Klozur® KP Slurry Injection via Hydraulic Fracturing: Fundamentals, Methods, and Lessons Learned

Webinar | September 22, 2021

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Presentation Outline

- Klozur® KP Chemistry
- Klozur® KP Case Studies
- Why KP?
- Lessons Learned
- Application:
  - Fracture Form
  - Managing Daylighting
  - Diffusion of Reagents

Chemistry
Dose
Contact
And
Monitoring

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Klozur® Persulfate
Differences between Sodium and Potassium Persulfates

KLOZUR® SP

- Environmental Grade Sodium Persulfate

KLOZUR® KP

- Environmental Grade Potassium Persulfate

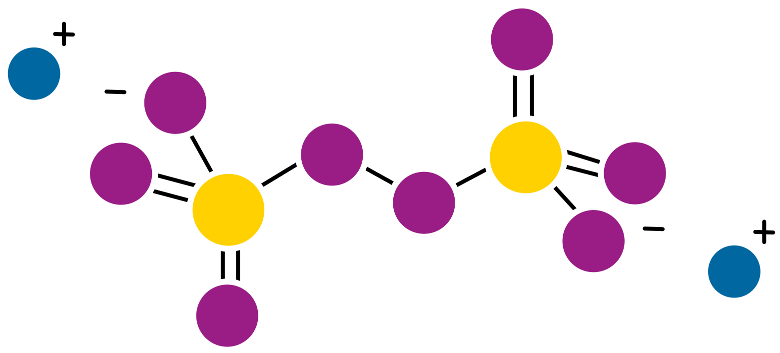
Key Differences:
- Solubility
- Na^+ vs K^+ residual

Temperature	Klozur® SP		Klozur® KP	
(℃)	wt%	g/L	wt%	g/L
0	36.5	480	1.6	17
10	40.1	540	2.6	29
20	41.8	570	4.5	47
25	42.3	580	5.7	59

Characteristic	Klozur® SP	Klozur® KP
Formula	$Na_2S_2O_8$	$K_2S_2O_8$
Molecular Weight	238.1	270.3
Color	White	White
Loose Bulk Density (g/cc)	1.12	1.30

All Klozur® persulfates release the persulfate anion

- Sodium and potassium persulfate are used in environmental remediation applications
- A strong oxidant
- Activation results in the formation of oxidative and reductive radicals
- Applicable across a broad range of contaminants
- Extended subsurface lifetime (weeks to months)
- Little to no gas evolution



Free Radical Chemistry:
Persulfates produce free radicals in many diverse reaction situations

$S_2O_8^{-2}$ + activator ⟶ $SO_4^{\bullet-}$ + ($SO_4^{\bullet-}$ or SO_4^{-2})

Activation produces a radical which is more powerful and kinetically fast

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Klozur® Persulfate Degradation Pathways

Oxidative	Either	Reductive
Petroleum Hydrocarbons	PCE, TCE, DCE and VC	Carbon Tetrachloride
MGP Residuals	Chlorobenzenes	1,1,1-Trichloroethane
BTEX	Chlorophenols	Dichloroethanes
PAHs	Select Pesticides	Select Pesticides
Oxygenates	Select Fluorinated Compounds	Select Energetics
1,4-Dioxane	PCBs	
	Select Energetics	

Activation Methods: Alkaline, Hydrogen Peroxide, and Heat

Activation Method: Iron Chelate, Klozur® One

Klozur® KP Reduces cVOC and BTEX by >99% at Former Industrial Site in Germany

Consultant: Riskcom
Contractor: Toterra Ltd.

Area:	200 m^2 (2,150 ft^2)
Interval:	7-11 m bgs (23-36 ft bgs)
Klozur® KP:	1,350 Kg (~3,000 lbs)
Activator:	200 Kg (441 lbs) iron lactate

Klozur® KP Case Study
Former Industrial Site in Germany

- 1 Year Post Application Monitoring
- Successful distribution of KP and activator over a 200 m^2 area (2,152 ft^2) with 3 injection locations
- Activated Klozur® KP resulted in up to 99% treatment of Target COCs

Date	Contaminant (mg/L)				
	PCE	TCE	cDCE	BTEX	PAH
Baseline	13,000	22,000	52,000	20,713	98
6 Months Post	8	23	3,800	47	5
Percent Reduction	99.9%	99.9%	92.7%	99.8%	94.5%
12 Months Post	4	6	13,000	2,570	104
Percent Reduction	99.97%	99.97%	75.0%	87.6%	-5.3%

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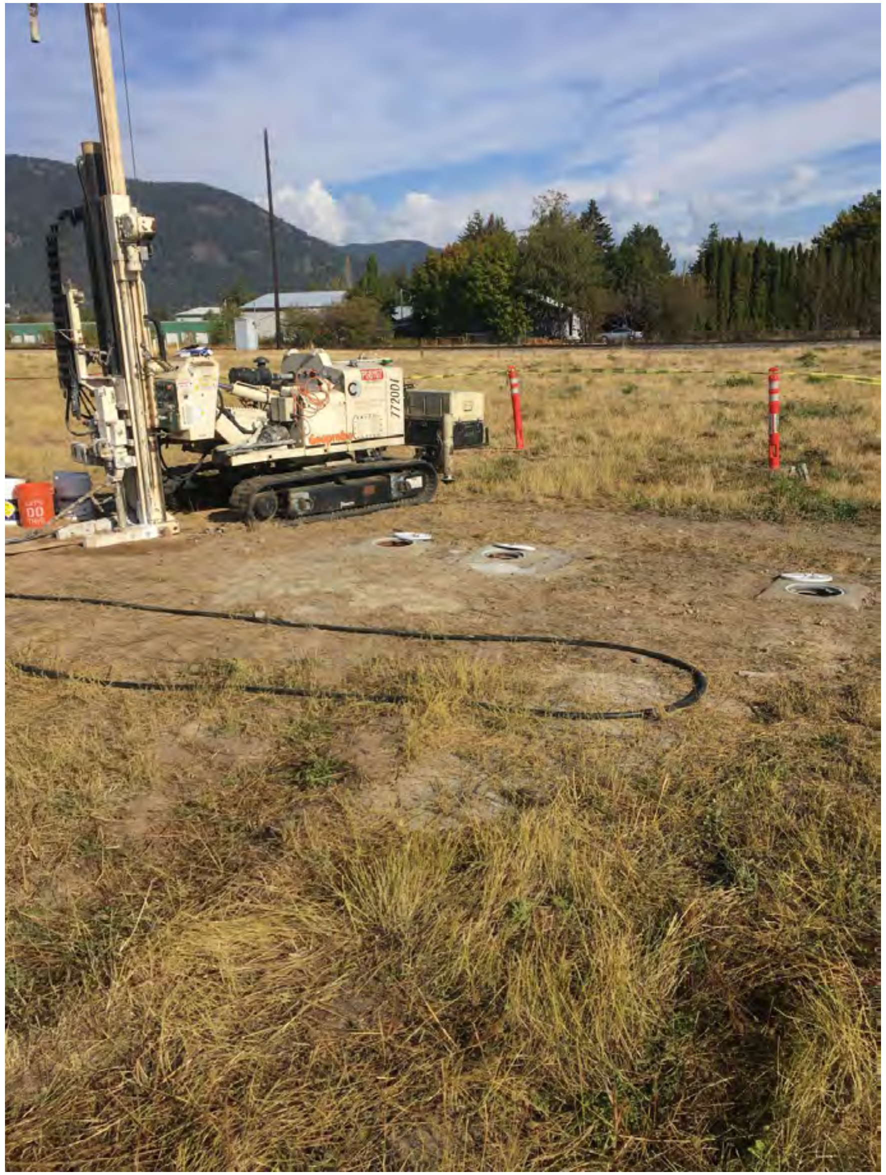
Klozur® KP Reduces Pentachlorophenol by up to 99 percent at Former Wood Treatment Site in Pacific Northwest USA

