

Anaerobic Biodegradation of Chlorobenzene, Dichlorobenzene and Benzene in Shallow Saturated Soils

Amita Oka, Ph.D.

Langan Engineering and Environmental Services, Inc.

Co-authors

Steven Florkiewicz, Stewart Abrams and Elana Seelman

April 2019

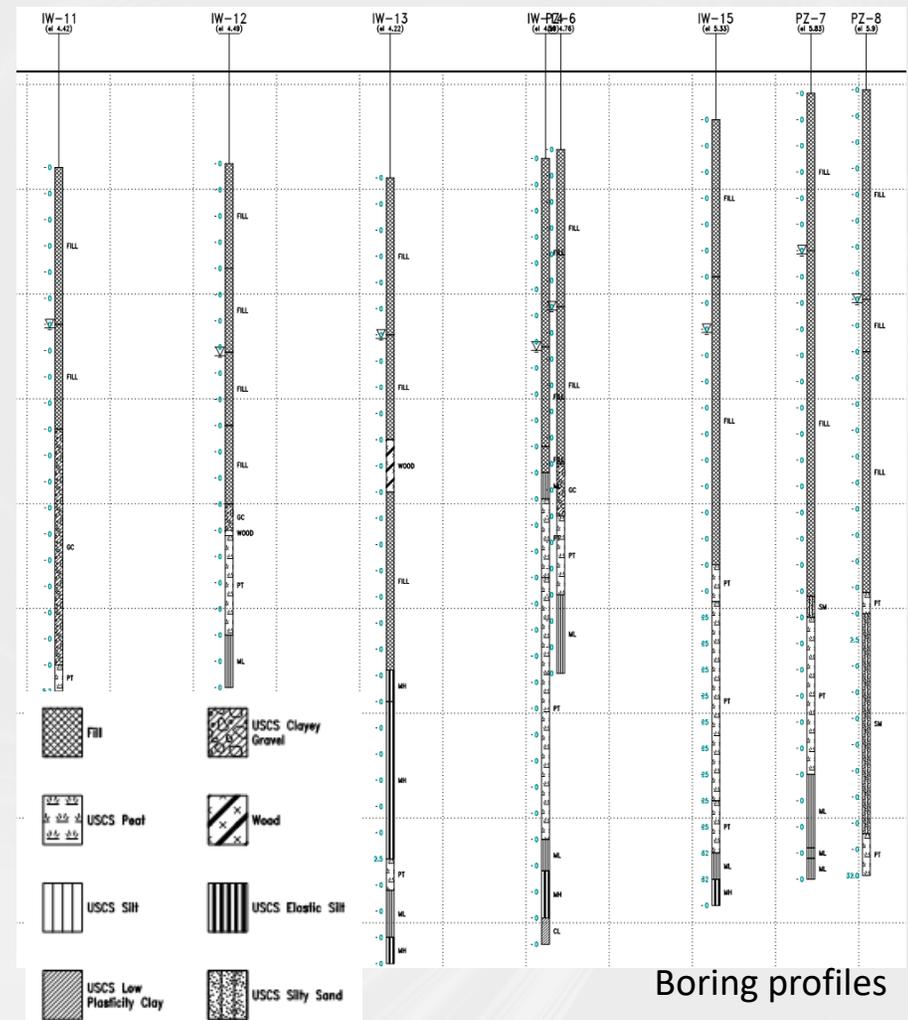
Site Background

- Bulk fuel storage facility in New Jersey
- Mixture of benzene, mono-, di-, and trichlorobenzene in soil and groundwater
- Managed under NJDEP SRP
- Mandatory remediation time frame of May 2021



Site Background

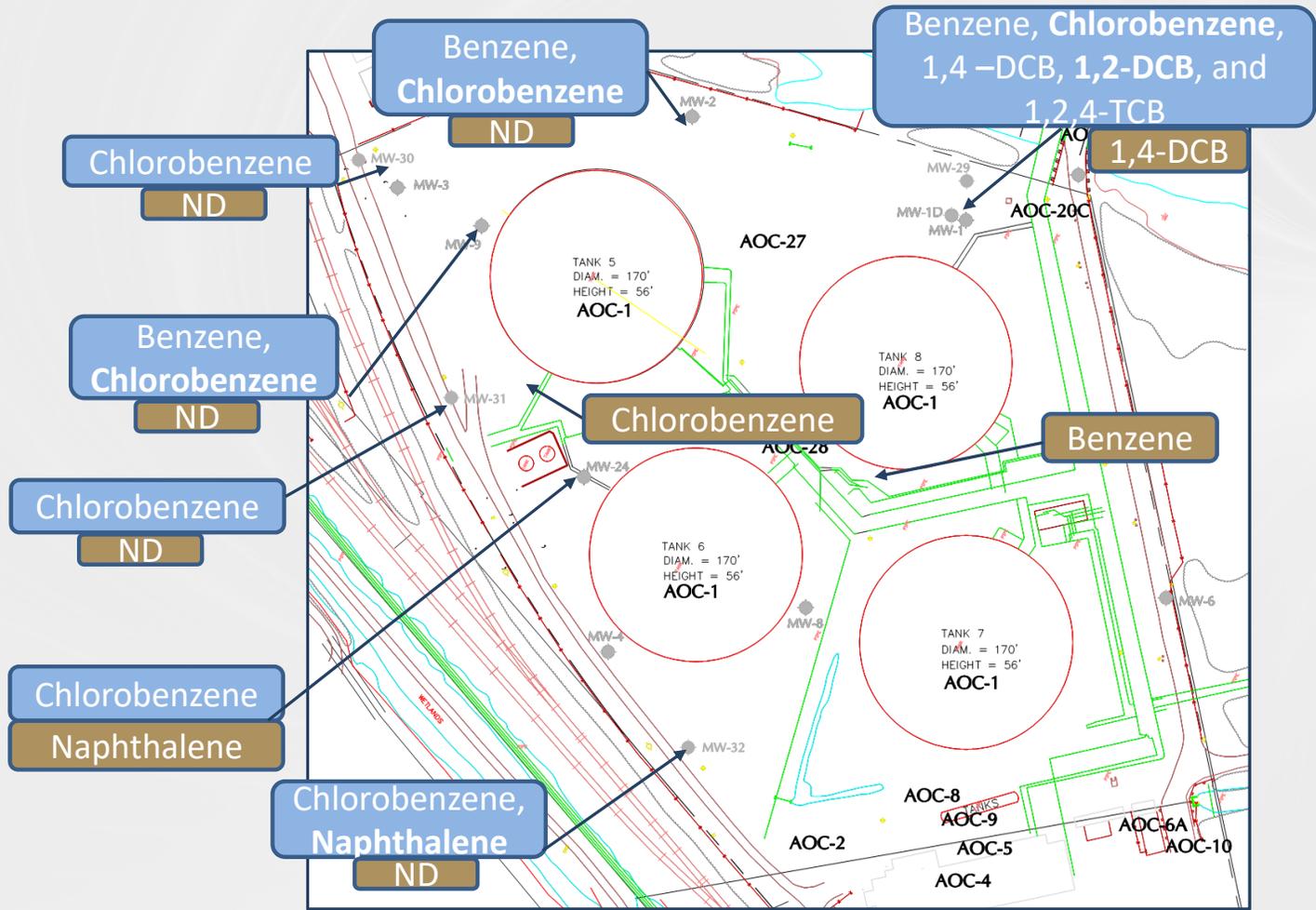
- Historic fill with underlying peat layer.
- Intermittent layers of silt, silty sand
- Water table 0.5 to 4 feet bgs
- Proximity to tidally influenced water bodies
- Treatment area is inside a containment berm



