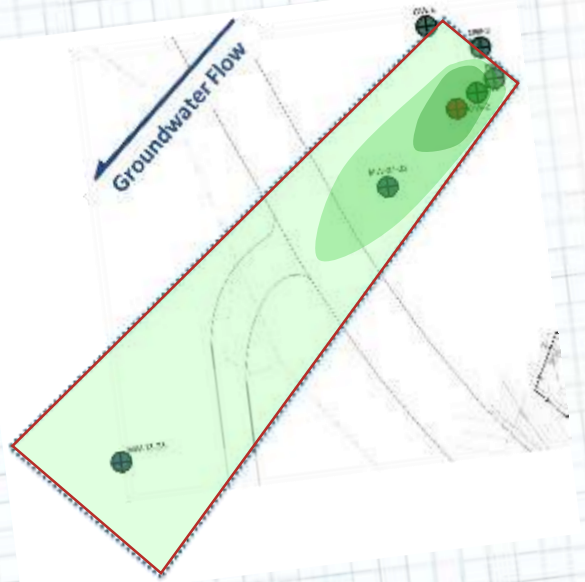
- qPCR
  - *Dehalococcoides*
  - *tceA*
  - *bvcA* and *vcrA*
  - *Dehalobacter*
  - *Dehalogenimonas*
- Compound Specific Isotope Analysis (CSIA)

Tracer Study

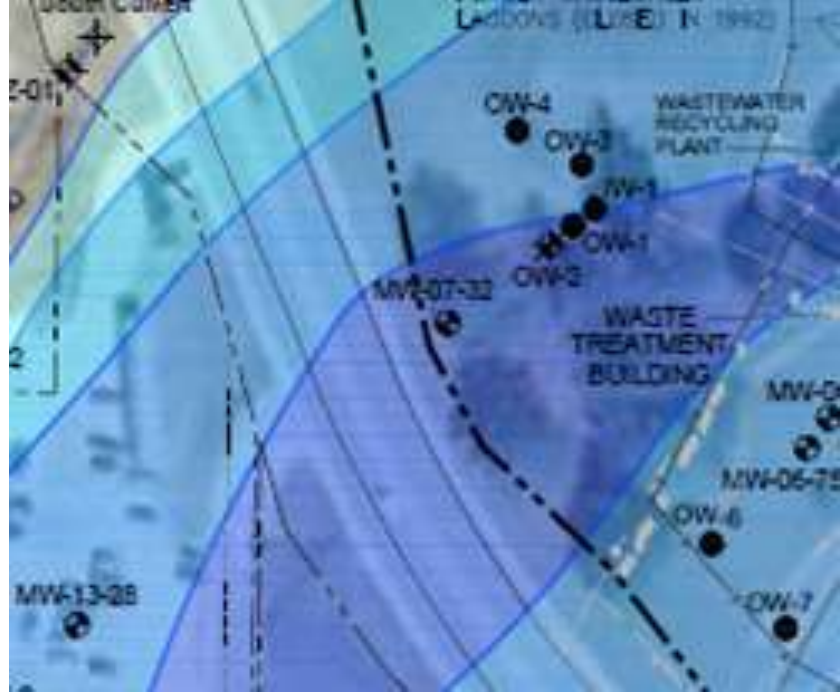
Tracer Results

Dye was detected within a couple months following injection (round numbers – µg/l):

- Near field: 100,000
- Mid-field: 10,000
- Far field: 1,000
- Very Far: 10

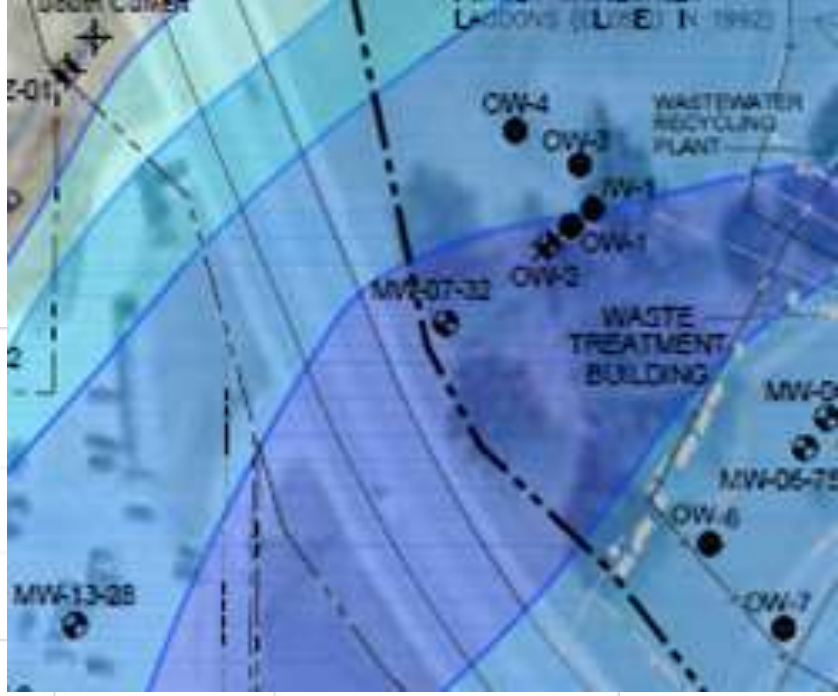


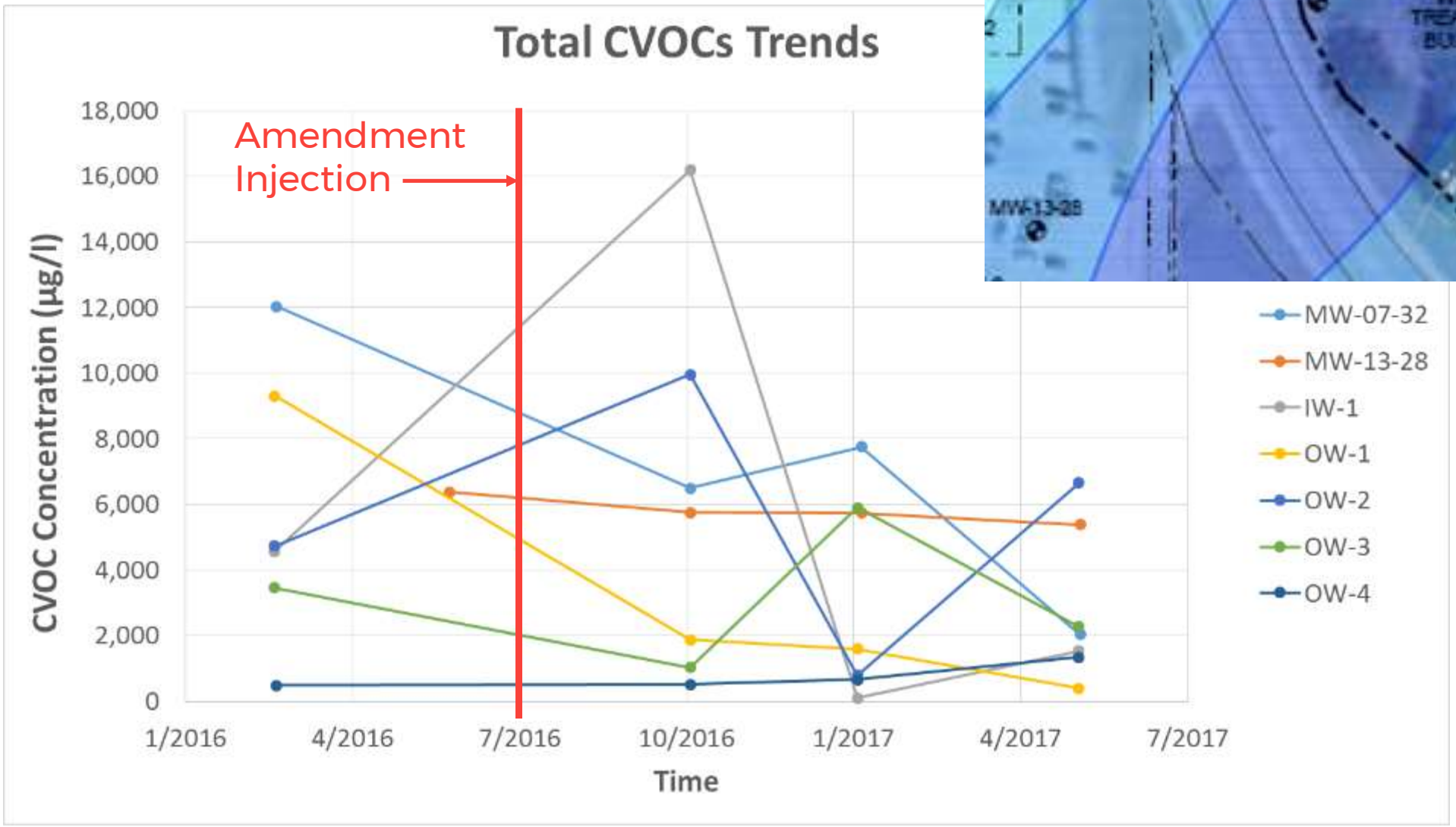
Geochemistry – Heat Map



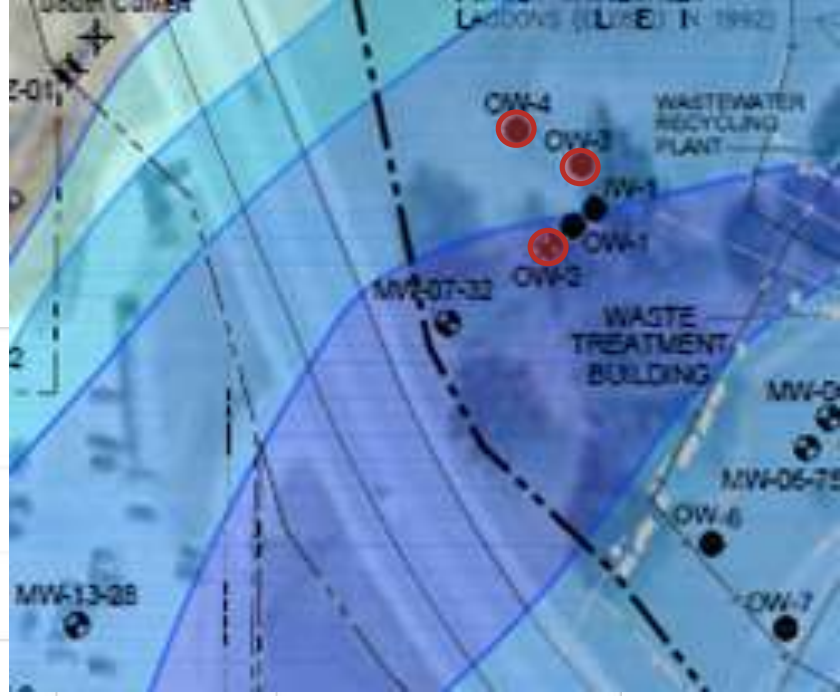
Well:	OW-2	OW-1	IW-1	OW-3	OW-4	MW-07-32	MW-13-28
Gradient Orientation:		up	up	cross	cross	down	down
Distance:	inj	20 ft	30 ft	50 ft	65 ft	80 ft	320 ft
Parameter							
Field Parameters							
pH (standard units)							
Specific Conductance (µS/cm)							
DO (mg/l)							
ORP (mV)							
Inorganics (mg/l)							
Nitrate							
Sulfate							
Sulfide							
Divalent Manganese							
Ferrous Iron							
Alkalinity (mg $CaCO_3$/l)							
DOC (mg/l)							

