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Injection of Potassium Persulfate via Hydraulic Fracturing to Address a Recalcitrant Fuel-Related and Chlorinated VOC Plume

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Mike Perlmutter, PE (mike.perlmutter@ch2m.com) (Atlanta, GA, USA)
Aleeca Forsberg, PG (Albuquerque, NM, USA)

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Presentation Outline

- Site background
- Remediation progress
- Volatile organic compound (VOC) recalcitrance at MW-12
- Remediation strategy
- Natural oxidant demand (NOD) treatability testing on site soil and groundwater
- Field application
- Results
- Summary and conclusion
- Subcontractors and costs

Site Background

- Former oilfield service facility in the western United States
- Fuel-related VOC impacts to site soil and groundwater were discovered during underground storage tank (UST) removal activities in late 1980s
  - Contaminants of concern include benzene, naphthalene, tetrachloroethene (PCE), 1,1-dichloroethene (DCE), and 1,1-dichloroethane (DCA)
  - Historically, maximum total VOCs up to 1 milligram per liter (mg/L)
- Hydrogeology
  - Silt and silty clay interbedded with clay layers and 0.5 to 1.5-foot thick stringers of cream colored gypsum/carbonate rubble, which constitute the primary water-bearing zones.
  - Groundwater level is approximately 11 to 14 feet below ground surface (under confined conditions)
  - Groundwater flow is to the northeast at approximately 1,000 feet per year