Site Background

Groundwater impacts over ~ 5 acres

Groundwater
Soil



Site Background

Source Area VOC Concentrations

Location:	MW-2		
Sampling Date:	May 2013	Feb 2014	May 2018
Units:	ug/L		
Chlorobenzene	1860	1410	1500
Benzene	100	129	110
1,4-Dichlorobenzene	172	91.1	NE

Location:	MW-1R		
Sampling Date:	May 2017	Aug 2017	May 2018
Units:	ug/L		
Chlorobenzene	3000	4400	120
Benzene	25	70	1.1
1,2-Dichlorobenzene	8700	3600	NE
1,4-Dichlorobenzene	390	280	NE
1,2,4-Trichlorobenzene	26	22	NE
Tetrachloroethene	NE	NE	NE

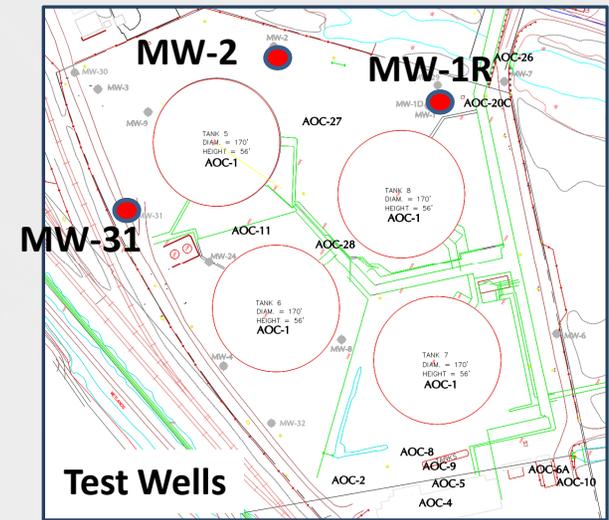
- Remedial goal - reduce concentrations to less than 10X groundwater quality standard
- Remedial constraints - minimum infrastructure and disruption to the facility operations

Remedial Strategy

- Evaluate potential for aerobic bioremediation
 - In-situ microcosm testing using Bio-Traps® (Aug to Sept 2014)
- Verify effectiveness of aerobic bioremediation with pilot testing
 - Oxygen infusion test using iSOC™ (May to Aug 2017)
- Phase I Remediation (June to Dec 2018)
 - Primary strategy
 - Contingent strategy

In-Situ Microcosm Testing

- Goal: Evaluate the potential for aerobic bioremediation
- Specific objectives
 - Evaluate the effect of oxygen release compound (ORC)
 - Evaluate effect of diammonium phosphate (DAP)
 - Evaluate effect of ENV477*, a 1,2-dichlorobenzene degrading culture
- Testing: Bio-Traps® (Microbial Insights Inc., TN) at three wells



Bio-Traps® Design

Units/ Well	MW-31	MW-2	MW-1R
MNA	×	×	×
ORC			×
DAP	×		
ORC + DAP		×	
BioAug + ORC			×

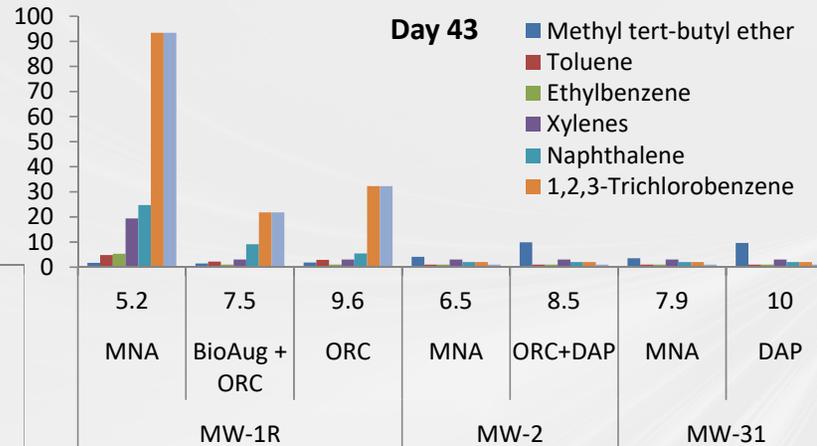
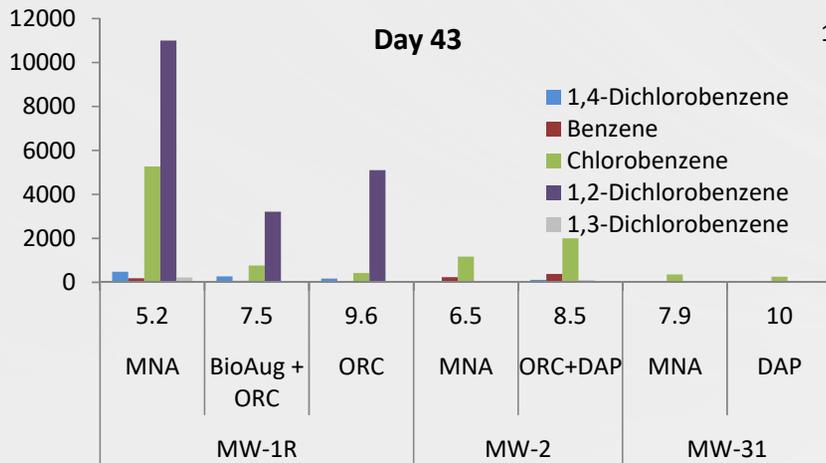
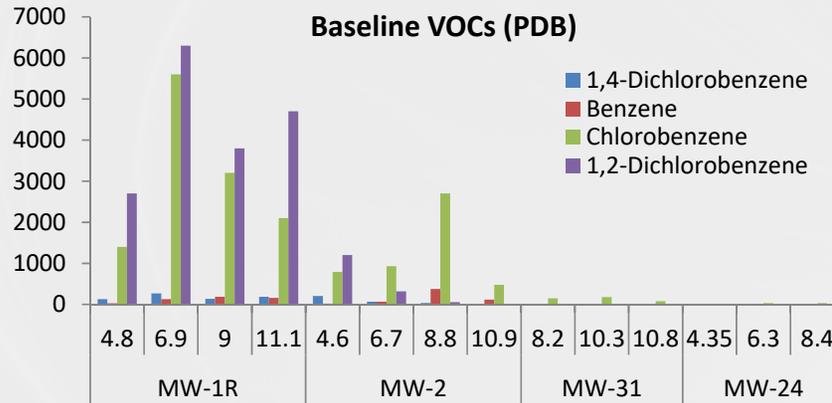
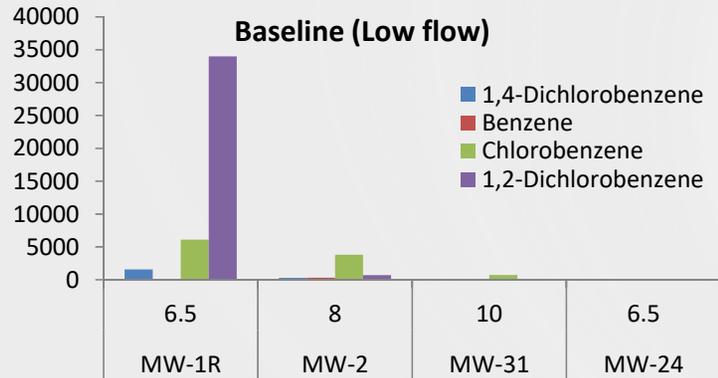
* ENV477 produced by APTIM, Lawrenceville, NJ