Consultant: ERM
Contractor: Cascade

Klozur KP:	4,400 lbs
Activator:	Hydrated Lime
Injection:	12 DPT locations
Spacing:	5 to 10 ft
Interval:	32 to 40 ft bgs



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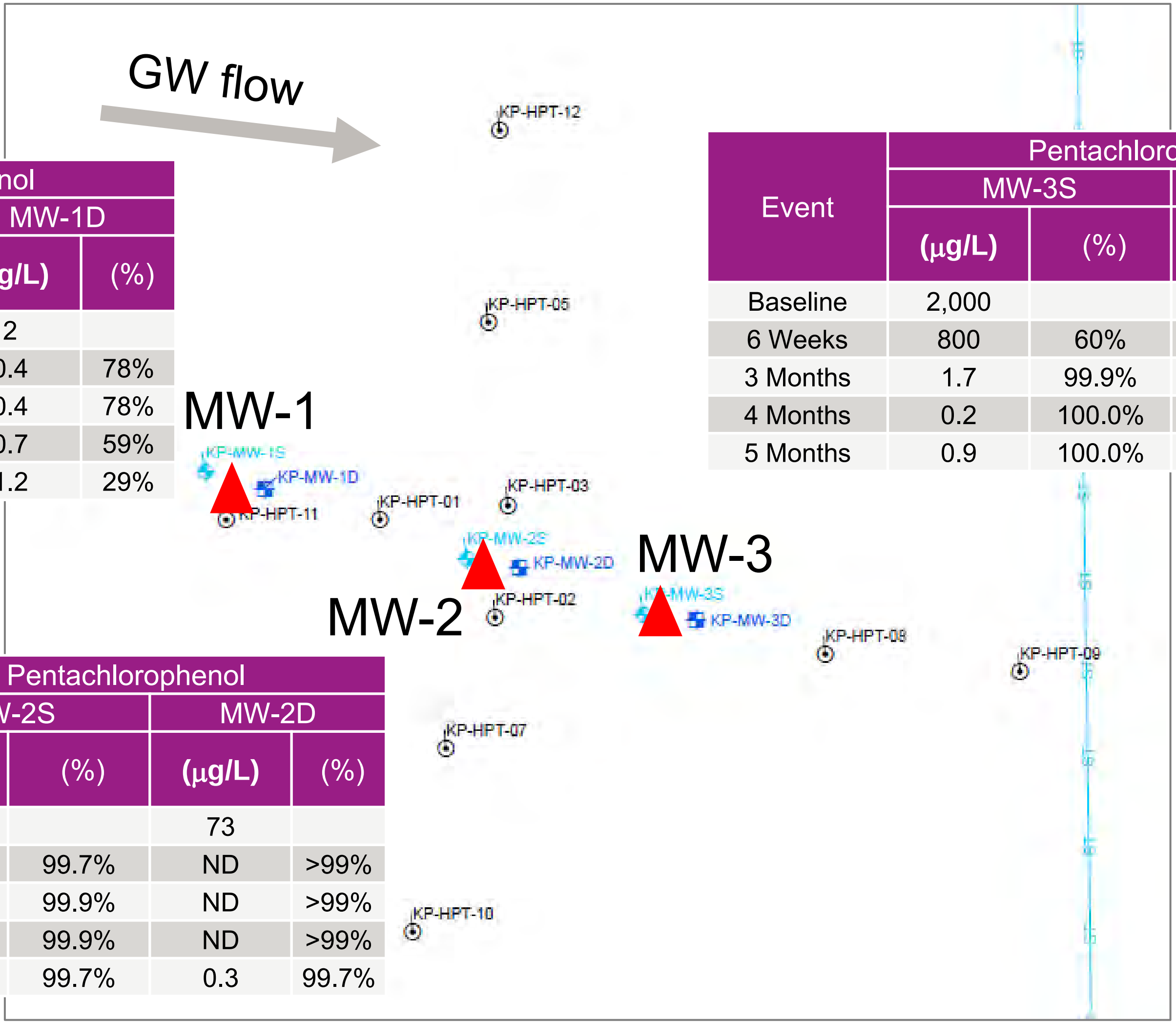
Klozur® KP Case Study
Pentachlorophenol Treatment



Event	Pentachlorophenol MW-1S (µg/L)	Pentachlorophenol MW-1S (%)	Pentachlorophenol MW-1D (µg/L)	Pentachlorophenol MW-1D (%)
Baseline	9		2	
6 Weeks	15	-69%	0.4	78%
3 Months	7	18%	0.4	78%
4 Months	ND	>99%	0.7	59%
5 Months	ND	>99%	1.2	29%

Event	Pentachlorophenol MW-3S (µg/L)	Pentachlorophenol MW-3S (%)	Pentachlorophenol MW-3D (µg/L)	Pentachlorophenol MW-3D (%)
Baseline	2,000		11	
6 Weeks	800	60%	13	-18%
3 Months	1.7	99.9%	13	-18%
4 Months	0.2	100.0%	ND	>99%
5 Months	0.9	100.0%	2	86%

Event	Pentachlorophenol MW-2S (µg/L)	Pentachlorophenol MW-2S (%)	Pentachlorophenol MW-2D (µg/L)	Pentachlorophenol MW-2D (%)
Baseline	1,700		73	
6 Weeks	5	99.7%	ND	>99%
3 Months	2	99.9%	ND	>99%
4 Months	1	99.9%	ND	>99%
5 Months	5	99.7%	0.3	99.7%

35 ft downgradient

DG-W

Event	PCP DG-W (µg/L)	PCP DG-W (%)
Baseline	9,700	
6 Weeks	6,300	35%
3 Months	330	97%
4 Months	140	99%
5 Months	470	95%

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Klozur® KP - Case Study
Summary

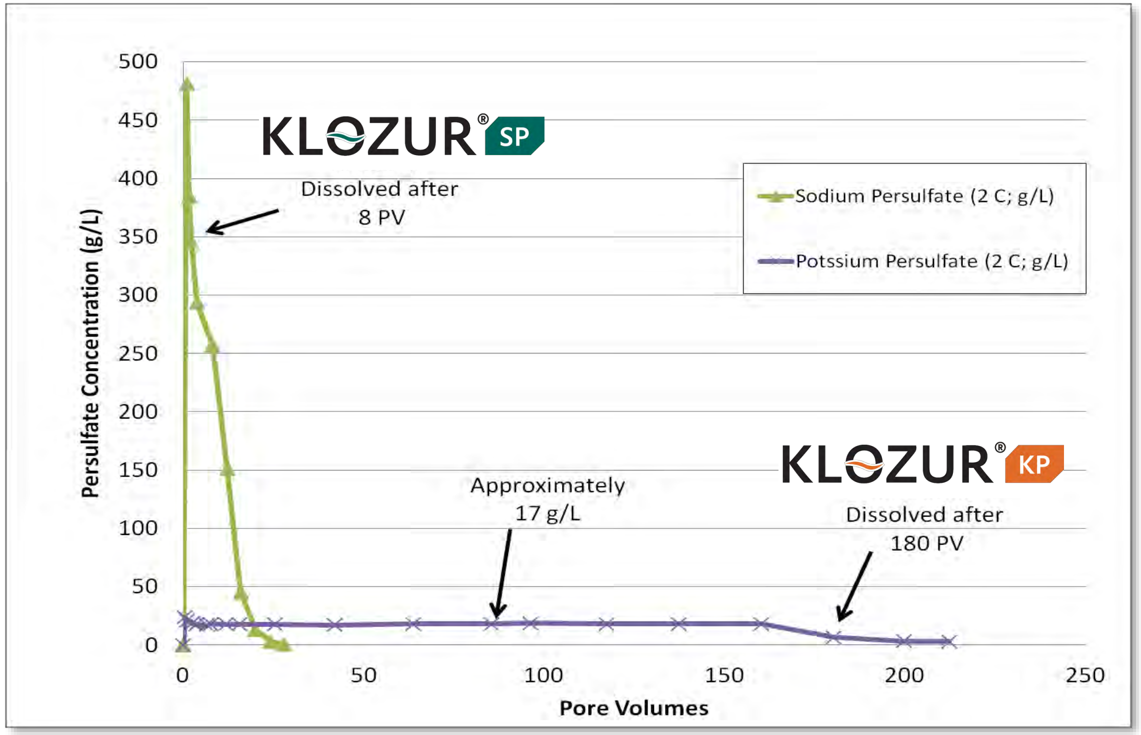
- Klozur® KP has been used at a variety of sites to remediate
  - Variety of contaminants
  - Co-mingled plumes
  - Variety of sites
- Treatment has been found to be ~99 percent reduction
- Hydrated lime is most common activator (alkaline activation) although iron-chelate has also been used.
- Once dissolved, remediation chemistry of Klozur® KP is the same as Klozur® SP

Why Klozur® KP?