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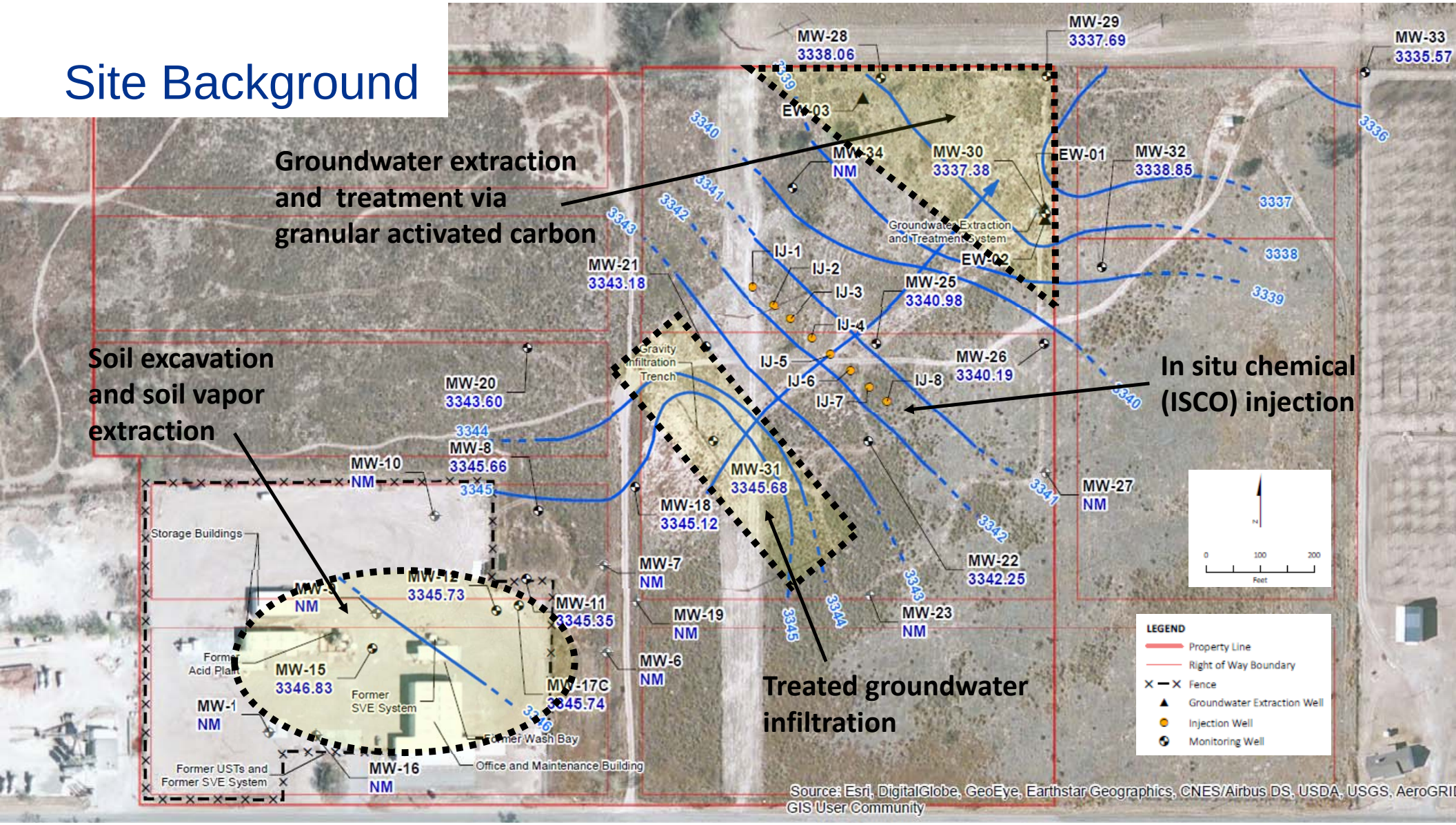
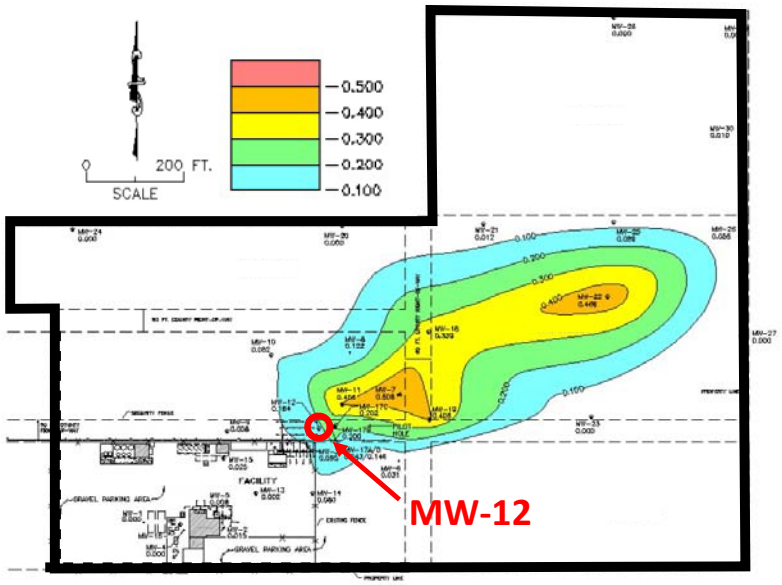
Site Background