Bio-Traps® image extracted from Microbial Insights Inc. website

In-Situ Microcosm Testing – Baseline Results

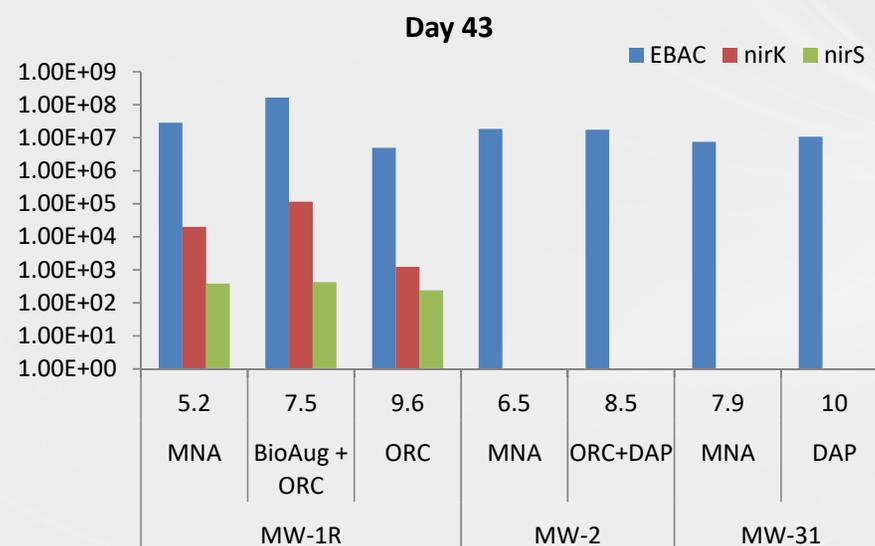
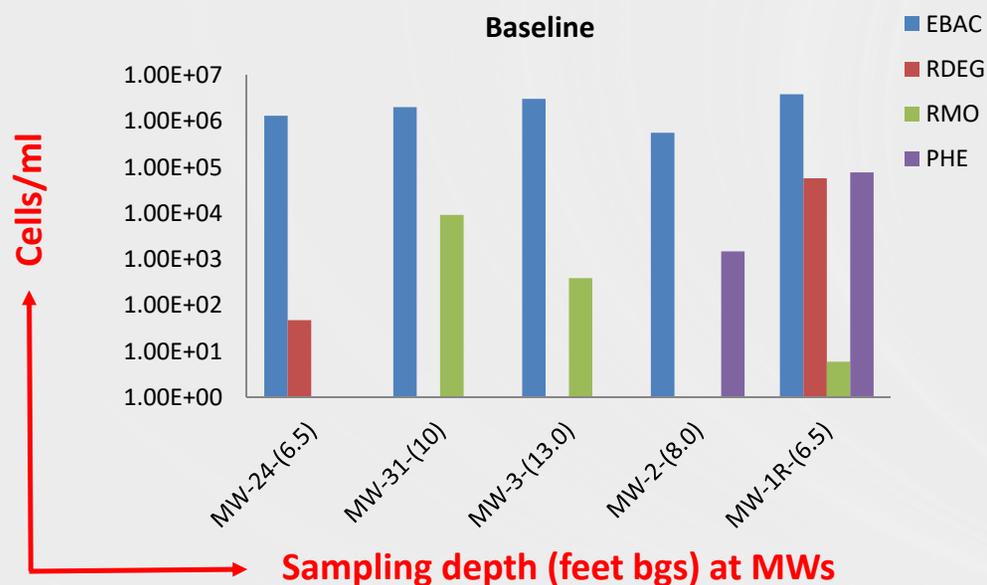
- ORP across wells sampled ranged from - 233 to -23 mV
- Nitrate < 1 mg/L
- Sulfate 4.6 to 270 mg/L
- Chloride
 - 340 to 890 mg/L
 - Salt water impact
- Low to moderate BOD and COD
 - COD 43 to 110 mg/L
 - BOD 4.3 to 26 mg/L

Bio-Trap Results - VOCs



Sampling depth (feet bgs) at MWs

Bio-Trap Results – Microbial Biomarkers



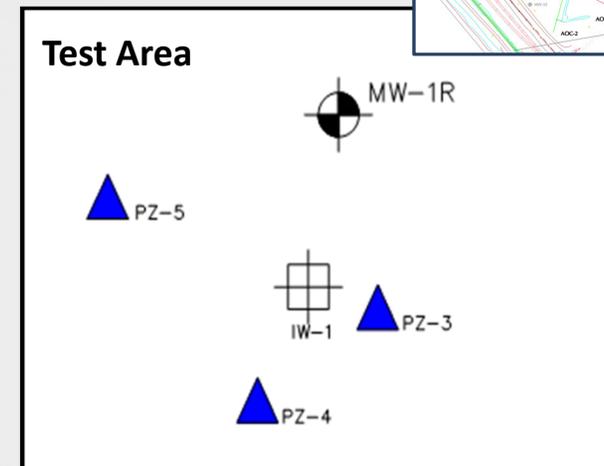
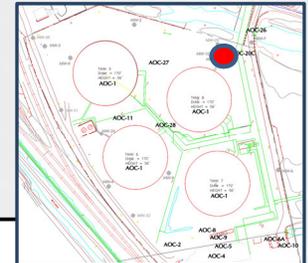
- EBAC - total bacteria
- nirK and nirS - nitrite reductase genes to track ENV 477
- RDEG - toluene monooxygenase
- RMO – ring hydroxylating toluene monooxygenase
- PHE - phenol hydroxylase

Conclusions

- Bacterial (gene) data was not conclusive
- VOC data suggested that ORC alone and ORC along with bioaugmentation was effective
- Effectiveness of DAP could not be verified

Field Pilot Testing

- Test goals: Assess effectiveness of oxygen infusion in establishing aerobic conditions and decreasing groundwater contaminants
- Setup: Oxygen infusion at IW-1 for 90 days
- Monitoring
 - Bimonthly OM&M
 - Baseline and day 90 groundwater sampling
 - VOCs
 - Geochemical parameters
 - Gene biomarkers
 - Plate counts