- Time

- Klozur® KP (potassium persulfate) dissolves over a period of time to maintain a consistent concentration

- Klozur® SP – dissolved and available at time of application
  – Typically reactive for 2-8 weeks



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What Do You Do with More Remediation Time?

- Treating Aqueous Phase Contaminants
  - Permeable Reactive Barriers (PRBs)
  - Source zones
- Longer Contact Time
  - Low permeable soils
  - Low solubility contaminants
  - Low contaminant concentrations
- High groundwater velocity

Conceptual Klozur® KP Persistence (months)							
Temp (◦C)			5	10	15	20	25
Solubility (g/L)			22	29	37	47	59
	(ft/yr)	(m/yr)					
Groundwater Seepage Velocity	10	**3**	315	239	187	147	117
	25	**8**	126	96	75	59	47
	50	**15**	63	48	37	29	23
	75	**23**	42	32	25	20	16
	100	**20**	31	24	19	15	12
	500	**152**	6	5	4	3	2

1% KP by w/w Soil

15% ePV

30 ft length parallel to groundwater flow

Assumes achieving 50% solubility in cross section or pore volume

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Groundwater Contamination

Aueous phase contaminants to migrate to solid state Klozur® KP

- Permeable Reactive Barriers (PRBs)
  - Treating groundwater contamination as it passes into PRB. Soil contamination directly downgradient of PRB.
    - Will require periodically refreshment
- Source zones/Groundwater plumes
  - Typically treated with Klozur® SP
  - Low K_{oc} contaminants are not on soil, primarily in aqueous phase
    - 1,4-Dioxane, vinyl chloride, MTBE, etc
  - Solid slurry displaces less groundwater

Contaminant	EPA K_{oc}	F_{oc}	Contaminant Distribution (%)	
			GW	Soil
1,4-Dioxane	17	0.005	70%	30%
1,1,1-TCA	110		27%	73%
1,2-DCA	38		51%	49%
1,1-DCA	53		43%	57%
DCE	38		51%	49%
Benzene	59		40%	60%
Toluene	182		18%	82%
Ethylbenzene	363		10%	90%
Xylene	386		9%	91%
TCE	166		19%	81%
Carbon Tetrachloride	174		19%	81%
1,2-Dichlorobenzene	617		6%	94%
Dieldrin	21,380		0%	100%
Note:	1. Assuming 1.5 g/cm^3 soil bulk density and effective pore volume of 0.15			

$$K_d = Koc * foc = \frac{Soil\ (\frac{g}{Kg})}{GW\ (\frac{g}{L})}$$

Longer Contact time: Low solubility contaminants

- Treatment time
  - Not just kinetics (PAHs/PCBs react very quickly with sulfate/hydroxyl radicals)
  - Time for entire mass to dissolve into aqueous phase
    - High Koc/low solubility
- Extended persistence allows for active oxidant to be present as contaminants slowly dissolve
  - Ex. Large PAHs, PCBs, and some pesticides
- Treatment time:
  - Contaminants treated within less than 8 weeks = treat with SP
  - Longer—treat with KP

PCB	**Day 56 PCB % Reduction**			
	Klozur® SP		Klozur® KP	
	Low	High	Low	High
Arochlor 1254	12%	26%	53%	53%

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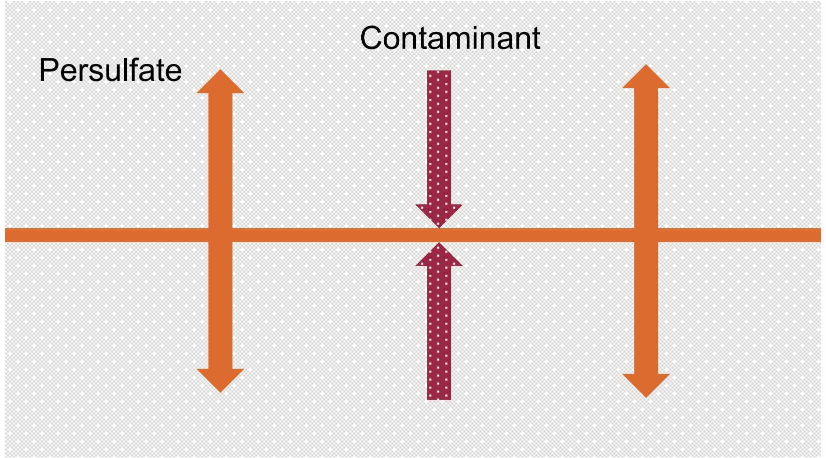
Longer Contact Time
Low Permeable Soils and Low Contaminant Concentrations

- Low permeable soils
  - Persulfate anion to diffuse into low permeable matrix
  - Contaminant to diffuse from low permeable matrix into active treatment zone

- Low contaminant concentrations
  - Time for diffusion of µg/L concentrations from matrix and reagent into matrix



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High Groundwater Velocities

- Is 2-4 months enough contact?

- Klozur® SP, which tends to persist 2-8 weeks, could flow out of target zone before completely reacted
  - 500 ft/yr is 42 ft/month or 10 ft/week

- As a solid, Klozur® KP would stay in treatment zone, slowly dissolving.

Conceptual Klozur® KP Persistence (months)							
Temp (◦C)			5	10	15	20	25
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Lessons Learned

- Monitoring
  - Have monitoring wells within the injection area/PRB
    - Monitor performance at the PRB
    - Monitor for the activity/persistence of the Klozur KP
  - Monitor for expected residuals (potassium, sodium, calcium, sulfate), residual persulfate, pH, conductivity, and ORP

- Site characterization
  - Groundwater flux is critical parameter (hydraulic conductive and groundwater gradient)
  - Effective/mobile porosity convert that to velocity

- Application
  - KP and HL being injected as high concentration solid slurries (50 to 70 percent by weight)
  - Care with fracture pressure and volumes applied per fracture to control distribution

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Summary

- Klozur® KP has same powerful chemistry as Klozur® SP
  - Persulfate anion
  - Oxidative and reductive pathways

- Klozur® KP has lower solubility that can allow more contact time in the subsurface
  - PRBs
  - Aqueous phase contaminants
  - Low solubility/high K_{oc} contaminants
  - Low permeable soils
  - Very high groundwater velocity sites

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Klozur® KP Slurry Injection via Hydraulic Fracturing

- Fracture Form and Hydraulic Fracturing Processes
- Distribution Mechanisms for Persulfate in Fractures
- Data Compiled from Six KP Projects in Five States
  - Reagent Loading and Field Productivity
  - Daylighting
  - Costs
- Klozur® KP Case Study – Industrial Site in New Mexico
- Q&A w/ Smith, Baird & Ross

Controlled Hydraulic Fracturing using KP

- Make a thick slurry
- Pump slurry into the formation
- Create a fracture in the formation
  - » Horizontal, sheetlike structure
  - » Solids-laden slurry simultaneously creates & fills fracture
- Monitor injections and record process data

Oxidant Distribution via Chemical Diffusion

K-Permanganate Frac

Oxidant Distribution via Chemical Diffusion

Klozur® KP Frac

Oxidant Distribution via Chemical Diffusion is Well Understood and Documented

Cavanagh, B.A., P.C. Johnson, and E.J. Daniels (2014), Reduction of Diffusive Contaminant Emissions from a Dissolved Source in a Lower Permeability Layer by Sodium Persulfate Treatment. *Environmental Science & Technology*, Vol 48