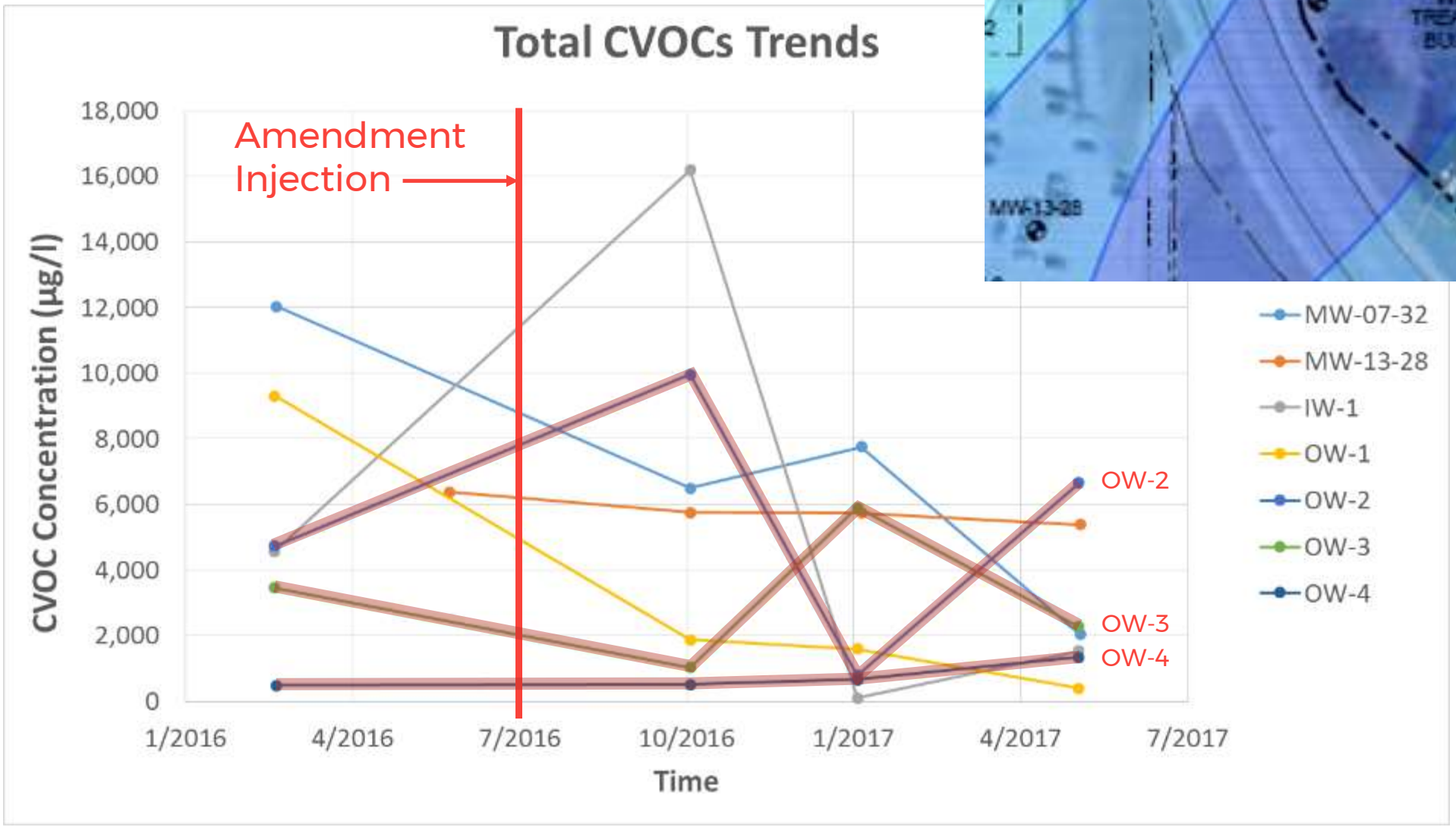
CVOCs


OW-4
OW-3
IW-1
OW-1
OW-2
MW-07-32
WASTEWATER RECYCLING PLANT
WASTE TREATMENT BUILDING
MW-13-28

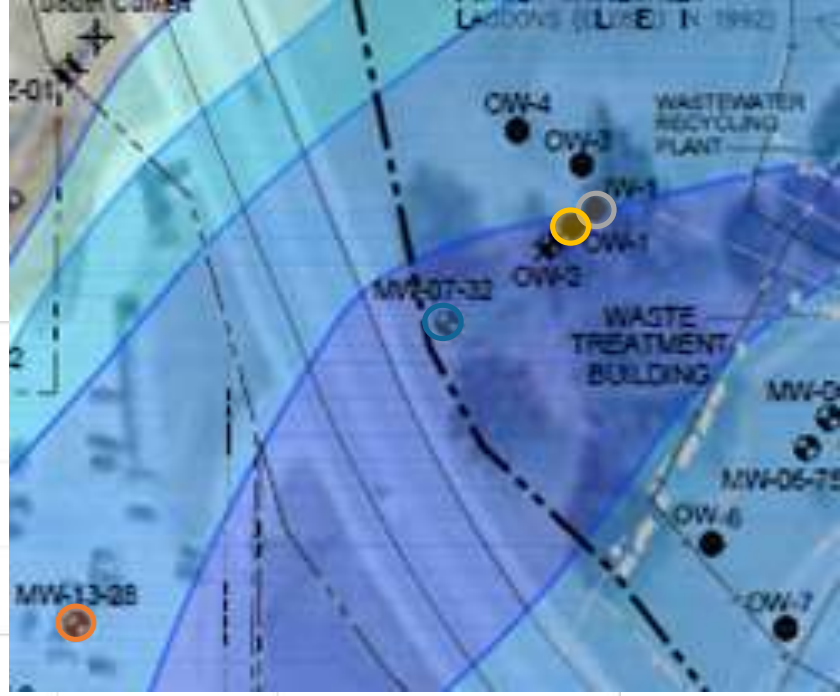

Total CVOCs Trends
Amendment Injection
CVOC Concentration (µg/l)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1/2016
4/2016
7/2016
10/2016
1/2017
4/2017
7/2017
Time
MW-07-32
MW-13-28
IW-1
OW-1
OW-2
OW-3
OW-4

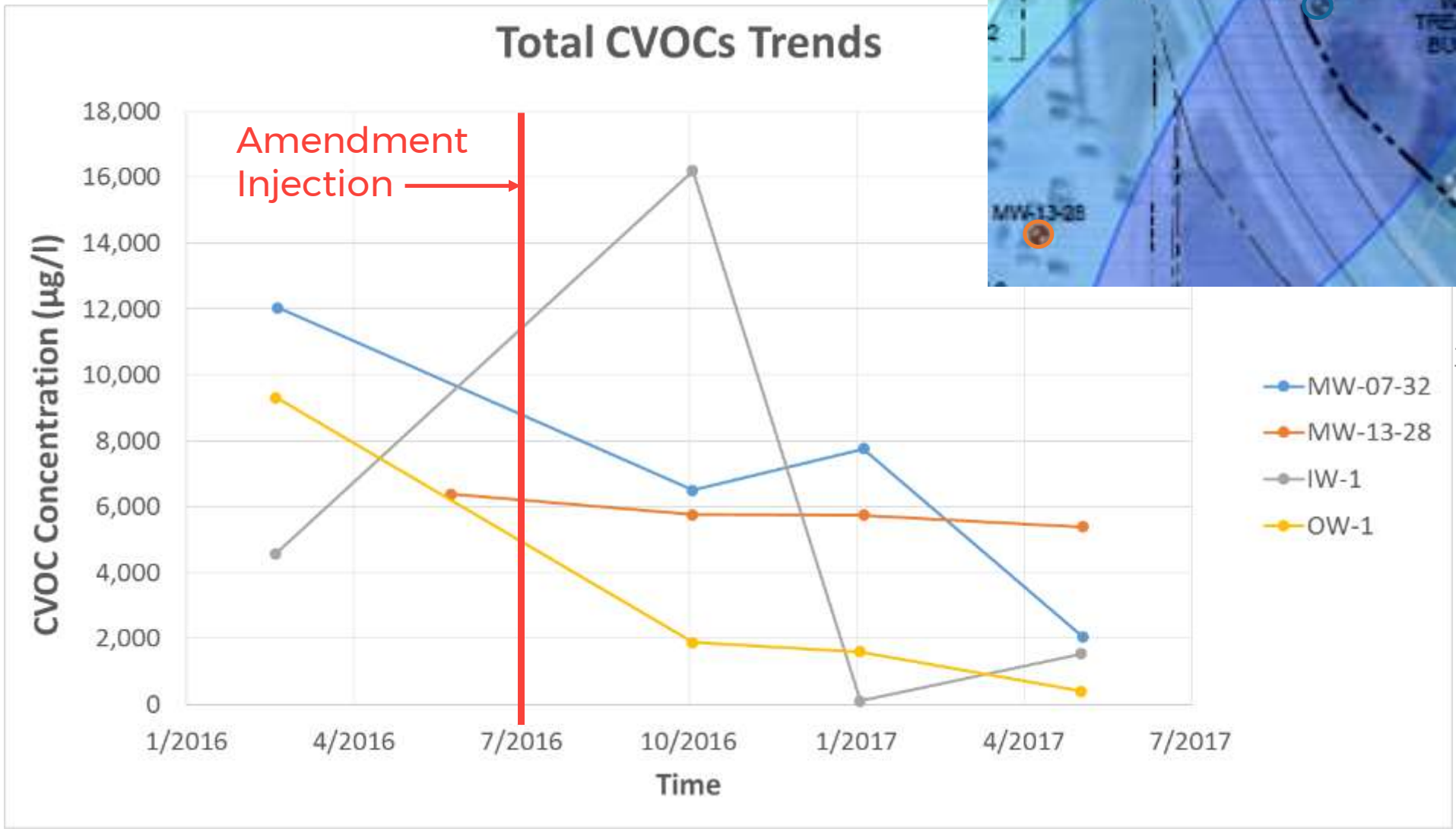
CVOCs


OW-4
OW-2
OW-1
OW-3
WASTEWATER RECYCLING PLANT
WASTE TREATMENT BUILDING
MW-07-32
MW-13-28

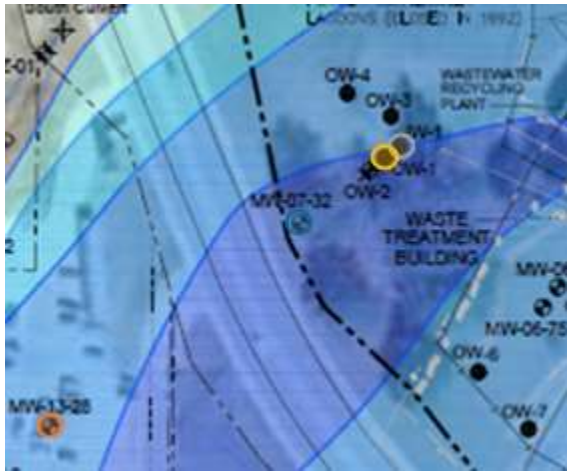

Total CVOCs Trends
Amendment Injection
CVOC Concentration (µg/l)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1/2016
4/2016
7/2016
10/2016
1/2017
4/2017
7/2017
Time
MW-07-32
MW-13-28
IW-1
OW-1
OW-2
OW-3
OW-4
OW-2
OW-3
OW-4