Remediation Progress

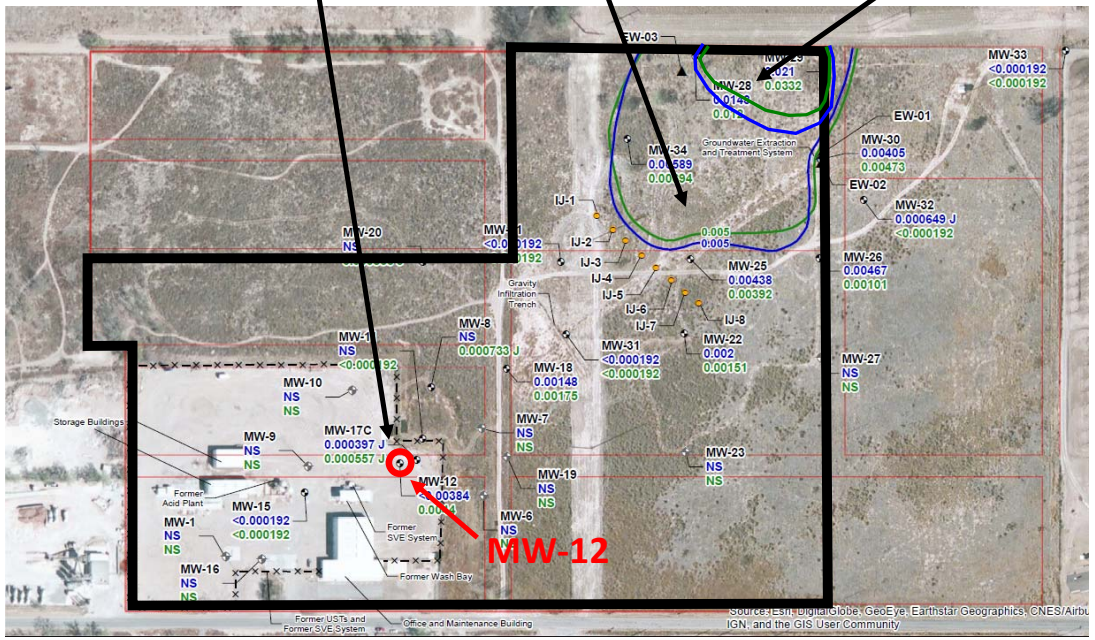


- **October 2000 Results (total VOC concentrations in mg/L)**

Benzene (0.0485)
Naphthalene (0.296)
1,1-DCA (0.0595)

1,1-DCE (maximum = 0.0332)

PCE (maximum = 0.0238)



- **October 2016 Results (individual VOC concentrations in mg/L)**

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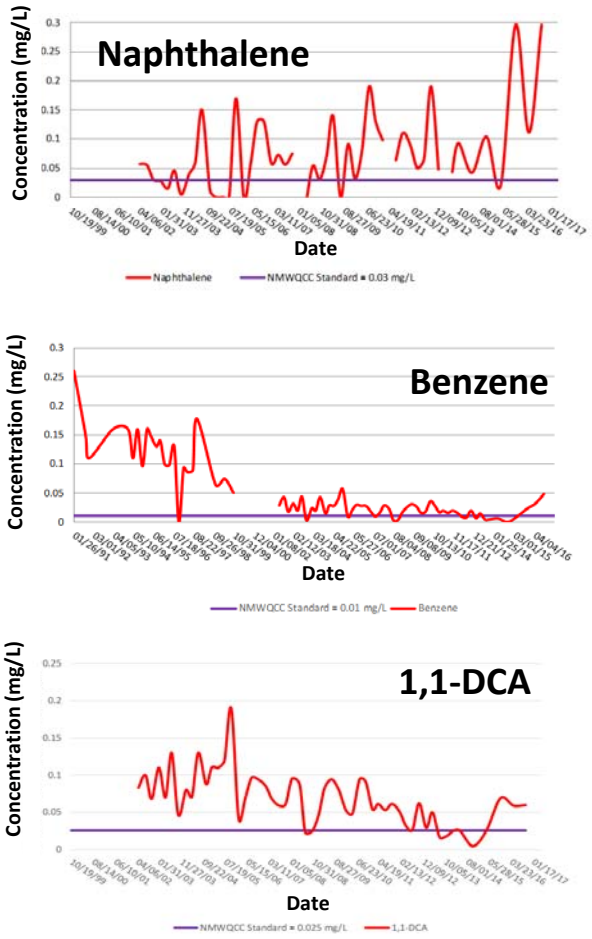
VOC Recalcitrance at MW-12



- Conducted soil and groundwater investigation
  - Photoionization detector (PID) readings in clay layer between 15 and 25 feet bgs were multiple orders-of-magnitude higher than more permeable zones
    - Suggests back-diffusion sustaining low concentration plume in source area (despite effectiveness of previous remedies in addressing the source area)