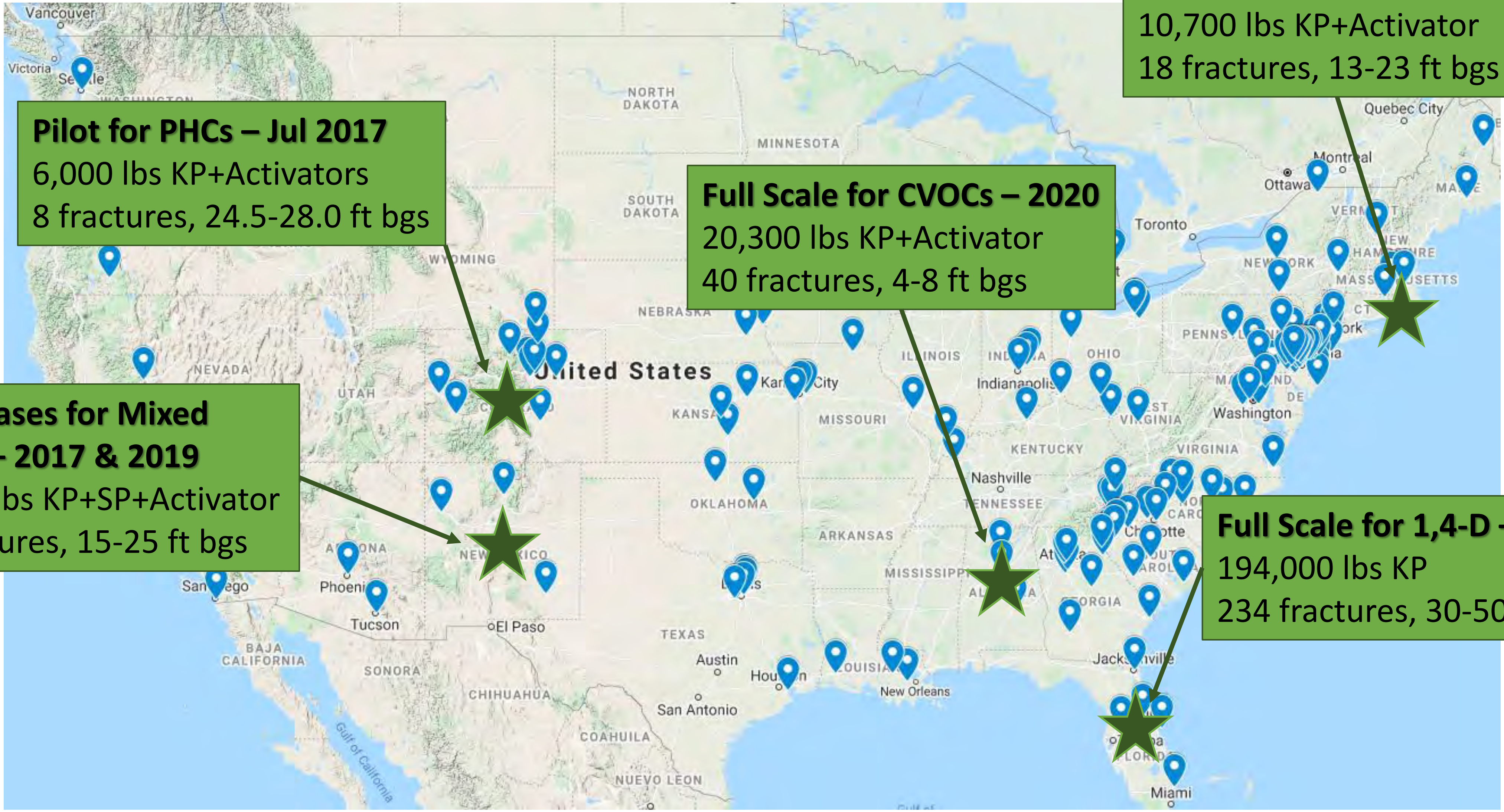
Hønning, J., M.M. Broholm, and P.L. Bjerg (2007), Role of Diffusion in Chemical Oxidation of PCE in a Dual Permeability System. *Environmental Science & Technology*, Vol 41, Issue 24

Johnson, R.L., P.G. Tratnyek, and R.O. Johnson (2008), Persulfate Persistence under Thermal Activation Conditions. *Environmental Science & Technology*, Vol 42, Issue 24

Siegrist, R. L., K.S. Lowe, L.C. Murdoch, T.L. Case and D.A. Pickering (1999), Oxidization By Fracture Emplaced Reactive Solids. *Journal of Environmental Engineering*, Vol 125, Issue 5

Struse, A.M., R.L. Siegrist, H.E. Dawson and M.A. Urynowicz (2002), Diffusive Transport of Permanganate during In Situ Oxidation. *Journal of Environmental Engineering*, Vol 128, Issue 4

Klozur® KP Injection Projects



Full Scale for CVOCs – 2021
10,700 lbs KP+Activator
18 fractures, 13-23 ft bgs

Pilot for PHCs – Jul 2017
6,000 lbs KP+Activators
8 fractures, 24.5-28.0 ft bgs

Full Scale for CVOCs – 2020
20,300 lbs KP+Activator
40 fractures, 4-8 ft bgs

Two Phases for Mixed Plume – 2017 & 2019
39,700 lbs KP+SP+Activator
71 fractures, 15-25 ft bgs

Full Scale for 1,4-D – 2019
194,000 lbs KP
234 fractures, 30-50 ft bgs

Reagent Loading & Field Productivity

Project	KP ± SP & Activators Dosing Range (by dry wt soil)	Pounds/Fracture (average)	Pounds/Day (average)
Colorado 2017	N/A	750	3,000
New Mexico 2017	See 'NM 2019' below	460	5,500
Florida 2019	0.19%	830	5,100
New Mexico 2019	0.21% (combined)	610	5,800
Alabama 2020	0.30%	500	3,400
New England 2021	0.72%	600	5,900