CVOCs


OW-4
OW-3
OW-1
OW-2
WASTEWATER RECYCLING PLANT
WASTE TREATMENT BUILDING
MW-07-32
MW-13-28


Total CVOCs Trends
Amendment Injection
CVOC Concentration (µg/l)
18,000
16,000
14,000
12,000
10,000
8,000
6,000
4,000
2,000
0
1/2016
4/2016
7/2016
10/2016
1/2017
4/2017
7/2017
Time
MW-07-32
MW-13-28
IW-1
OW-1
Distance from OW-2
80 ft
320 ft
30 ft
20 ft

Mole Fractions



A	Drawn By: STS 06/22/2017	Checked: MB 06/01/2017	DWG Name:
		Approved: JS 06/01/2017	

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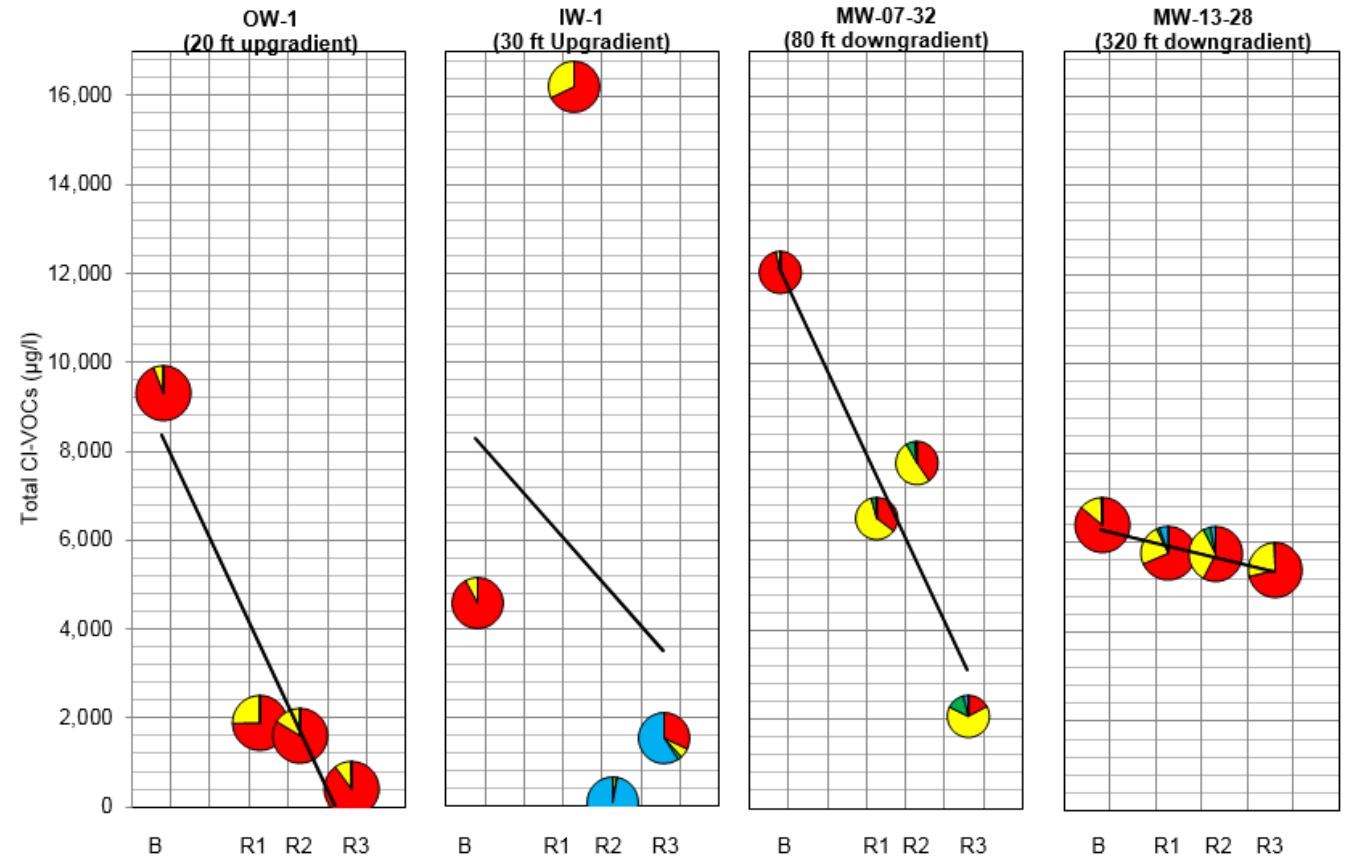
Biogeochemical Pilot Test
Performance Monitoring

FIGURE 2



NOTES:

1. AMMENDMENT ADDED JULY, 2016
2. B = BASELINE SAMPLE PRIOR TO TREATMENT MARCH, 2016; R1 = OCTOBER, 2016; R2 = JANUARY, 2017; R3 = May, 2017
3. µg/l = MICROGRAMS PER LITER; E's = TOTAL ETHENE/ETHANES; TCE = TOTAL TRICHLOROETHENE-ANE; DCE = TOTAL DICHLOROETHENE-ANE; CVL = TOTAL VINAL CHLORIDE.
4. WHEN A COMPOUND WAS NOT DETECTED ABOVE THE LABORATORY REPORTING LIMIT, A CONCENTRATION OF ZERO WAS ENTERED INTO THE TOTAL.

Mole Fractions

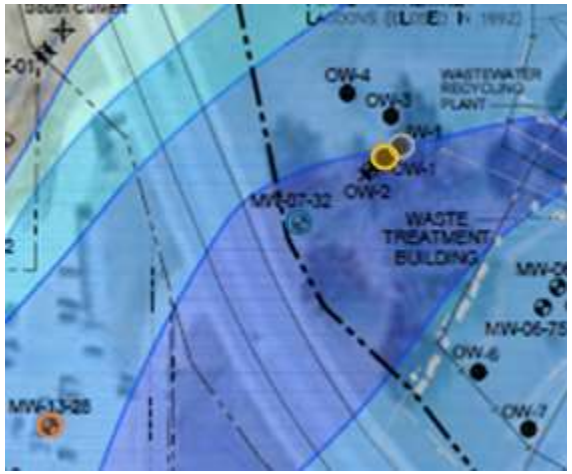


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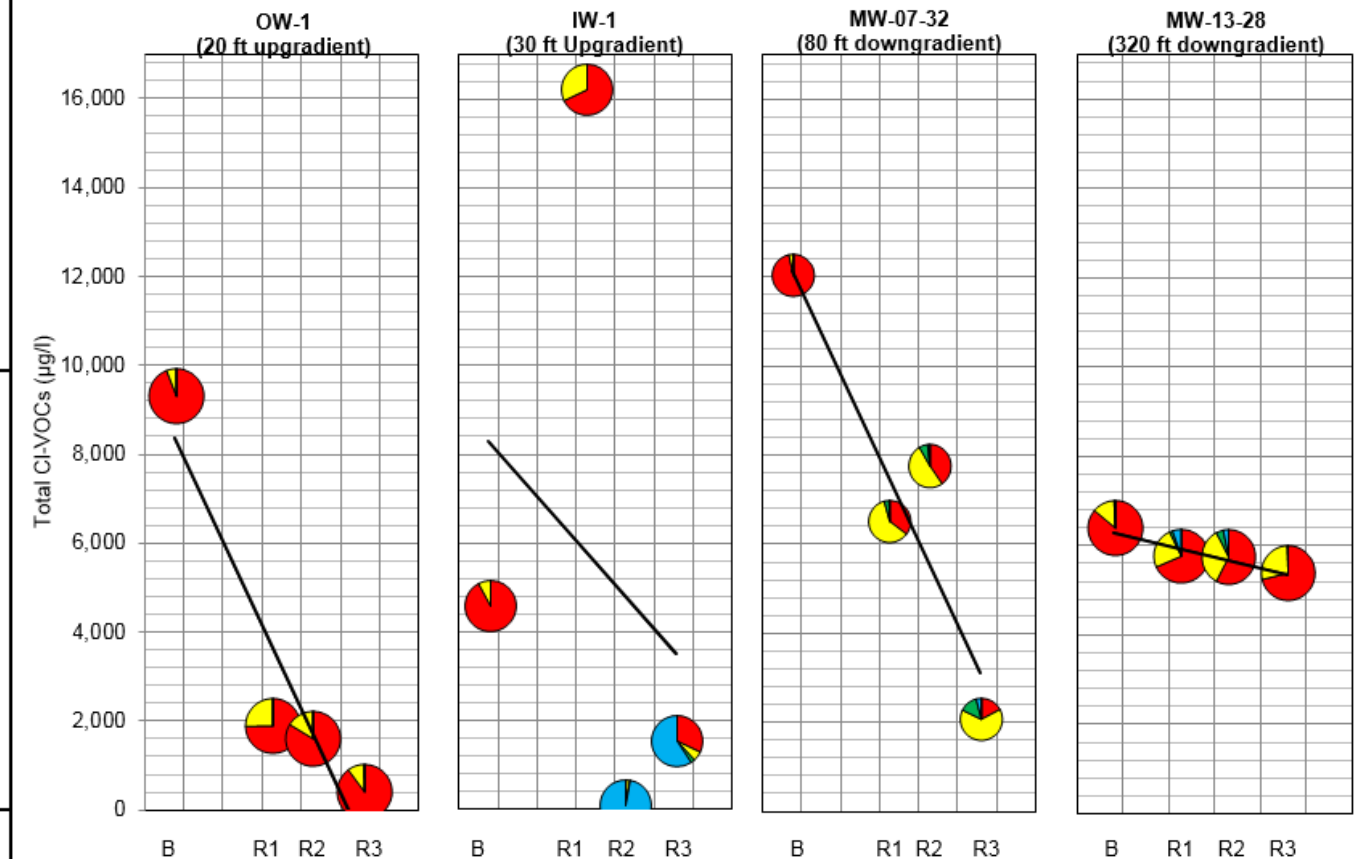
FIGURE 2