IW DISTANCES	
SAMPLE POINT	DISTANCE TO IW-1
MW-1R	20.2
PZ-3	9.2
PZ-4	15.1
PZ-5	27

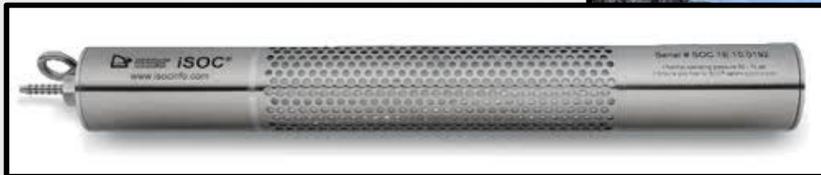
Field Pilot Testing – VOC Results

	IW-1		PZ-4		MW-1R		PZ-3		PZ-5	
	Baseline	Post PT								
Chlorobenzene	4,000	2,600	34,000	52,000	3,000	4,400	3,900	2,800	5,600	6,000
Benzene	81	310	3,100	4,100	25	70	100	120	110	150
1,2-Dichlorobenzene	15	27	4,700	1,300	8,700	3,600	14		20,000	19,000
1,3-Dichlorobenzene	14	7	120	130	53	100	23	10	84	70
1,4-Dichlorobenzene	49	28	670	830	390	280	59	35	840	660
1,2,4-Trichlorobenzene	100	62	500		26	24	50		120	110

- VOCs – Up to 30% reduction observed
- Low recharge at PZ-4 - data may not be representative
- Microbial and geochemical data did not show significant changes

Field Pilot Testing Results

ISOC Unit Before Test



iSOC Unit – Day 90



- ORP at all wells except IW-1 was negative
- Dissolved oxygen at all monitoring locations was mostly <1 mg/L
- Dissolved oxygen at IW-1 decreased shortly after infusion was stopped
- Results showed that establishing aerobic groundwater conditions for full-scale will be challenging

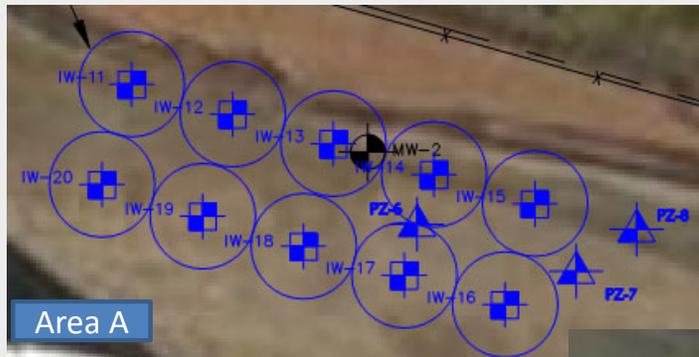
Phase I Remediation – Anaerobic Bioremediation

- Goal: Assess effectiveness of anaerobic bioremediation in decreasing groundwater contaminant concentrations

Treatment Areas

Area A	Area B
MW-2 Benzene and chlorobenzene	MW-1R Benzene, chlorobenzene , 1,4 - and 1,2-DCB , and 1,2,4-TCB
Sulfate Reduction	Step 1 - Sulfate reduction Step 2 - bio-stimulation/bioaugmentation (reductive dechlorination)

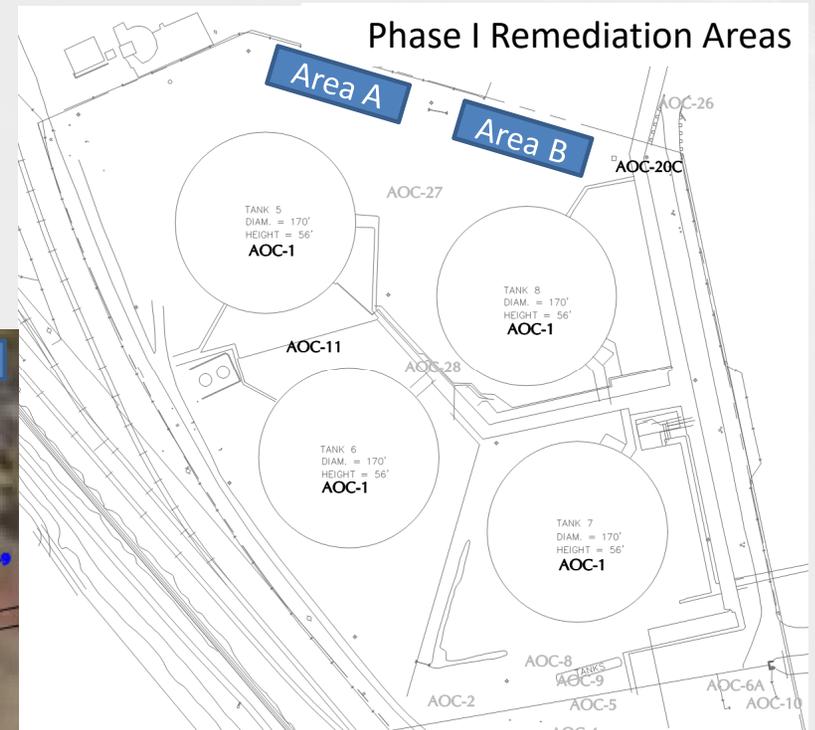
Phase I Remediation



Treatment Areas

Treatment Zone

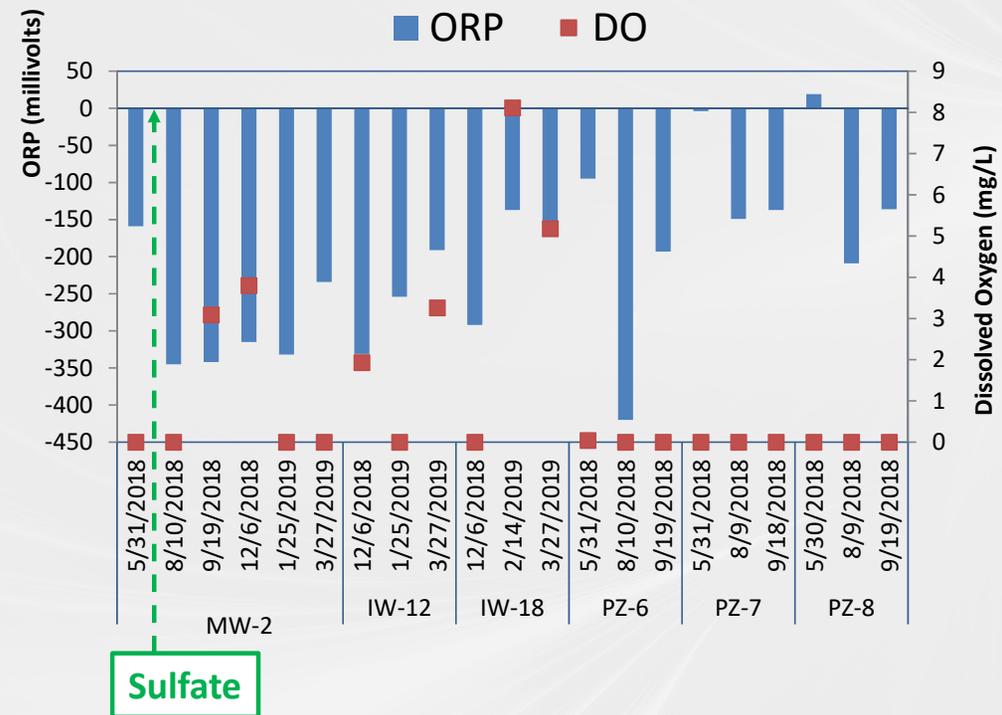
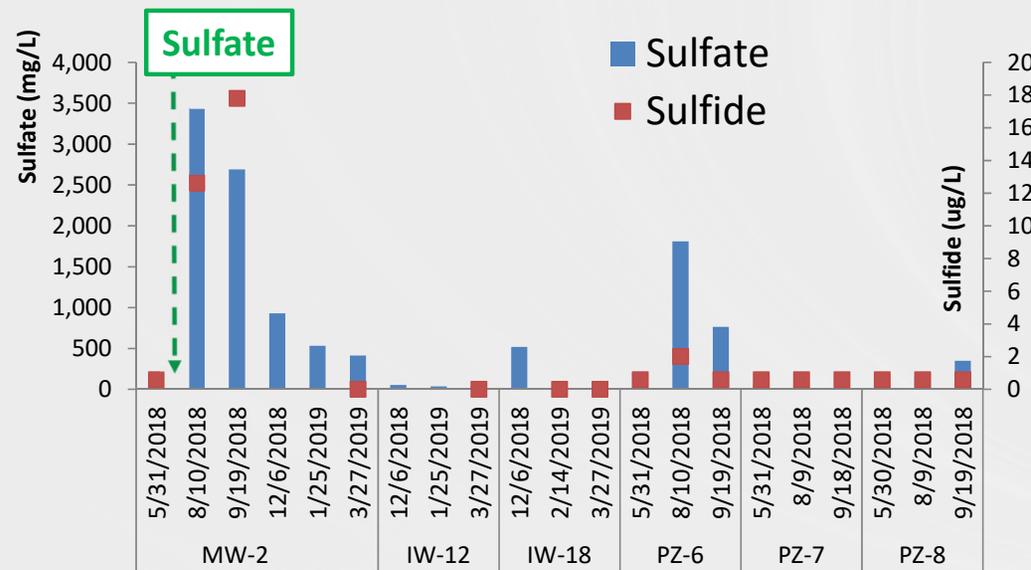
- 3000 square feet/area
- 5 to 7 feet of treatment thickness
- 10 injection wells/area