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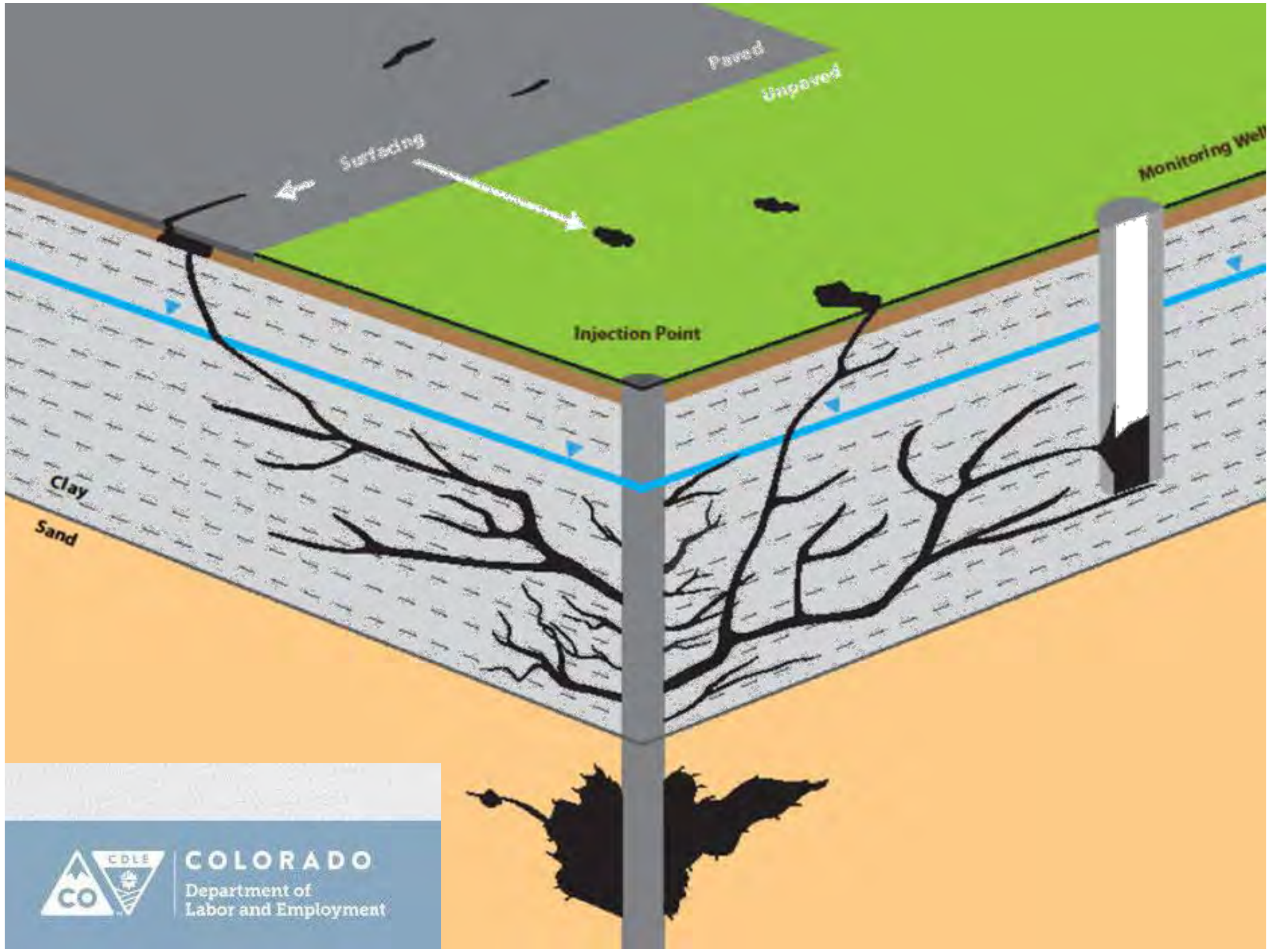
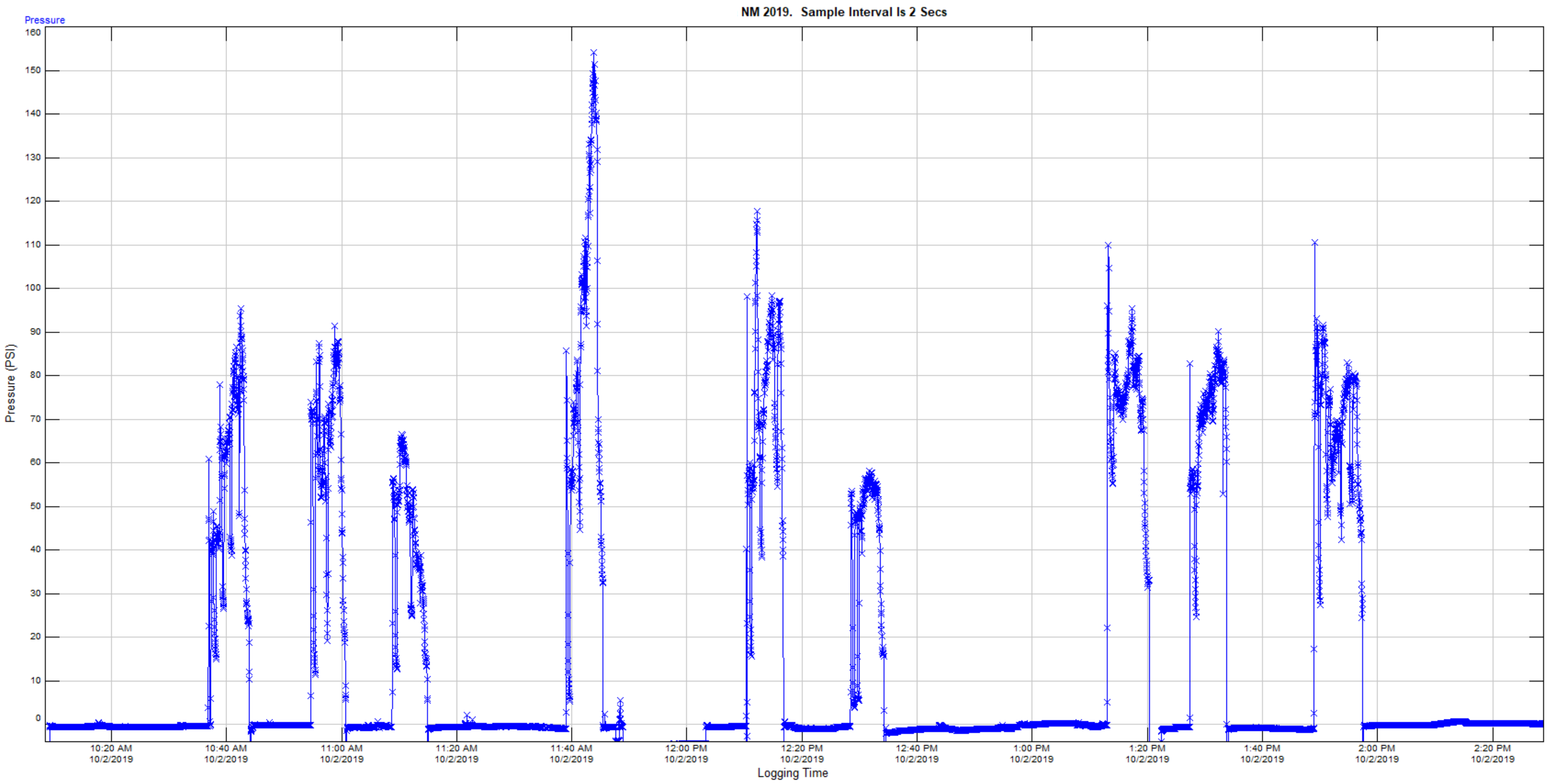
Daylighting is a Common Problem

Often a BIG One



- Indicative of steeply dipping fractures
- Multiple causes, commonly manmade
- Excessive amounts can kill an injection project
- Can be minimized and possibly eliminated

Daylighting can be Minimized or Eliminated



Daylighting at Klozur® KP Projects

Project	Injection Interval (ft bgs)	Daylighting Observations	Fracs Attempted	Daylighting Rate
Florida 2019	25-59	1	234	< 1%
New Mexico 2017 & 2019	15-25	5	71	7%
Alabama 2020	4-8	5	40	13%
New England 2021	13-23	0	18	0%
Total		**11**	**363**	**5%**