Biogeochemical Pilot Test
Performance Monitoring



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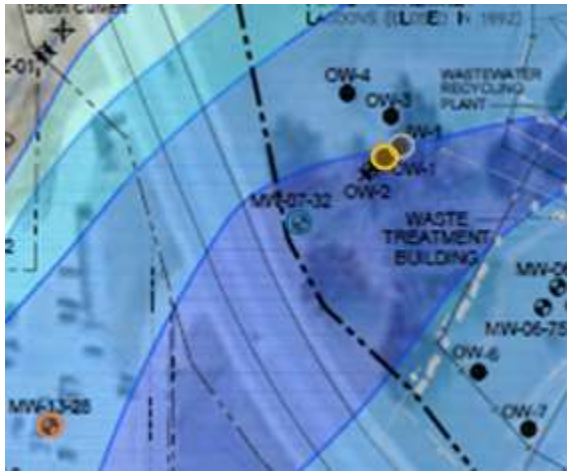
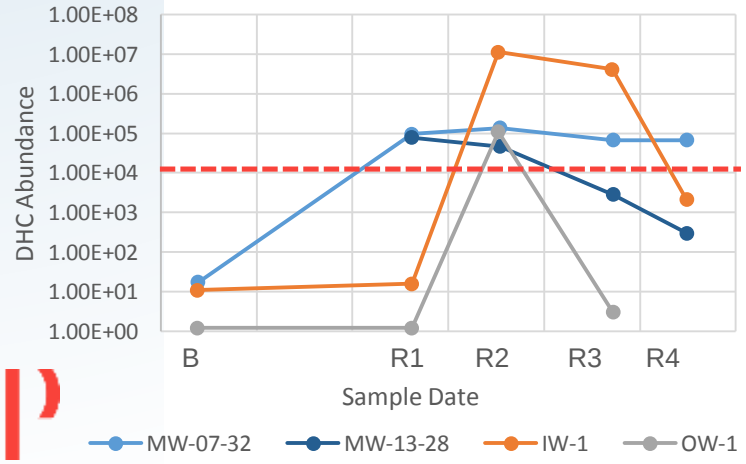
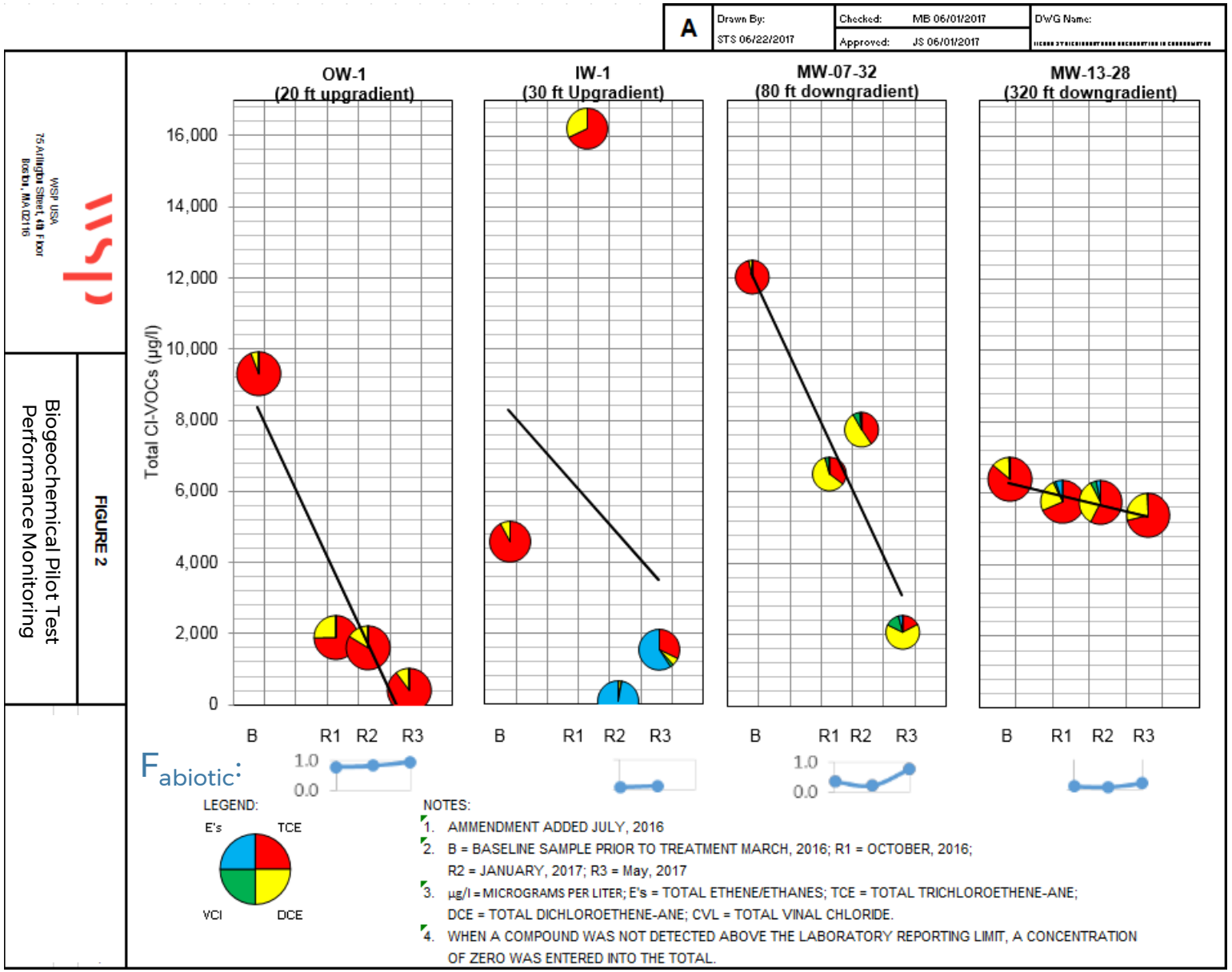
4. WHEN A COMPOUND WAS NOT DETECTED ABOVE THE LABORATORY REPORTING LIMIT, A CONCENTRATION OF ZERO WAS ENTERED INTO THE TOTAL.

qPCR



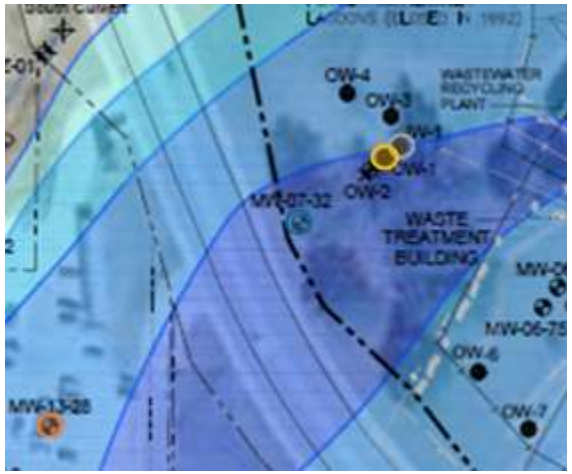
qPCR Dehalococcoides

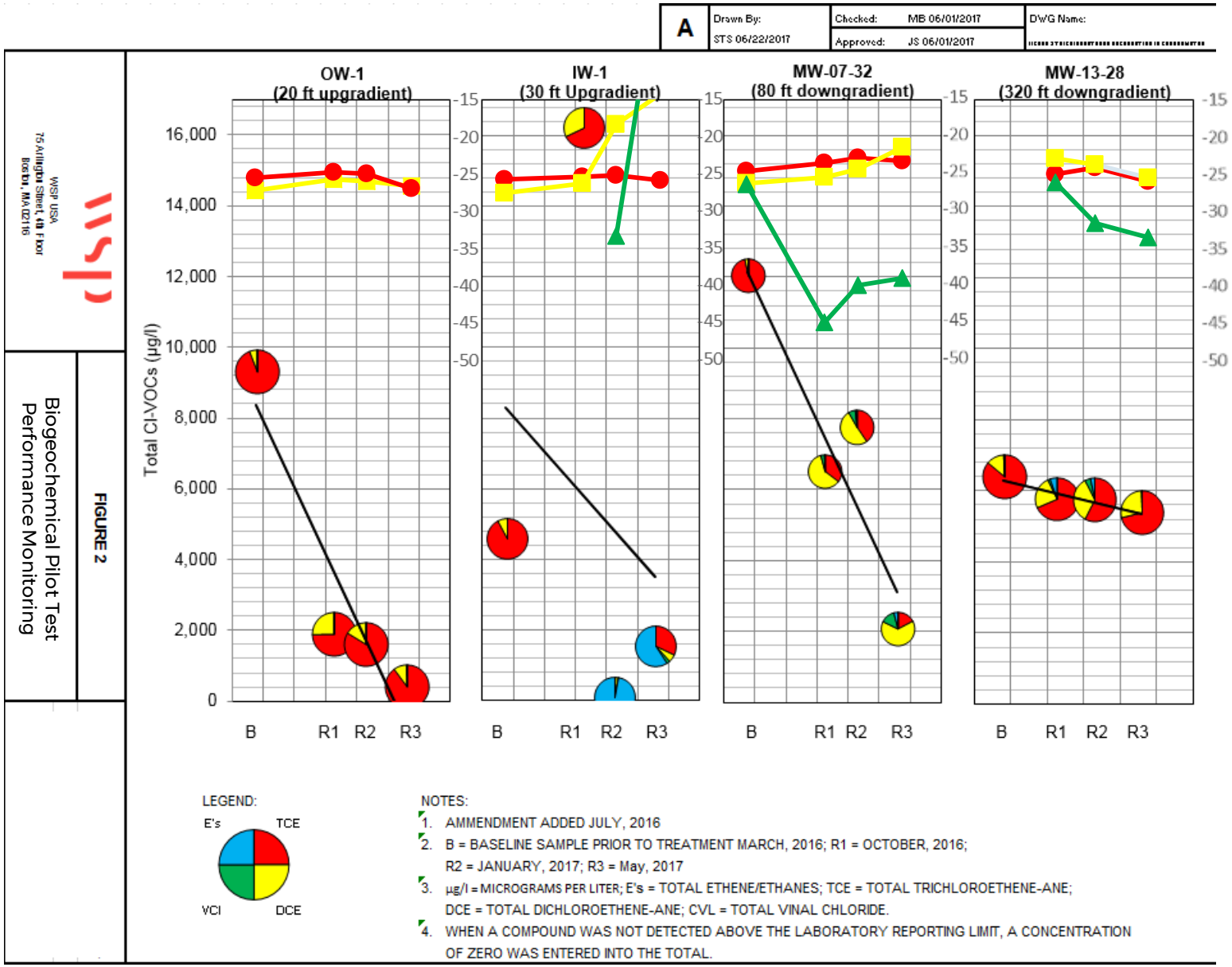




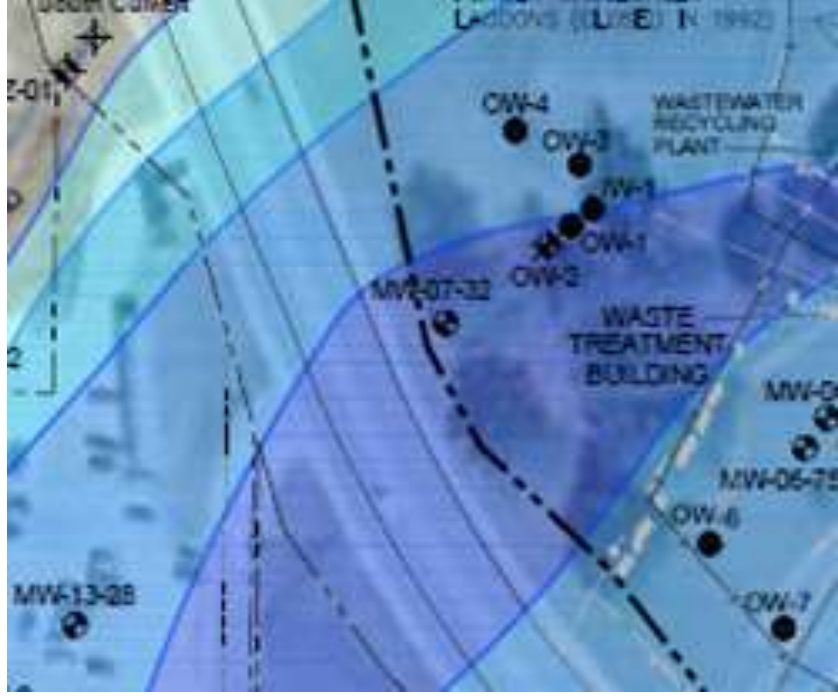
2016 Pilot Test

CSIA





2016 Pilot Test - Summary



Well:	OW-1	IW-1	MW-07-32	MW-13-28	OW-3	OW-4
Gradient Orientation:	up	up	down	down	cross/up	cross/up
Distance:	20 ft	30 ft	80 ft	320 ft	50	65
Delivery						
Dye						
Geochemistry						
Efficacy						
CVOC Trends						
CSIA						
Mechanism						
qPCR						
$F_{abiotic}$	abiotic	biotic	mix	biotic		