Phase I Remediation

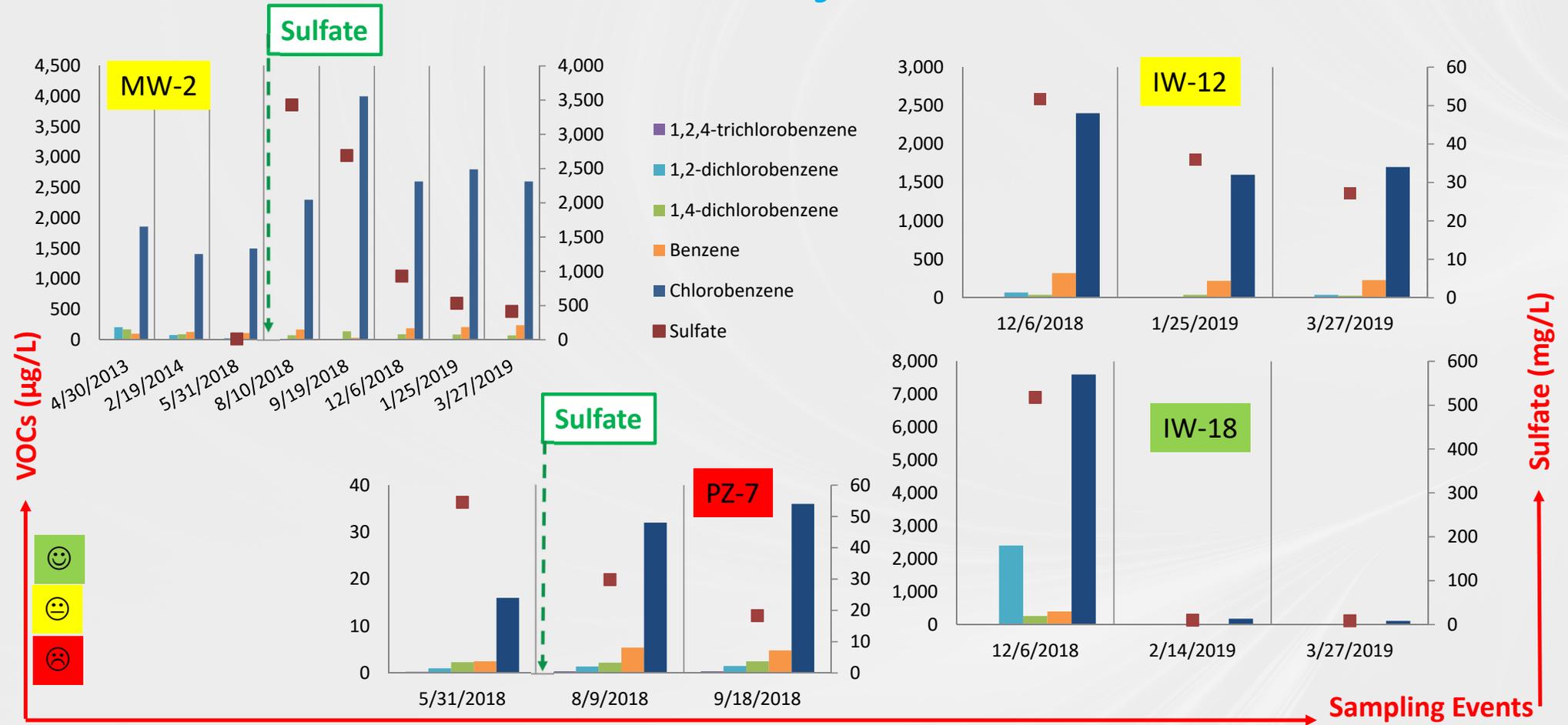
	Treatment Area A	Treatment Area B
Contaminants	Benzene and chlorobenzene	Benzene, chlorobenzene , 1,4-DCB, 1,2-DCB , and 1,2,4-TCB
Sulfate + Nutrients Injections in June/July 2018	<ul style="list-style-type: none"> • 5,100 lbs of sulfate salts (Nutrisulfate)[®] and 1700 lbs of Nutrimens[®] • Injections completed over 10 work days, 0.5 gpm/well • 6300 gallons injected 	
Lactate and SDC-9 Injections in Dec 2018	-	<ul style="list-style-type: none"> • 2200 lbs of 60% lactate (QRS[™]-SL) • 14L DHC microbial consortium • 3700 gallons injected over 7 work days
Injection Wells	<ul style="list-style-type: none"> • IW-11 to IW-20 • <50% target well volume injected at IW-13, IW-14 and IW-19 	<ul style="list-style-type: none"> • IW-1 to IW-10 • <50% target well volume injected at IW-1, IW-3, IW-5 during lactate injections