Example Klozur® KP Project Costs

Drilling, KP ± Activators, Fracturing

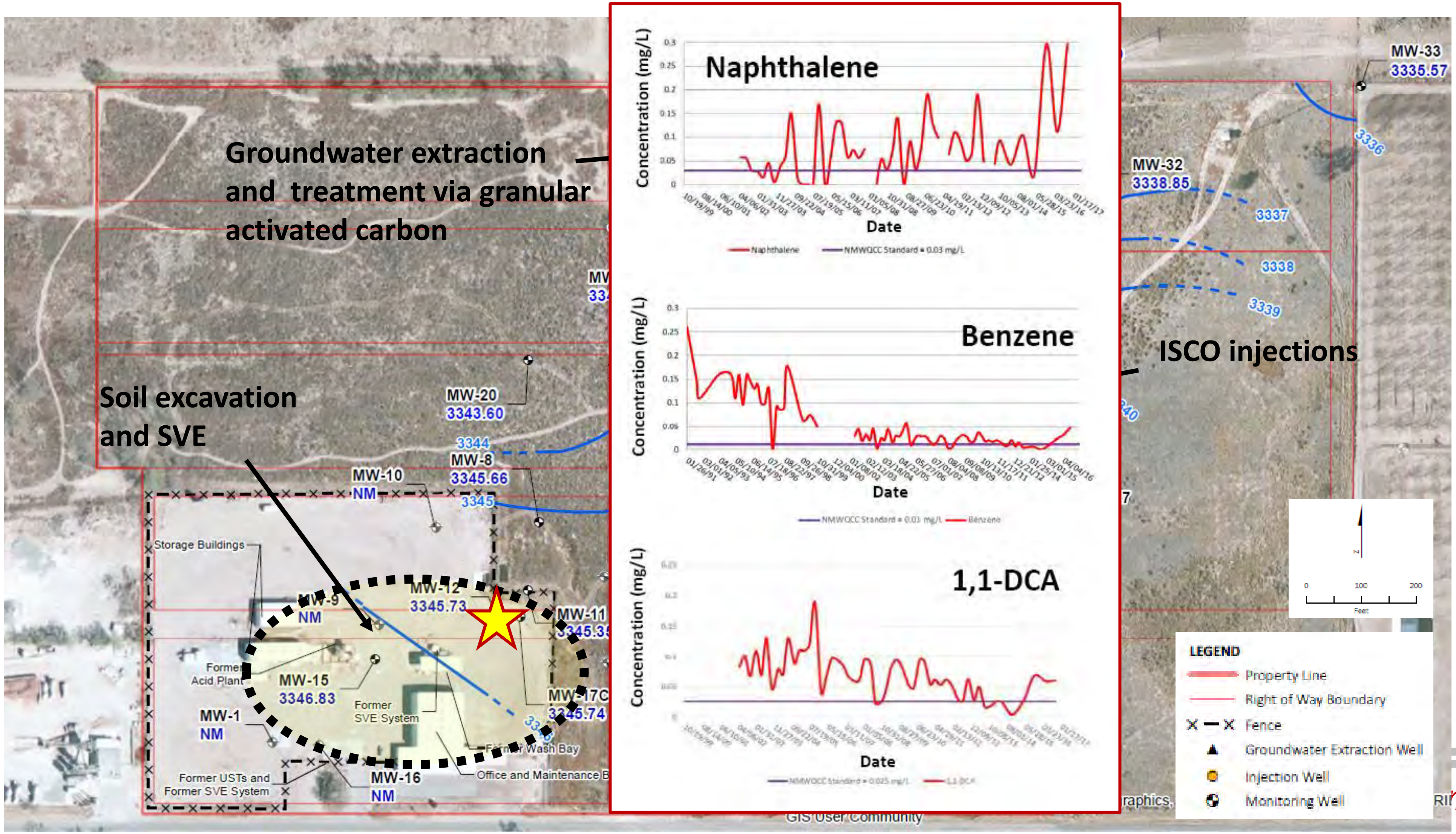
Project	Amendments	Amendment Mass (lbs)	Treatment Area (square feet)	Treatment Unit Cost ($/cy)
New Mexico 2017 & 2019	Klozur® KP Klozur® SP Fe-EDTA	39,700	12,500	$84
Alabama 2020	Klozur® KP Hydrated Lime	20,300	15,300	$54
Florida 2019	Klozur® KP	194,000	47,500	$55
New England 2021	Klozur® KP Hydrated Lime	10,700	1,350	$222

Klozur® KP Case Study

Industrial Site in New Mexico

- Former industrial service facility
- Alluvial overbank deposits: Silt and silty clay with clay layers and lenses of carbonate rubble
- Primary CoCs: naphthalene, benzene, and 1,1-DCA
- Source and plume remediation approach over time based on varied CoCs, hydrogeology, and property boundary

Treatment of Residual Source Zone



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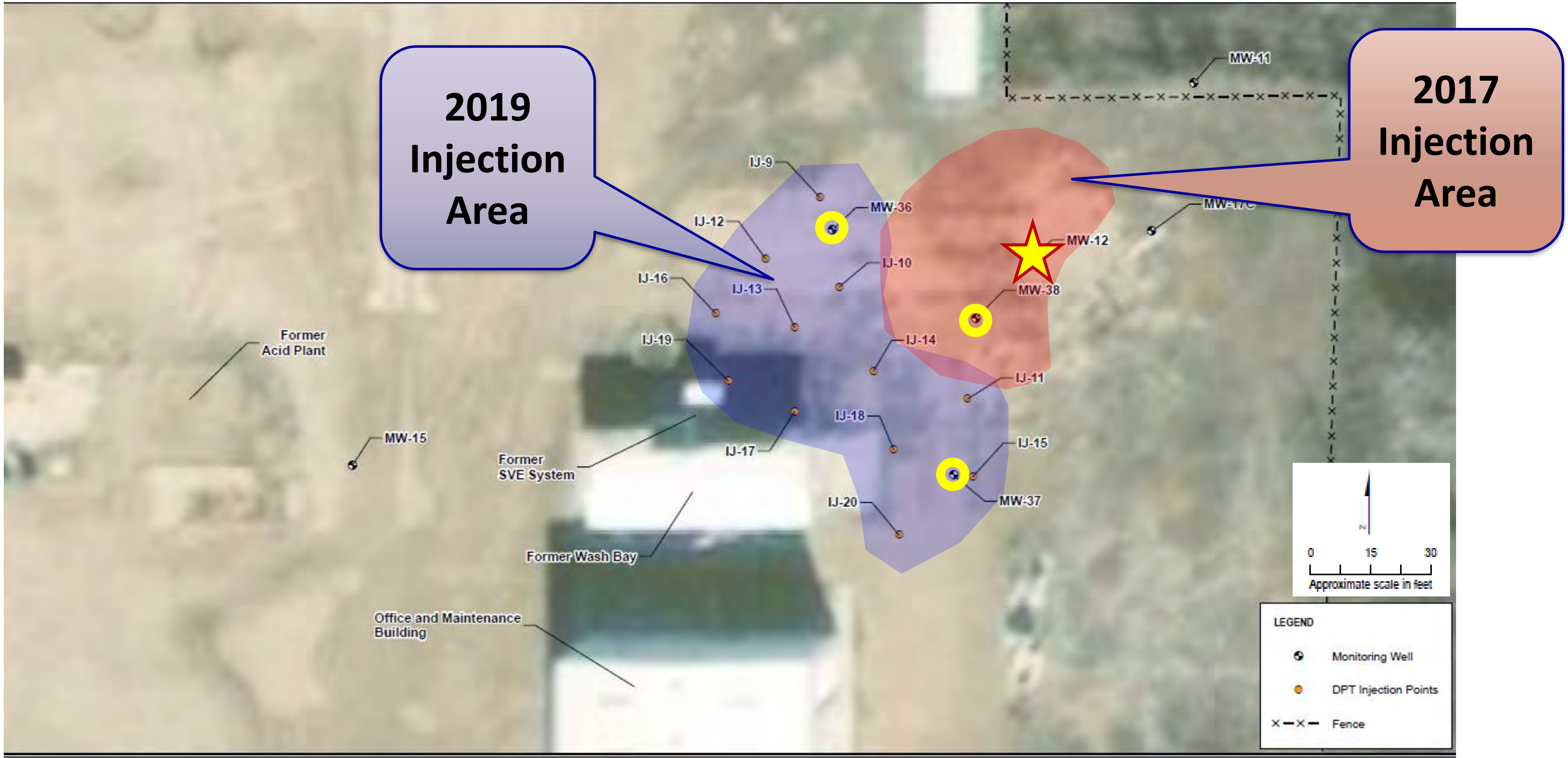
Remedial Goal, Approach, and Additional Considerations