PlumeStop Pilot Test

The Reagent – what it is

PLUME STOP® Liquid Activated Carbon

- A highly dispersive, injectable sorbent and microbial growth matrix

- Colloidal activated carbon (1 – 2 µm)
  - Size of a bacterium – suspends as 'liquid'
  - Huge surface area – extremely fast sorption
- Proprietary anti-clumping / distribution supporting surface treatment (patent applied for)
  - Core innovation
  - Enables wide-area, low-pressure distribution through the soil matrix without clogging

Subsurface Distribution

Liquid Activated Carbon
(LAC™)

- 1” diameter glass columns
- Sandy soil with 11% silt/clay
- Gravity feed

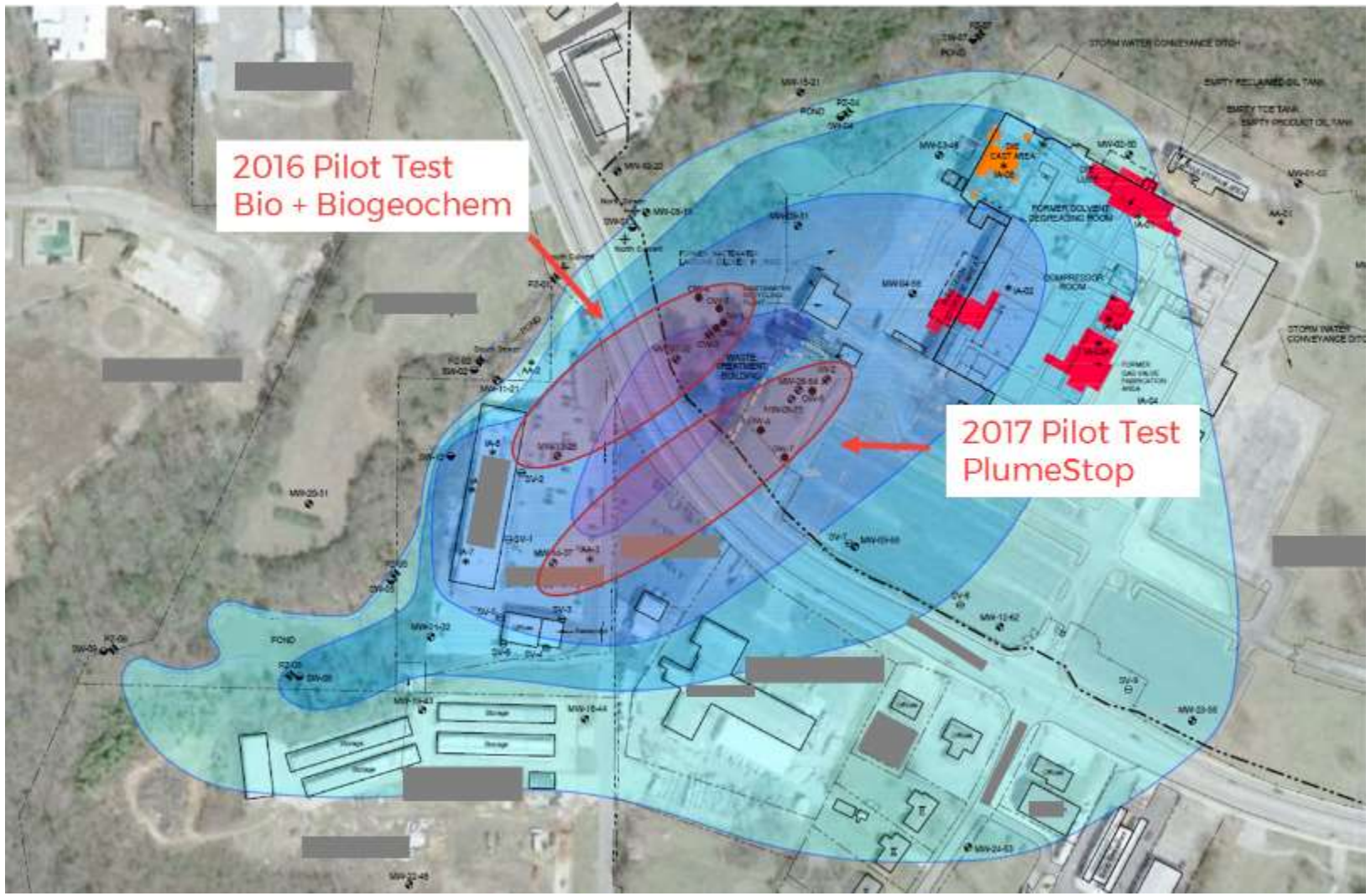
Powdered Activated Carbon
(PAC)

Liquid Activated Carbon
(LAC™)

Powdered Activated Carbon
(PAC)

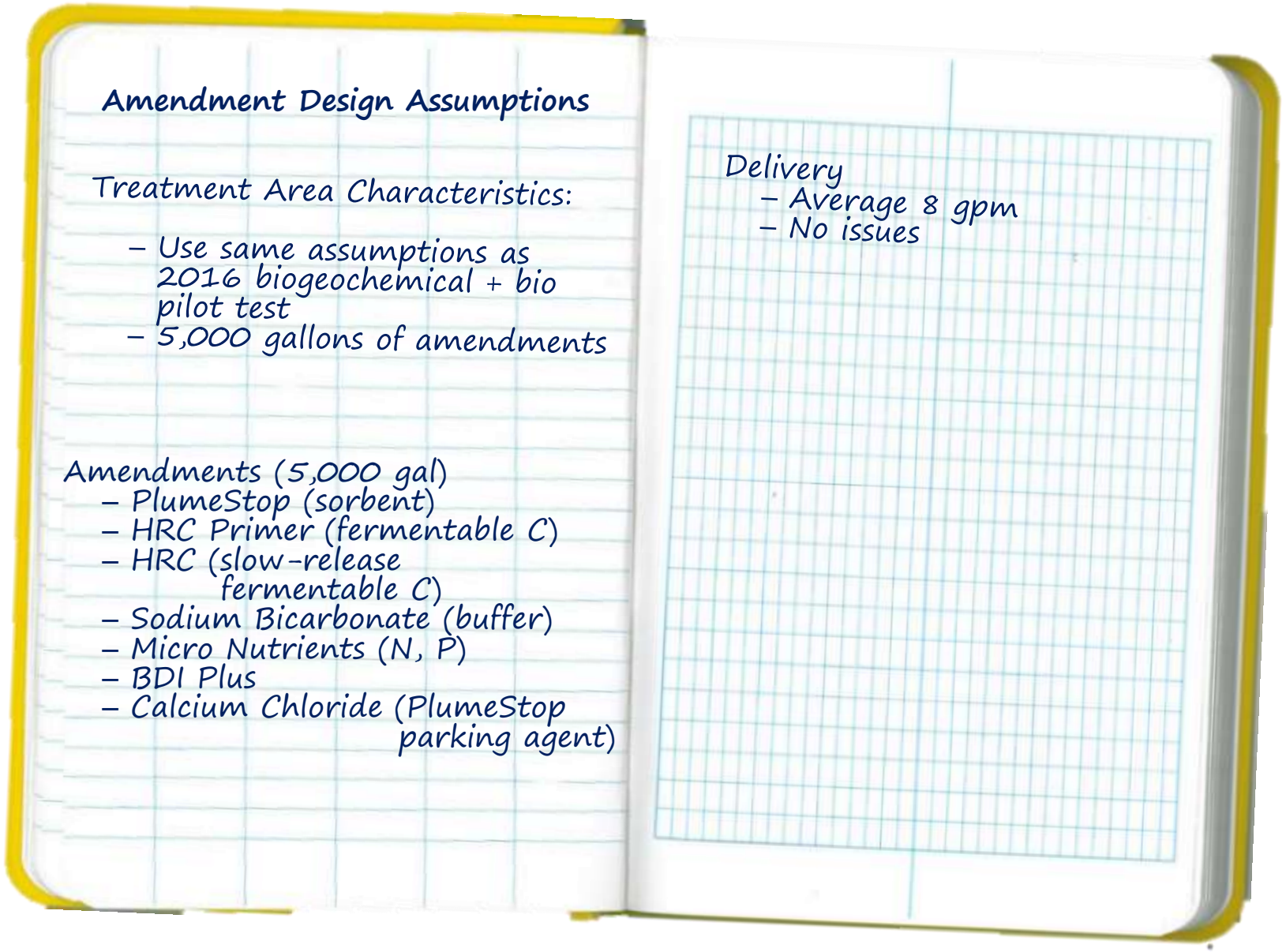
Time Lapse = 12 minute

PlumeStop Pilot Test Layout



PlumeStop Pilot Layout

PlumeStop Amendment



Performance Monitoring Plan
(baseline plus four quarterly sampling events)

Chemical

- VOCs
  - Parents
  - Daughters
- Dissolved Gases
  - Ethene
  - Ethane
  - Acetylene
- VFAs