Treatment Area A – Sulfate Injections - Results

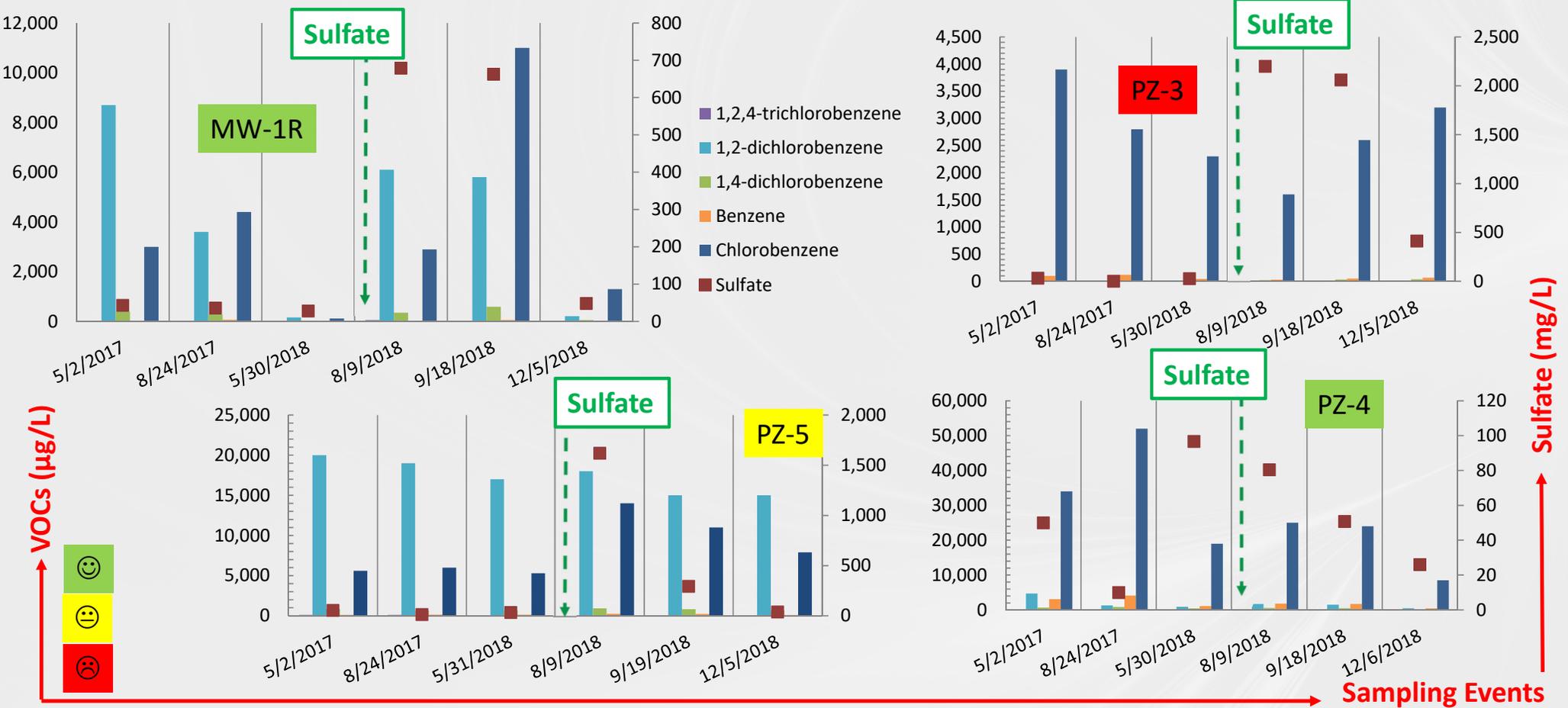


- Anaerobic conditions were established in the treatment area

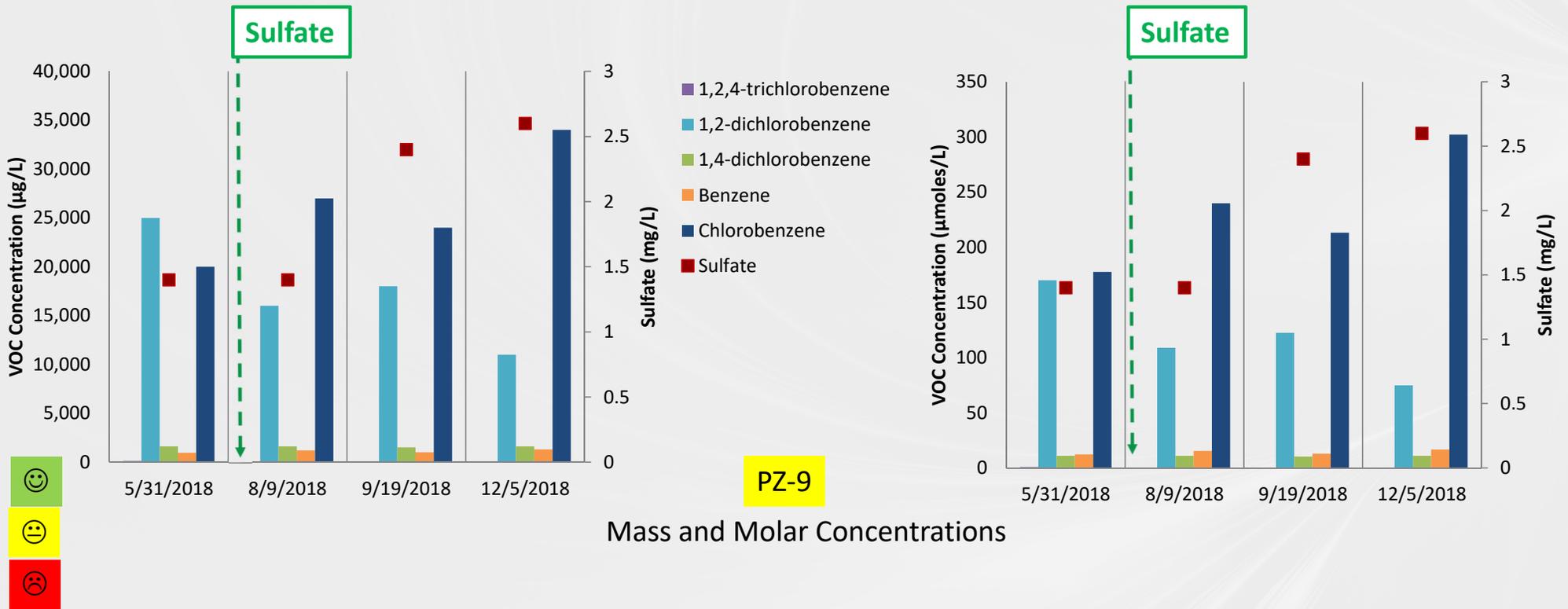
Treatment Area A – Sulfate Injections – VOC Results