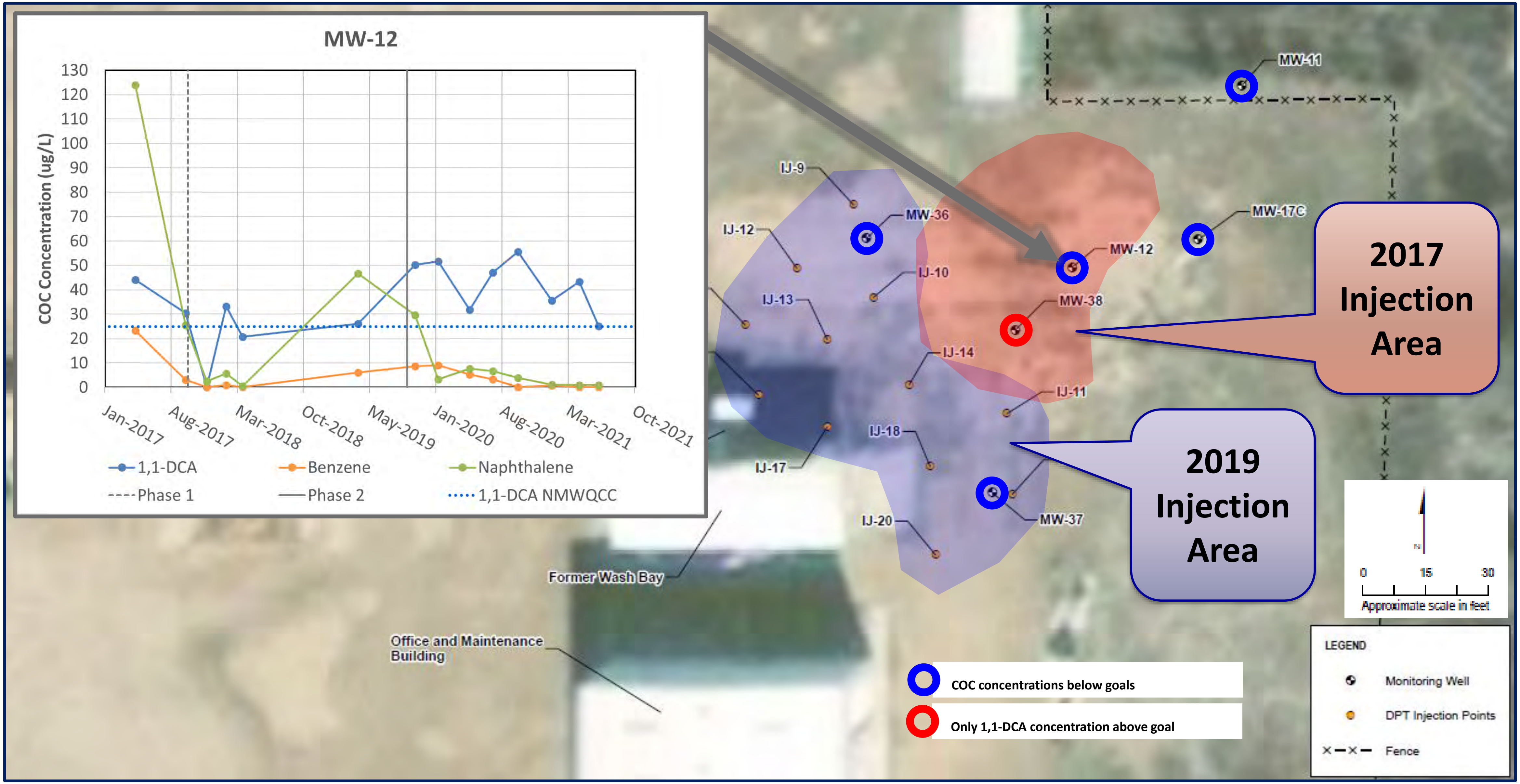
- Goal: Obtain NFA without long-term monitoring
- Approach
  - Phased ISCO for treatment of residual source
  - Hydraulic control of far downgradient plume
  - Source polishing of 1,1-DCA with enhanced dichlorination
- Decision Points and Tasks
  - Remedial design investigation to characterize source
  - Treatability testing for optimal activation
  - Execute Phase 1 injections and Phase 2, if necessary

Treatment Areas & Performance MWs



In-Situ Access to Contaminants

Treatment Areas & Results



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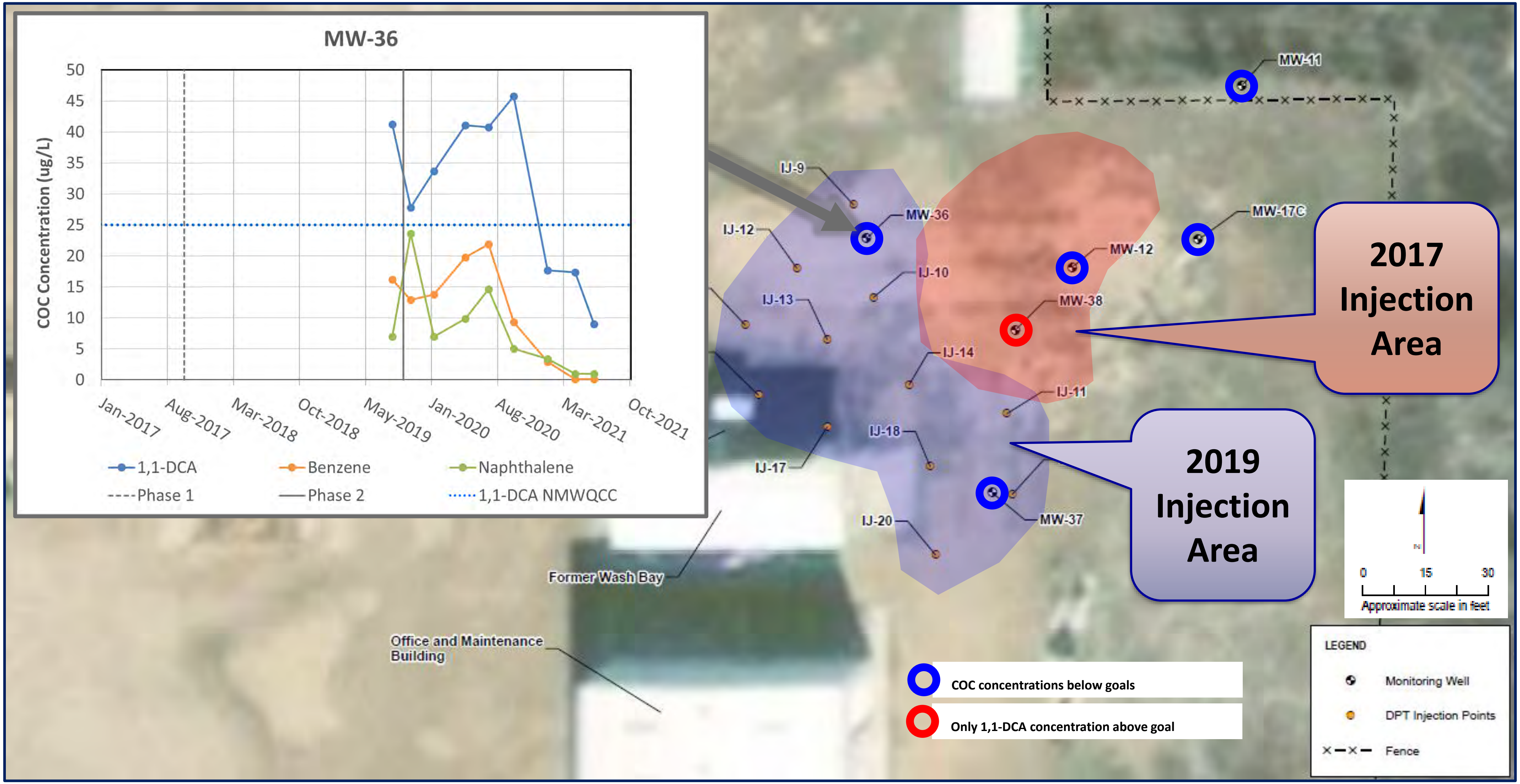