Geochemical

- Field Measurements
  - ORP, DO
  - pH
  - Etc.
- Methane

MBTs

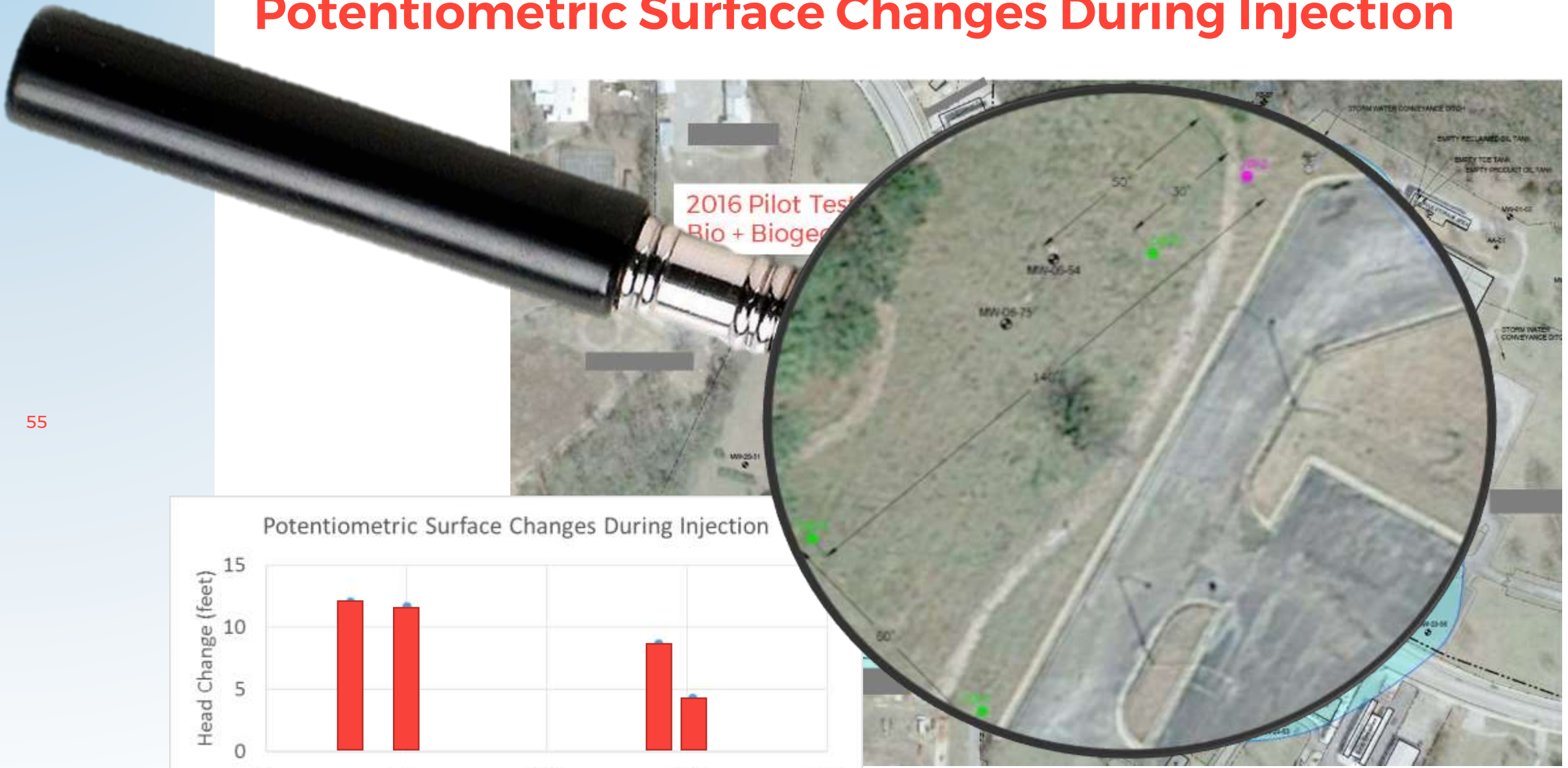
- qPCR
  - *Dehalococcoides*
  - *tceA*
  - *bvcA* and *vcrA*
  - *Dehalobacter*
  - *Dehalogenimonas*
- Compound Specific Isotope Analysis (CSIA)

Crushed Sandstone Core *In Situ* Microcosms

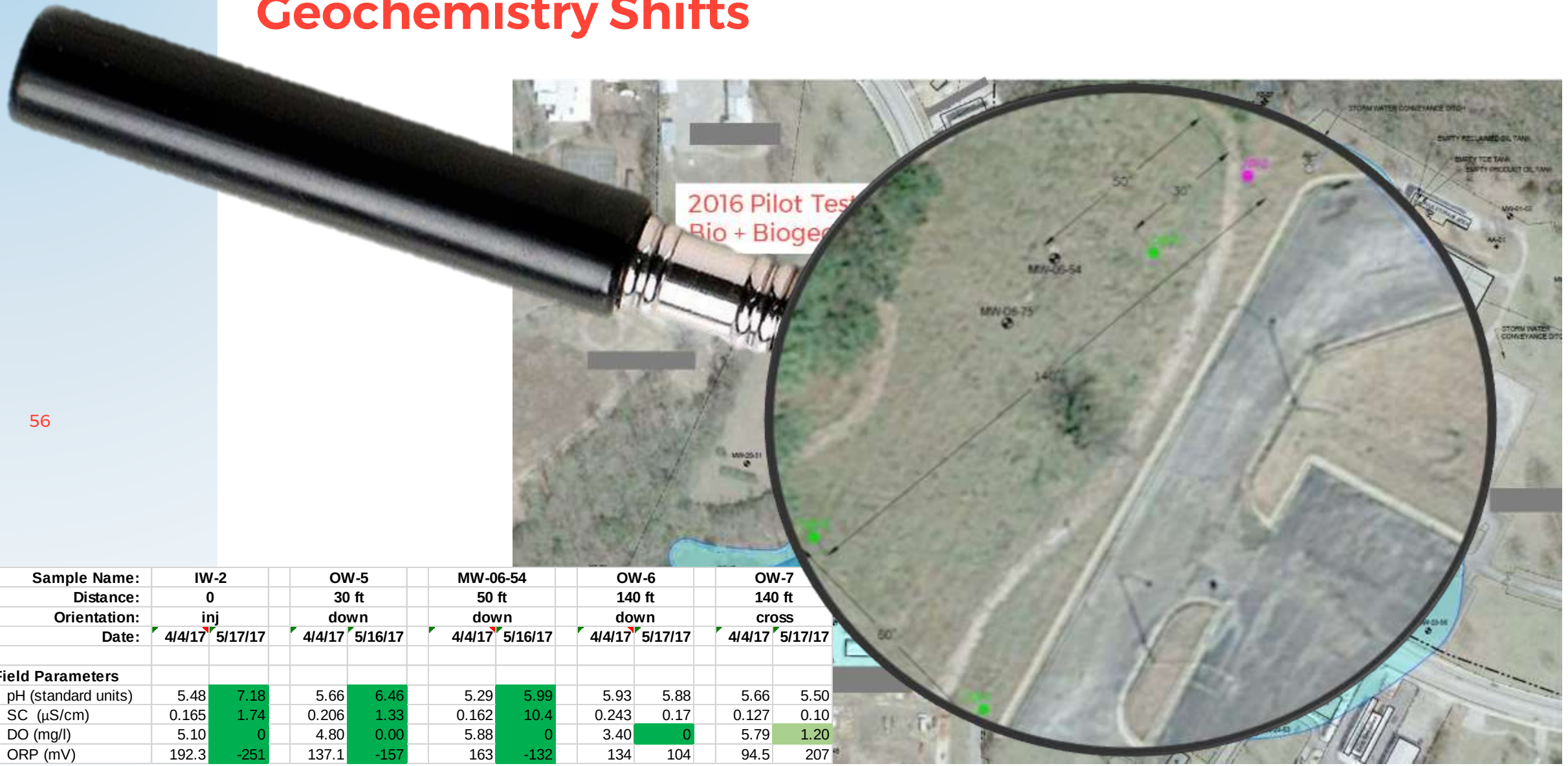
- VOCs
- VFAs
- Dissolved Gases
  - Ethene
  - Ethane
- Field Measurements
  - ORP, DO
  - pH
  - Etc.
- qPCR
- CSIA