Treatment Area B – Sulfate Injections – VOC Results



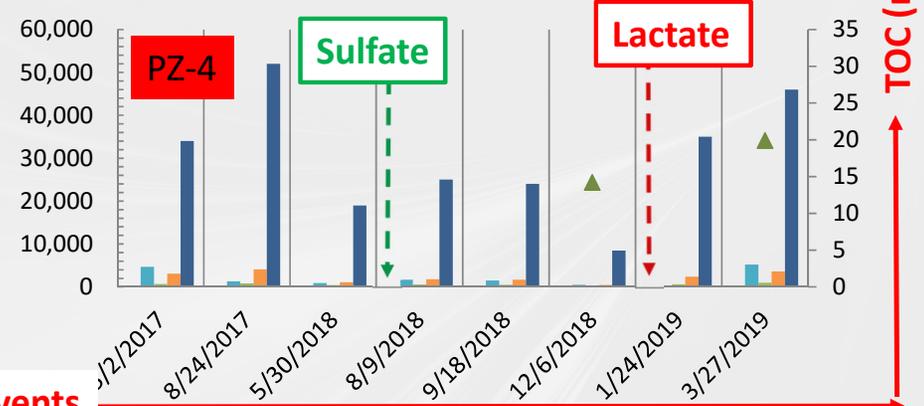
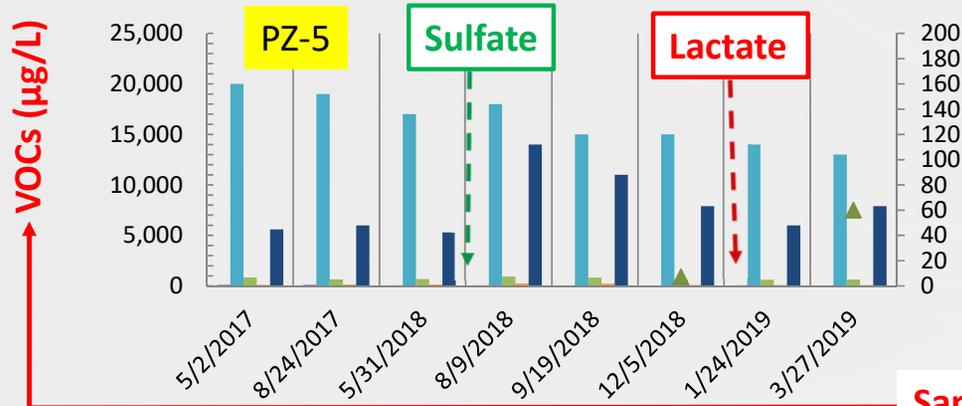
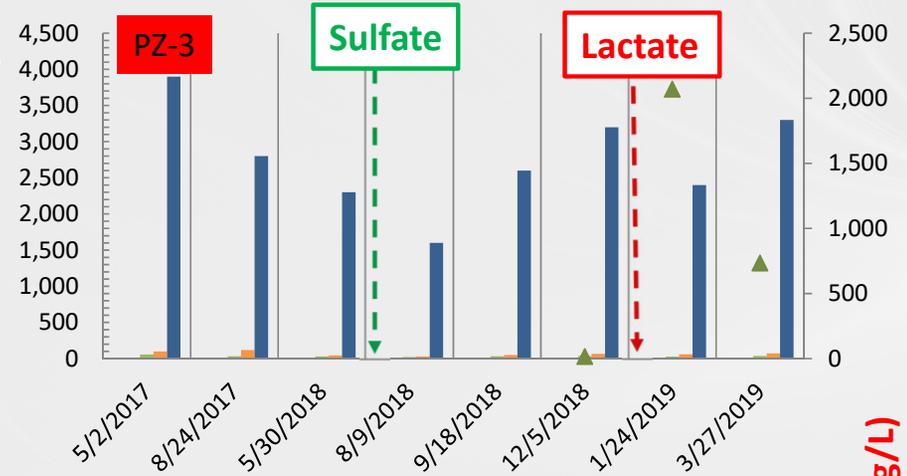
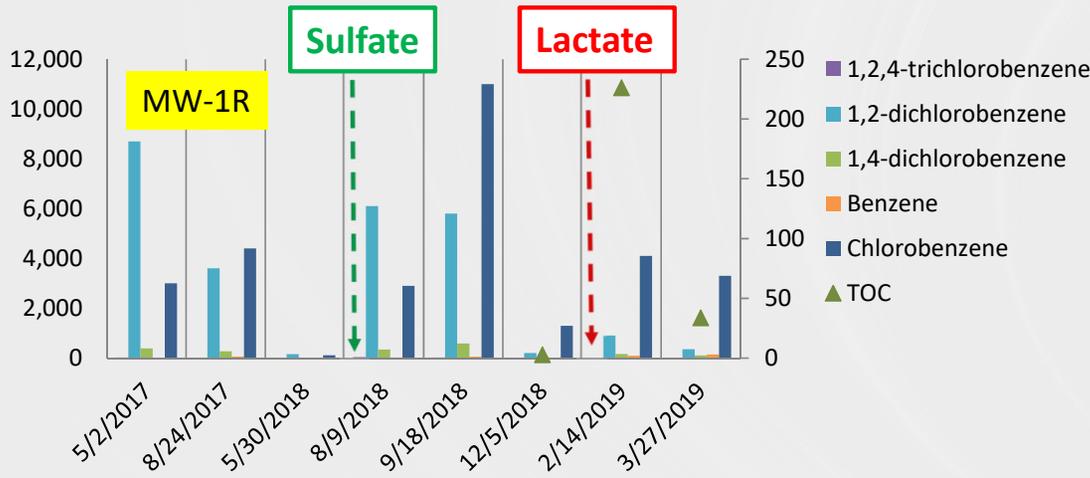
Treatment Area B – Sulfate Injections – VOC Results