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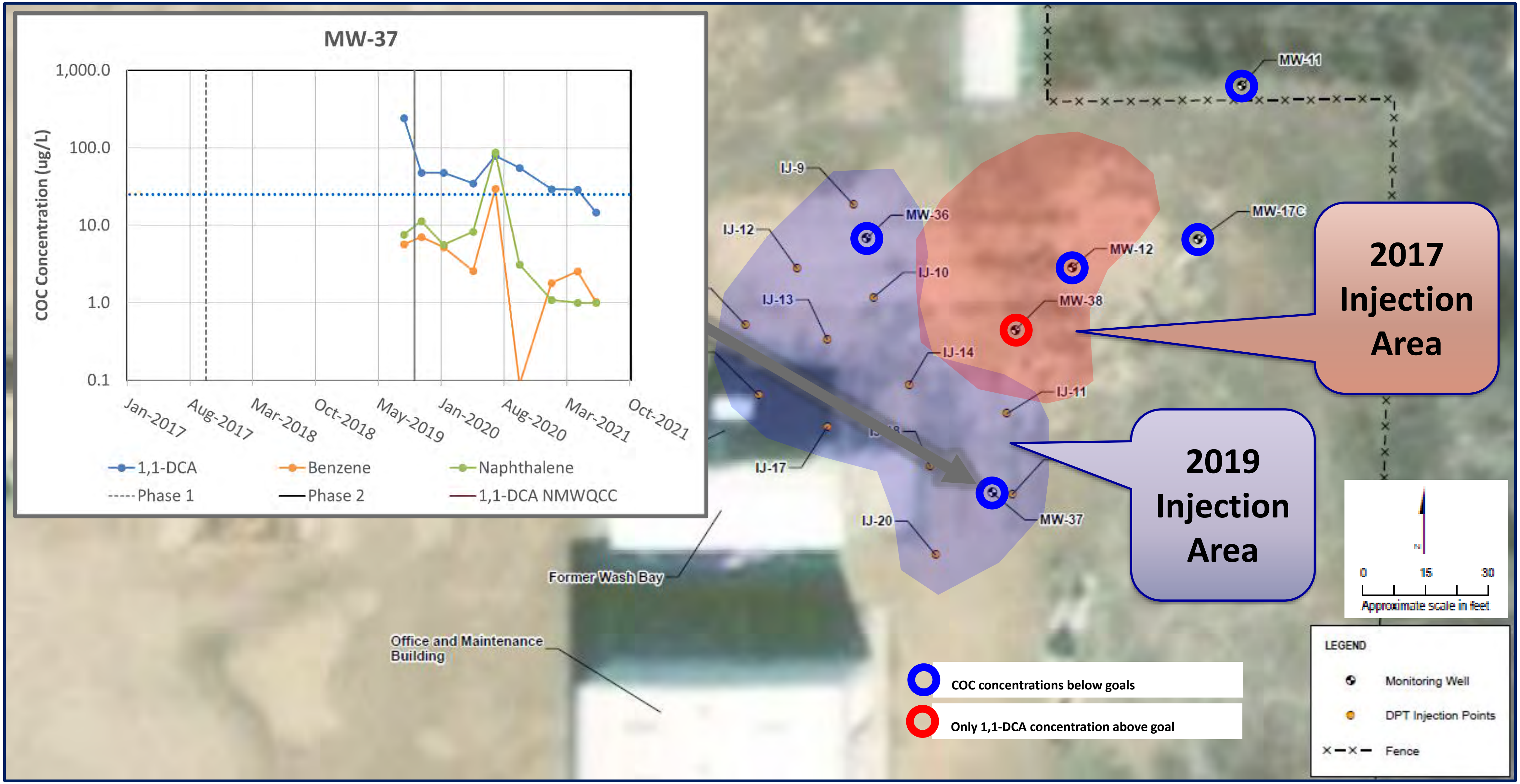

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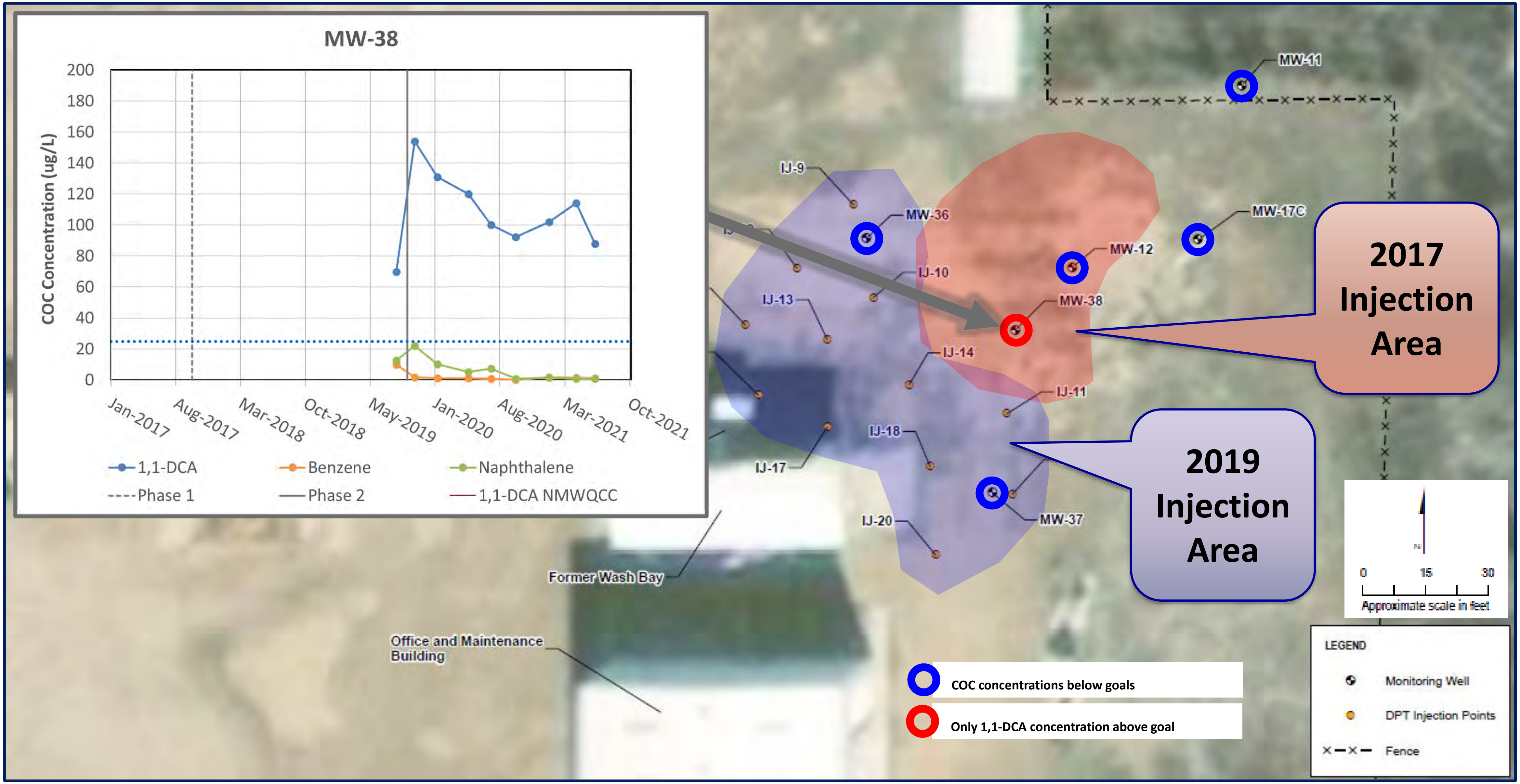

Klozur® KP via Hydraulic Fracturing

Conclusions

- Several case studies show the versatility, successful application, and treatment capabilities of Klozur® KP.
- Oxidant distribution via chemical diffusion is well-understood.
- Good fracture form is paramount. It can be attained with understanding of principles and application of proper techniques.
- Daylighting can be minimized or possibly eliminated.
- High-dose delivery of activated KP in low-k units is well-established.
- Treatment using this approach is cost effective. Total project costs are typically less than $85 per cubic yard.

Questions?

Drew Baird, PG
Senior Geologist
FRx, Inc
dbaird@frx-inc.com

Chapman Ross, PE
Director of Technology
FRx, Inc
cross@frx-inc.com

Brant Smith, PhD, PE
Director of Technology
Evonik Active Oxygens, LLC
brant.smith@evonik.com
remediation@evonik.com

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