In Situ Microcosms

Potentiometric Surface Changes During Injection



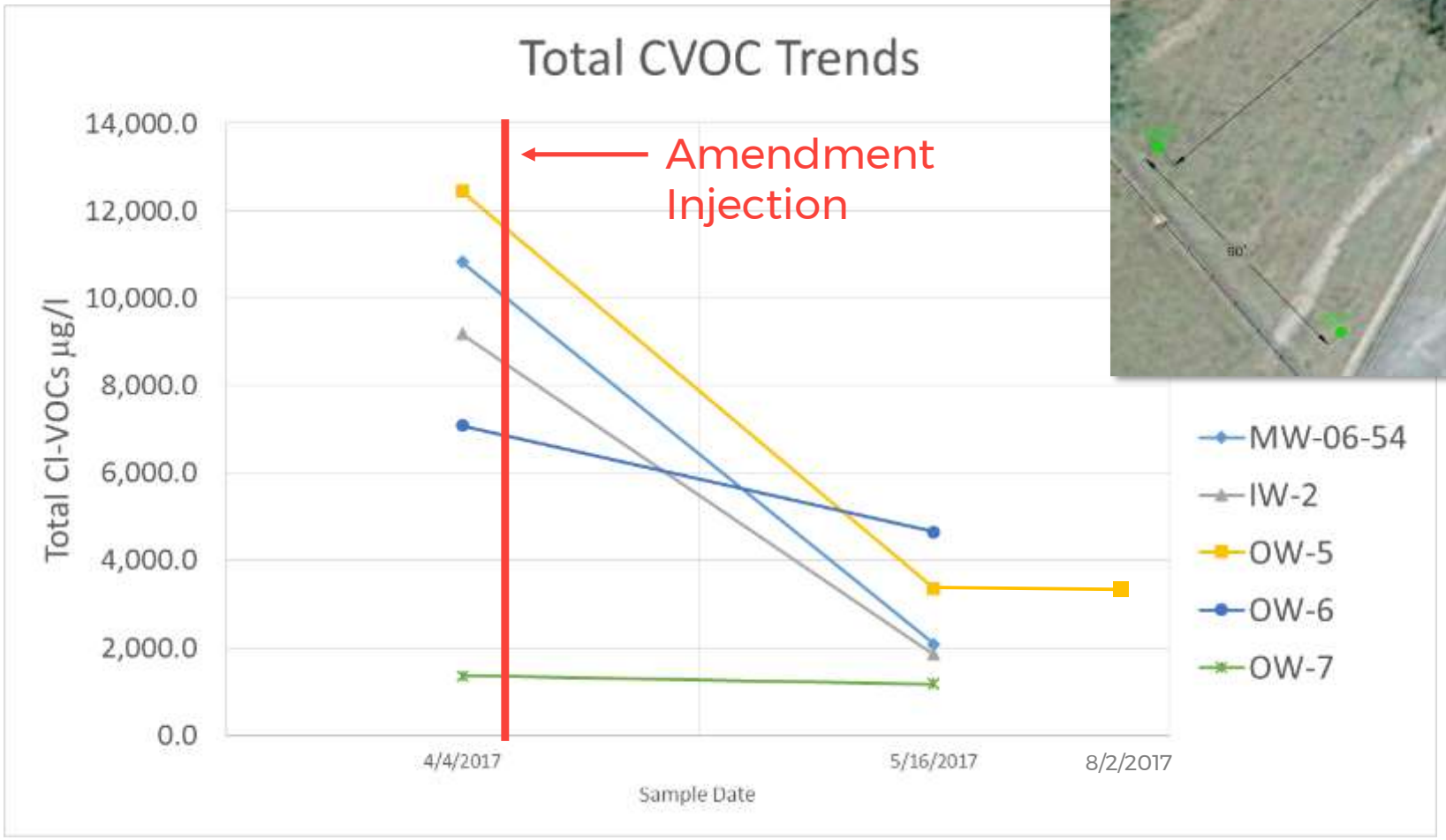
Geochemistry Shifts



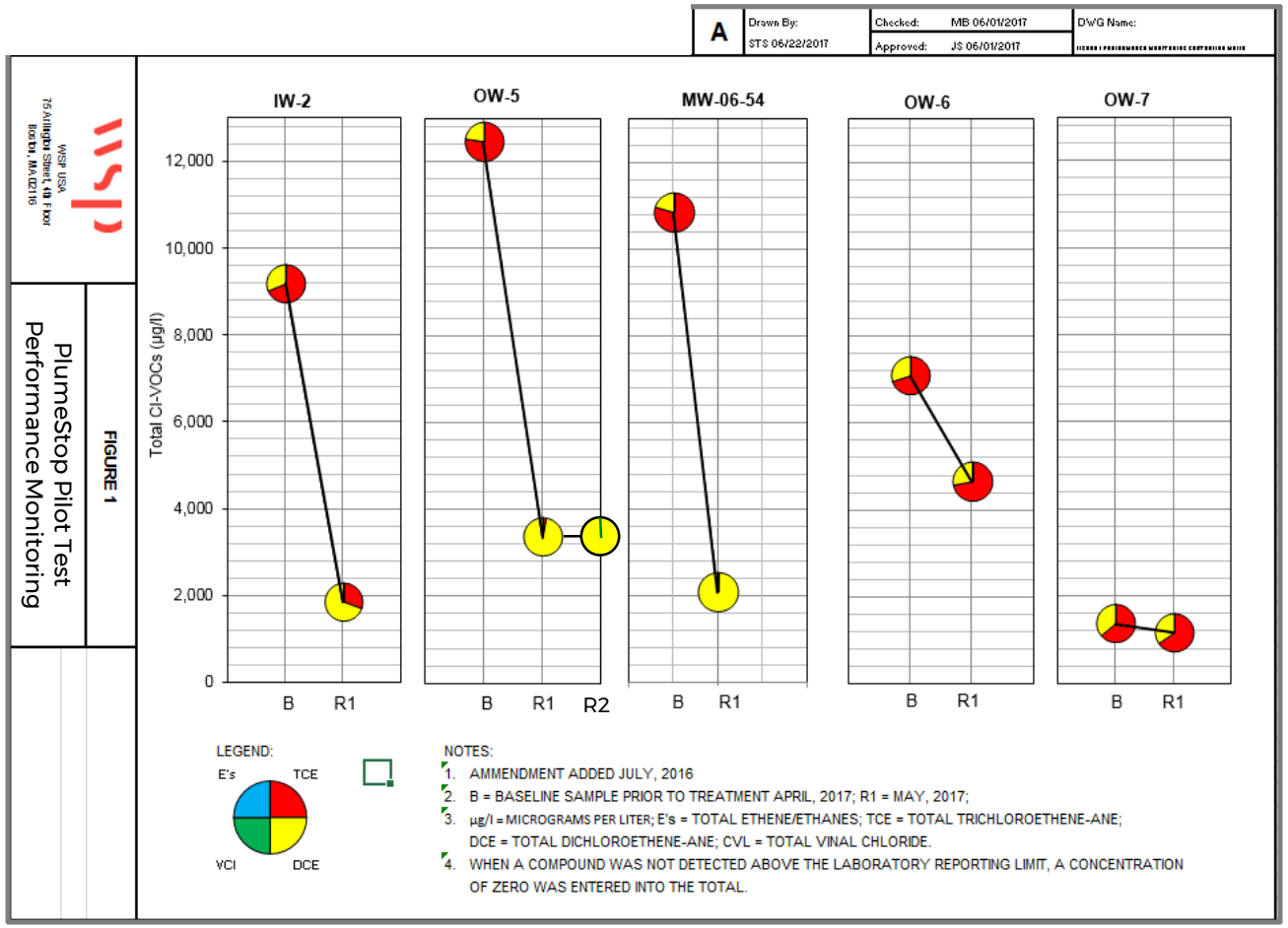
Sample Name:	IW-2		OW-5		MW-06-54		OW-6		OW-7	
Distance:	0		30 ft		50 ft		140 ft		140 ft	
Orientation:	inj		down		down		down		cross	
Date:	4/4/17	5/17/17	4/4/17	5/16/17	4/4/17	5/16/17	4/4/17	5/17/17	4/4/17	5/17/17
Field Parameters										
pH (standard units)	5.48	7.18	5.66	6.46	5.29	5.99	5.93	5.88	5.66	5.50
SC (µS/cm)	0.165	1.74	0.206	1.33	0.162	10.4	0.243	0.17	0.127	0.10
DO (mg/l)	5.10	0	4.80	0.00	5.88	0	3.40	0	5.79	1.20
ORP (mV)	192.3	-251	137.1	-157	163	-132	134	104	94.5	207

CVOCs

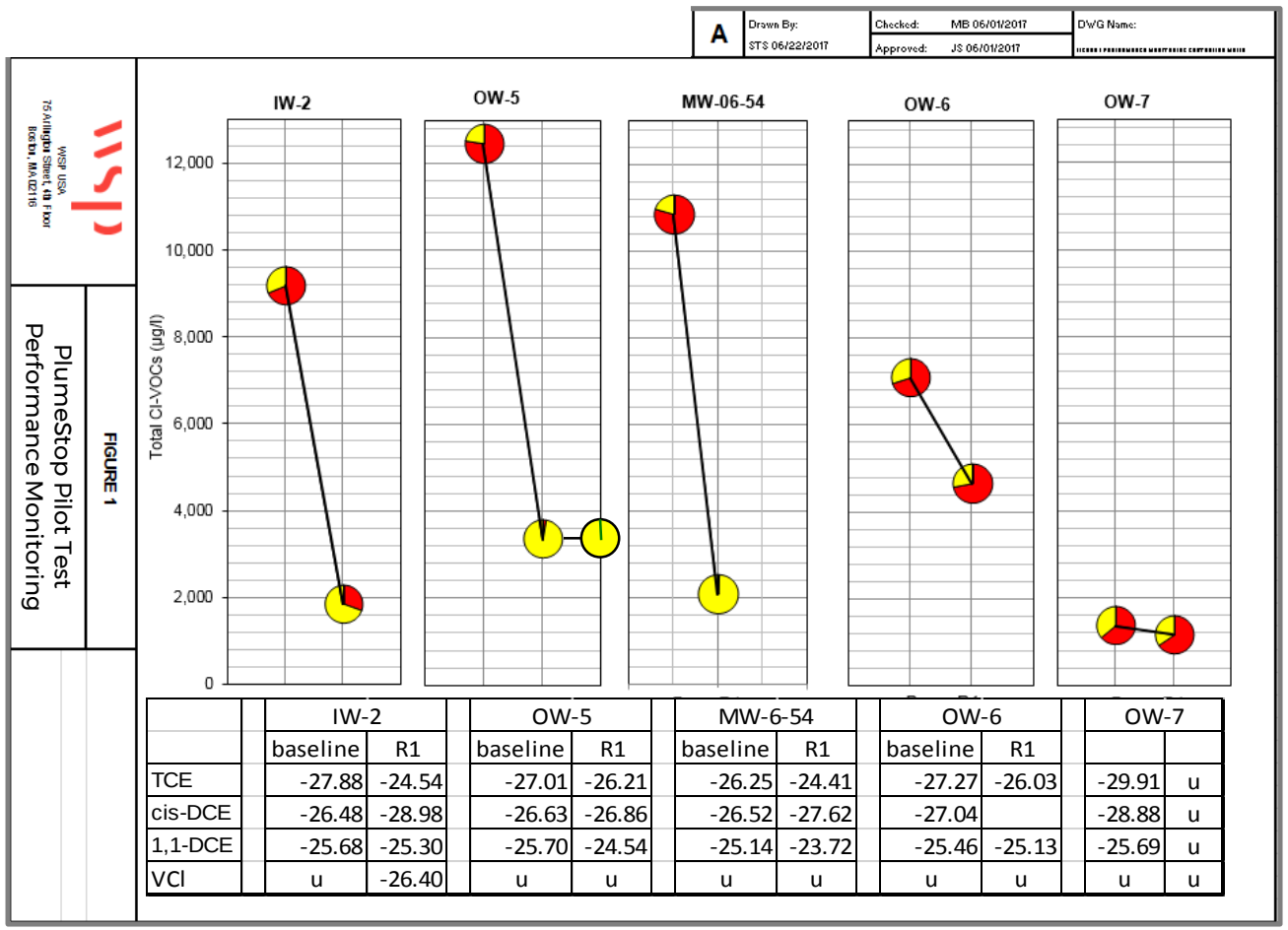

MW-06-54
MW-06-75
140'
90'
50'


Total CVOC Trends
Amendment Injection
Total Cl-VOCs µg/l
14,000.0
12,000.0
10,000.0
8,000.0
6,000.0
4,000.0
2,000.0
0.0
4/4/2017
5/16/2017
8/2/2017
Sample Date
MW-06-54
IW-2
OW-5
OW-6
OW-7

Mole Fraction

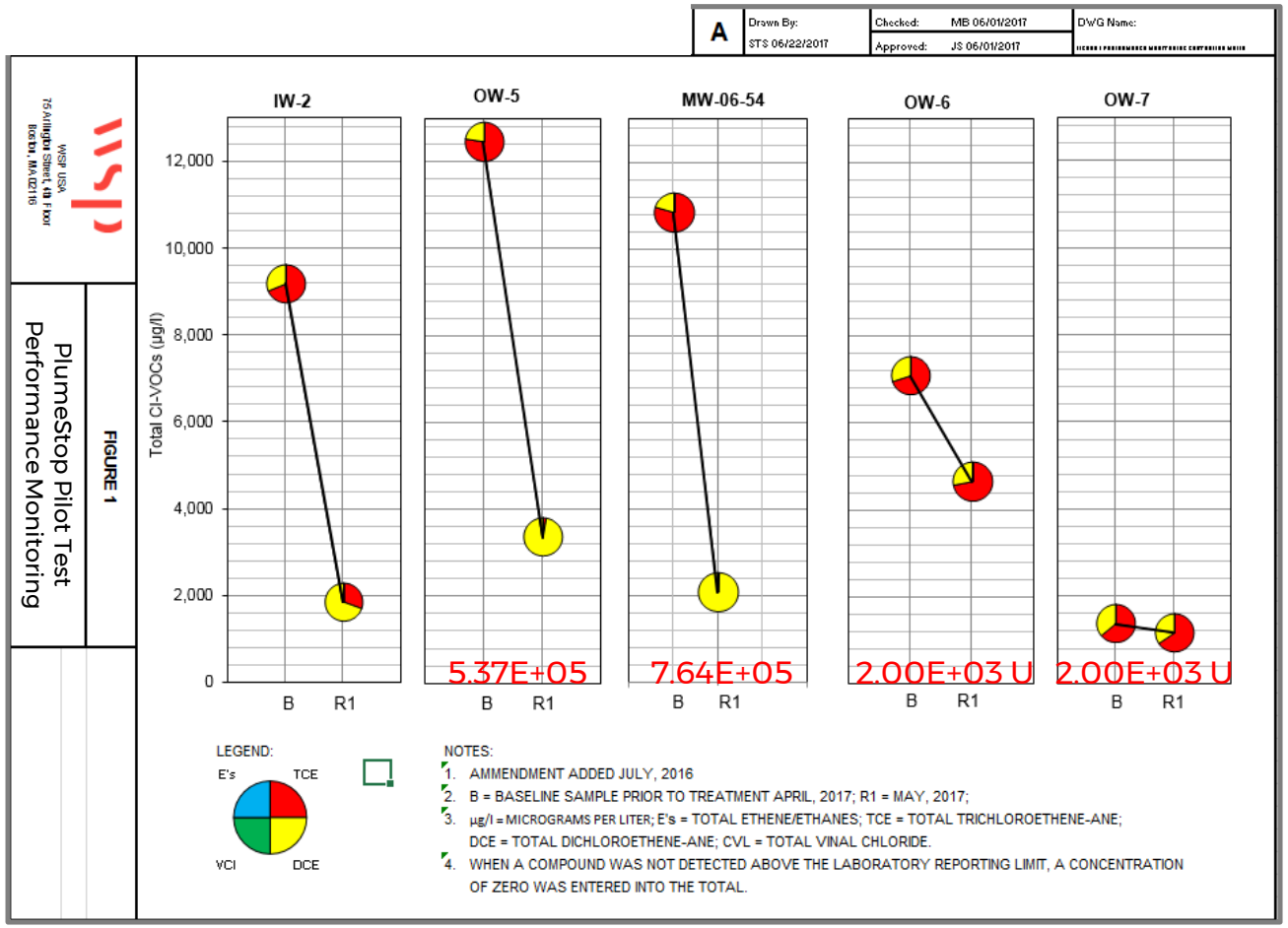


Mole Fraction With CSIA



	IW-2		OW-5		MW-6-54		OW-6		OW-7	
	baseline	R1	baseline	R1	baseline	R1	baseline	R1		
TCE	-27.88	-24.54	-27.01	-26.21	-26.25	-24.41	-27.27	-26.03	-29.91	u
cis-DCE	-26.48	-28.98	-26.63	-26.86	-26.52	-27.62	-27.04		-28.88	u
1,1-DCE	-25.68	-25.30	-25.70	-24.54	-25.14	-23.72	-25.46	-25.13	-25.69	u
VCl	u	-26.40	u	u	u	u	u	u	u	u