Sulfate Injections – Results Summary

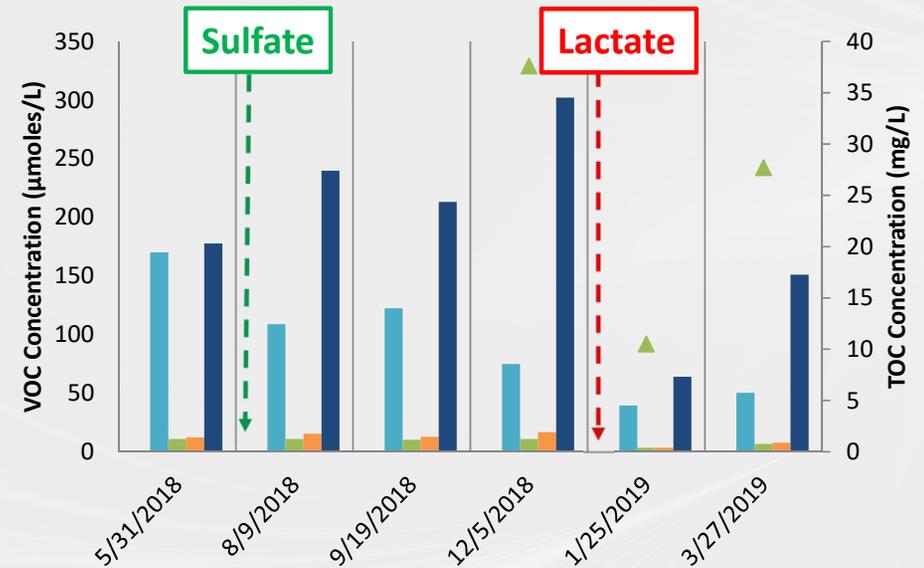
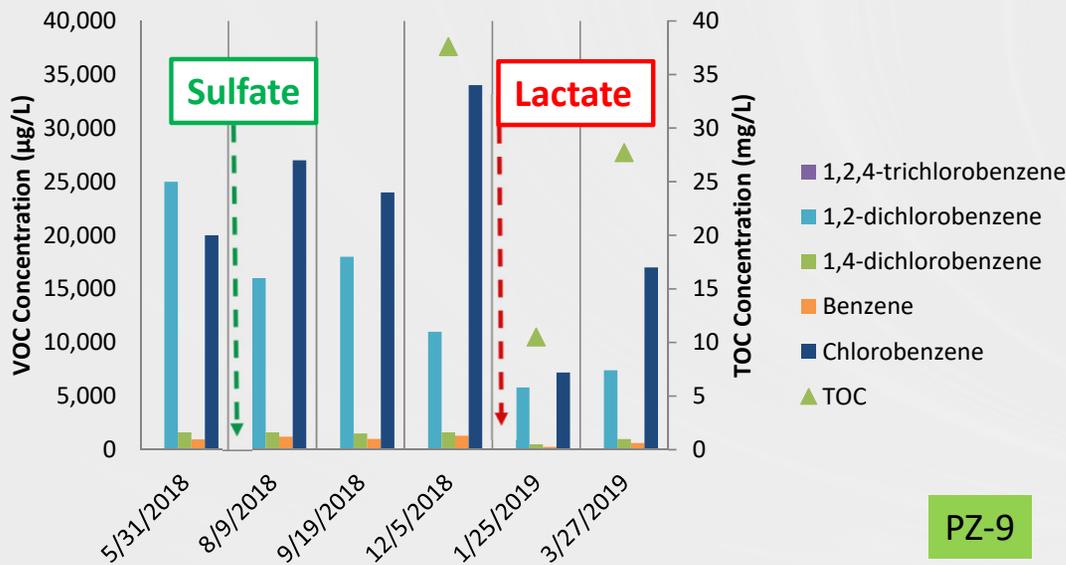
	Treatment Area A	Treatment Area B
Contaminants	Benzene and chlorobenzene	Benzene, chlorobenzene, 1,4 - and 1,2-DCB, and 1,2,4-TCB
Sulfate	Up To 3400 mg/L	Up to 2200 mg/L
Sulfide	Up to 18 ug/L	62 ug/L
VOCs	<p>Four wells with relatively high VOCs</p> <ul style="list-style-type: none"> • Chlorobenzene concentrations decreased 30% , 35% and 95% in 3 of 4 wells • One well with 1,2-DCB - ~100% decrease • No spikes in benzene 	<p>Five wells with relatively high VOCs</p> <ul style="list-style-type: none"> • Chlorobenzene concentrations decreased in 3 of 5 wells between 43 to 88% • 1,2-DCB decreased by 16 to 96% in 3 of 4 wells • No spikes in benzene

Treatment Area B – Lactate Injections – VOC Results



Sampling Events

Treatment Area B – Lactate Injections – VOC Results

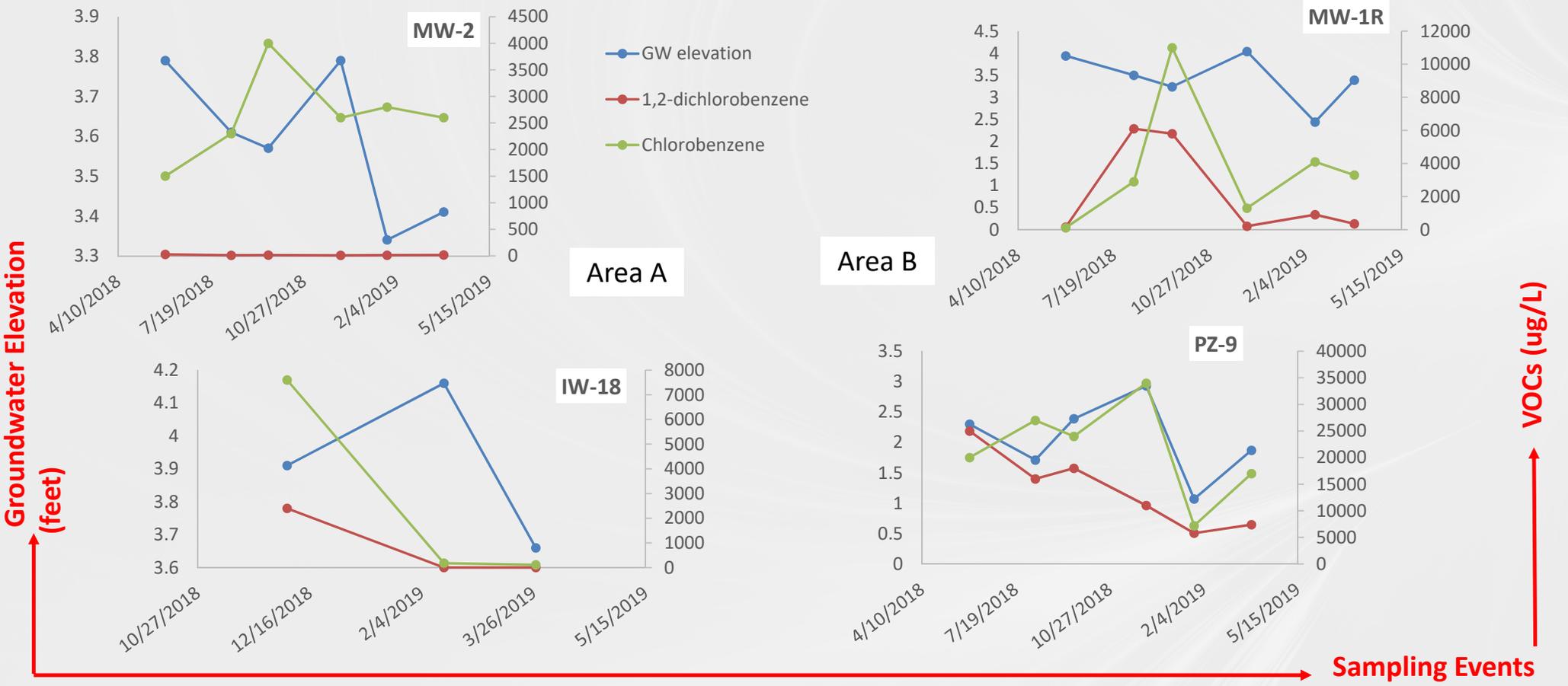


Mass and Molar Concentrations

Lactate Injections – Results Summary

	Treatment Area B
Contaminants	Benzene, chlorobenzene, 1,4-DCB, 1,2-DCB, and 1,2,4-TCB
Sulfate	<ul style="list-style-type: none">• Before injection only PZ-3 has relatively high sulfate concentrations (~400 mg/L)• Three months after lactate injections the sulfate concentrations in all wells is <50 mg/L
TOC	Uneven distribution. <100 mg/L mostly. One well with 730 mg/L
VOCs	<p>Five wells with relatively high VOCs</p> <ul style="list-style-type: none">• Chlorobenzene concentrations decreased 19 and 50% in two wells• 1,2-DCB decreased 13 to 60%• No comparable spikes in benzene

Groundwater Elevation and VOCs



Summary

- Decrease in chlorobenzene and 1,2-DCB concentrations was observed after sulfate injections and lactate injections
- Increase in groundwater concentrations of VOCs was observed after both injection events, indicating desorption of VOCs from soil matrix
- Effect of changes in groundwater elevation need to be accounted for during interpretation of data
- Additional data is needed to conclusively demonstrate effect of lactate injections
- Data shows beneficial effects of sulfate injection in decreasing chlorobenzene and 1,2-DCB concentrations.