Mole Fraction With qPCR for DHC

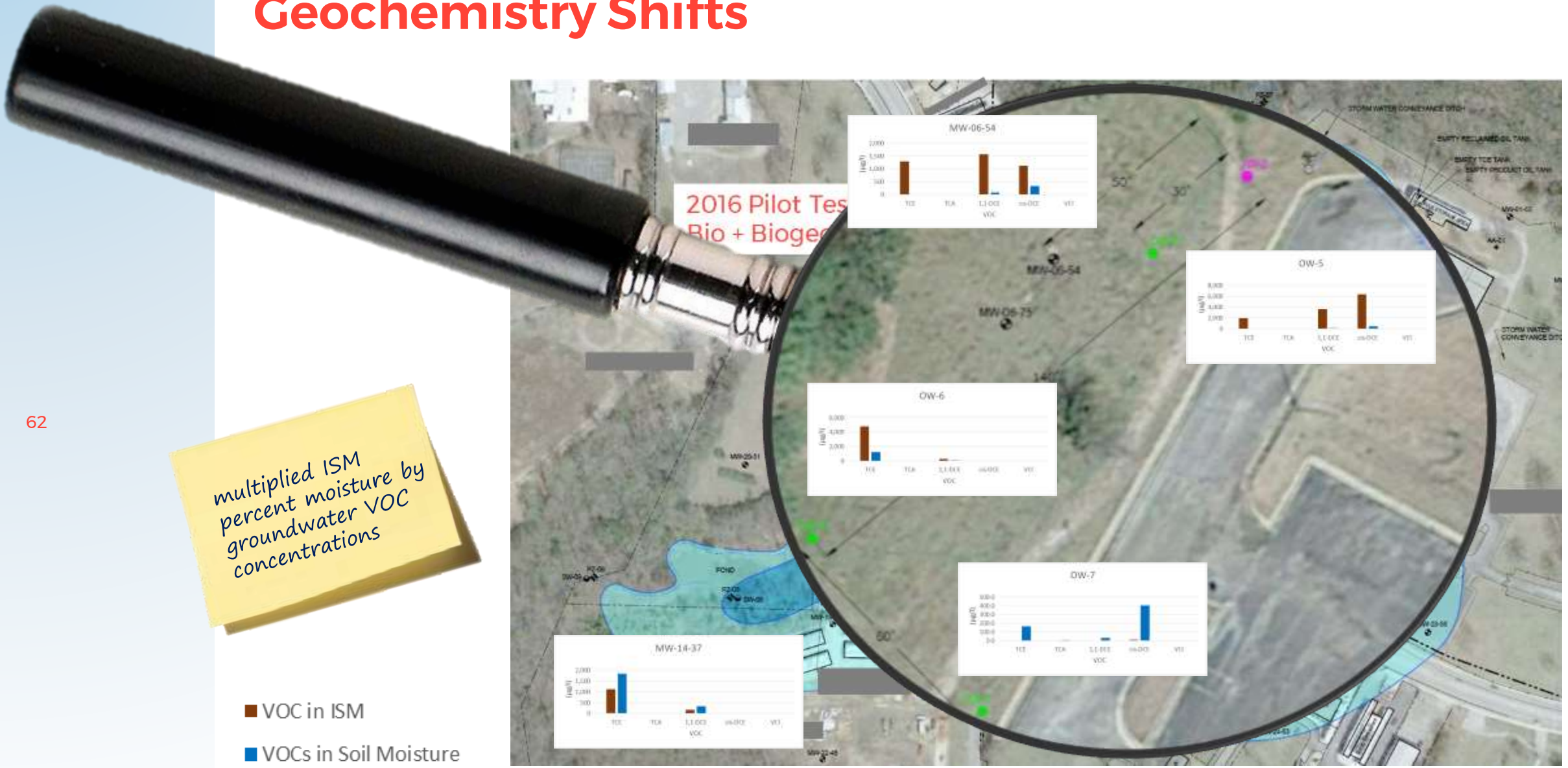


← qPCR (cells/g)
Collected from ISMs
Pre-treatment qPCR groundwater data = ND

End Products

- Dissolved gas data was collected from the ISMs
- A headspace method was used to quantify ethene in the crushed sandstone matrix
- The data are being assessed
- We know that ethene and ethane are present and
- The amount of ethene increased significantly from the May samples to the August samples

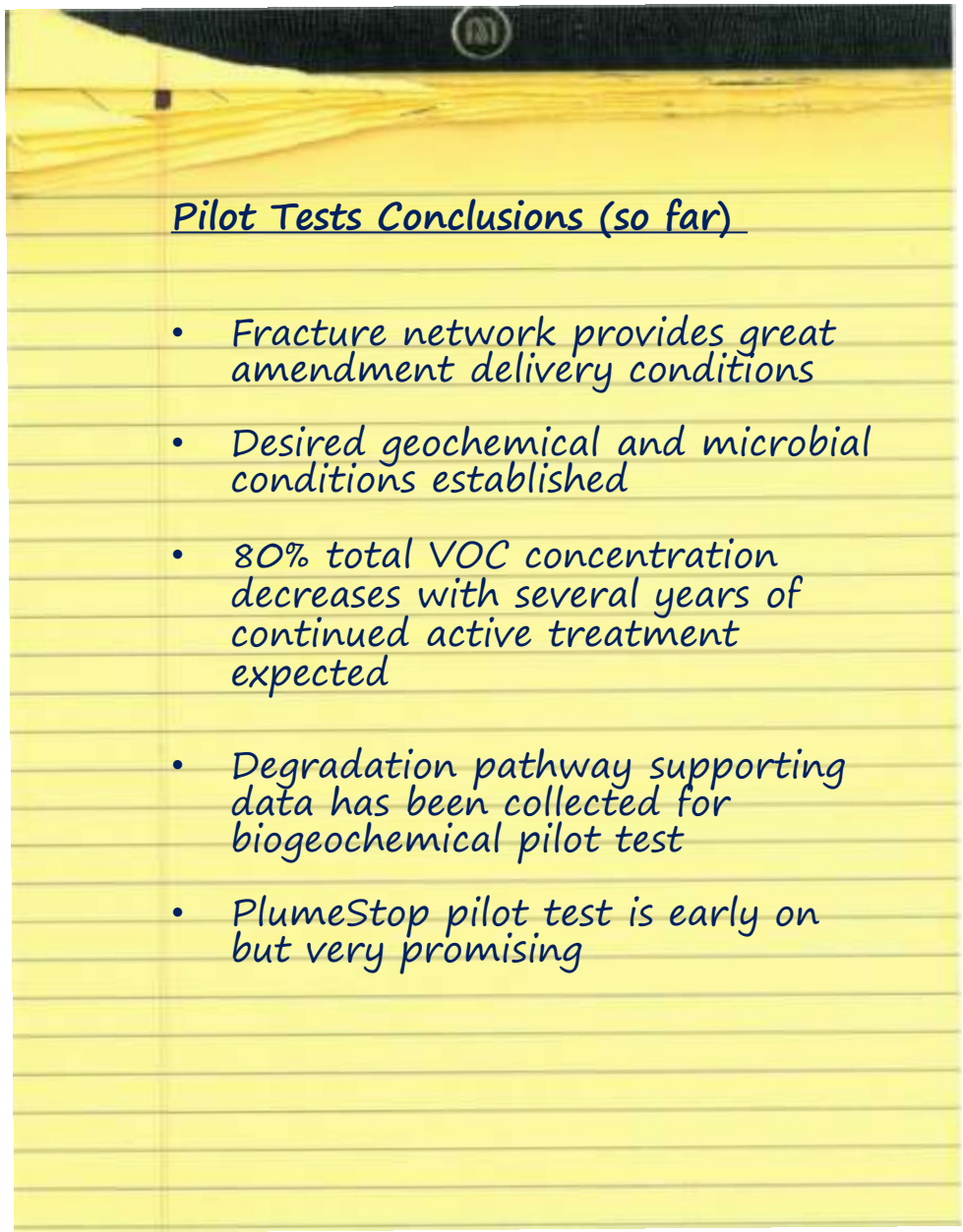
Geochemistry Shifts



multiplied ISM percent moisture by groundwater VOC concentrations

PlumeStop Pilot Conclusion

Conclusions



Conclusions

Greener Cleanups: EPA Spreadsheets for Environmental Footprint Analysis - August 2014

Environmental Footprint Summary

Core Element	Metric		Unit of Measure	Footprint	
				InSitu Treatment	Pump and Treat
Materials & Waste	M&W-1	Refined materials used on-site	Tons	0	4
	M&W-5	On-site hazardous waste disposed of off-site	Tons	10	10
Water (used on-site)	W-1	Public water use	MG	1	0.0
Energy	E-1	Total energy used (on-site and off-Site)	MMBtu	770	29,365
	E-4	On-site grid electricity use	MWh	0	2,200.0
Air	A-1	On-site NOx, SOx, and PM emissions	Pounds	158	431
	A-3	Total NOx, SOx, and PM emissions	Pounds	1,011	32,396
	A-3A	Total NOx emissions	Pounds	696	8,513
	A-3B	Total SOx emissions	Pounds	267	23,692
	A-3C	Total PM emissions	Pounds	48	191
	A-4	Total HAP emissions	Pounds	8	740
	A-5	Total greenhouse gas emissions	Tons CO2e*	62	1,803
Land & Ecosystems					

** Total greenhouse gases emissions (in CO2e) include consideration of CO2, CH4, and N2O (Nitrous oxide) emissions.*

"MMBtu" = millions of Btus

"MG" = millions of gallons

"CO2e" = carbon dioxide equivalents of global warming potential

"MWh" = megawatt hours (i.e., thousands of kilowatt-hours or millions of Watt-hours)

"Tons" = short tons (2,000 pounds)

Notes:

- P&T: 20 wells, AS, GAC
- In Situ: 20 wells
- O&M: 20 years, 5 injections

WSP

?

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