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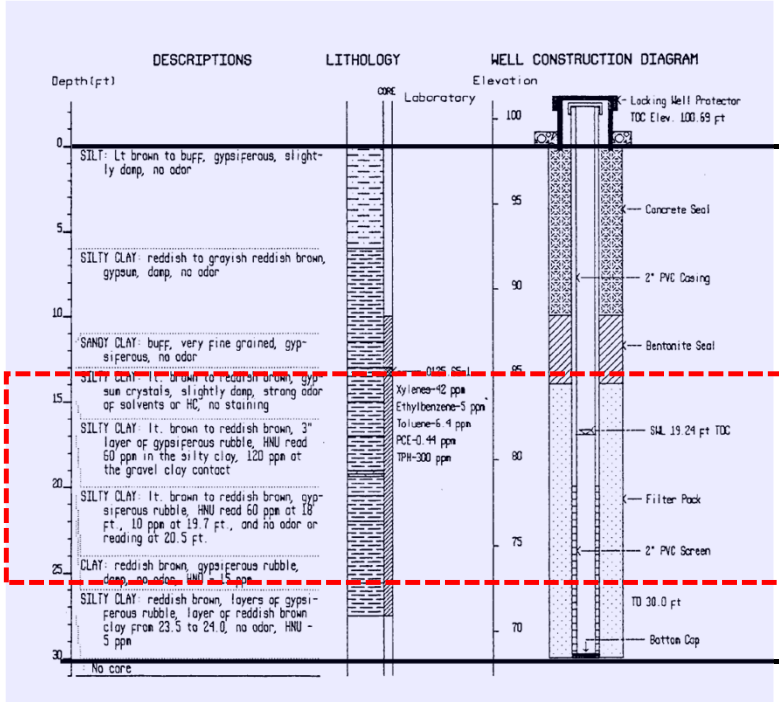
VOC Recalcitrance at MW-12



DEPTH BELOW SURFACE (ft)	SAMPLE INTERVAL (ft)	RECOVERY (ft)	#/TYPE	USCS CODE	SOIL DESCRIPTION: SOIL NAME, USCS GROUP SYMBOL, COLOR, MOISTURE CONTENT, RELATIVE DENSITY, OR CONSISTENCY, SOIL STRUCTURE, MINERALOGY	COMMENTS: Notes/Comments	PID Results (ppm)
5	2 - 3	0 - 5		ML	SILT, (ML), 10YR 8/4 & 10YR 8/3, Dry, Soft, Non-Plastic, Non-cohesive, Trace Caliche Rubble	No Staining, No Odor	3.1
	5 - 6						2.7
10		9 - 10		ML	SILT, (ML), 10YR 7/3, Dry, Soft, Non-Plastic, Non-cohesive, Trace Caliche Rubble	No Staining, No Odor	6.7
		13 - 15		CL	LEAN CLAY WITH SAND, (CL), Stringers of Caliche Rubble with Sand, 7.5YR 4/4, 7.5YR 5/2, Dry to Moist, Soft to Medium Density, Low to Medium Plasticity, Cohesive	No Staining, No Odor	4.2 3.5
15						trong Petroleum Odor, Staining	149
	16 - 17	16 - 20		CH	FAT CLAY, (CH), Stringers of Caliche Rubble with Sand 2 - 6 inches Thick, 7.5YR 5/2, 10YR 5/2, Moist, Medium to High Density, Medium to High Plasticity, Cohesive	Strong Petroleum Odor, Dark Black Staining	1884
	18 - 19						1704
20	20 - 21						1180
		20- 25		CH	FAT CLAY, (CH), Stringers of Caliche Rubble with Sand 2 - 6 inches Thick, 10YR 5/2, Moist to Wet, Medium to High Density, Medium to High Plasticity, Cohesive	No Staining, No Odor	16.5 5.8
25							6.3
	25 - 30	25 - 30		CH	FAT CLAY, (CH), Stringers of Caliche Rubble with Sand 2 - 6 inches Thick, 10YR 6/3, Moist to Wet, Medium to High Density, Medium to High Plasticity, Cohesive	No Staining, No Odor	6.7 8.1
30							5.0

- MW-12 Boring Log and Well Construction Diagram (1991)
- SB-09 Boring Log (2014) (next to MW-12)

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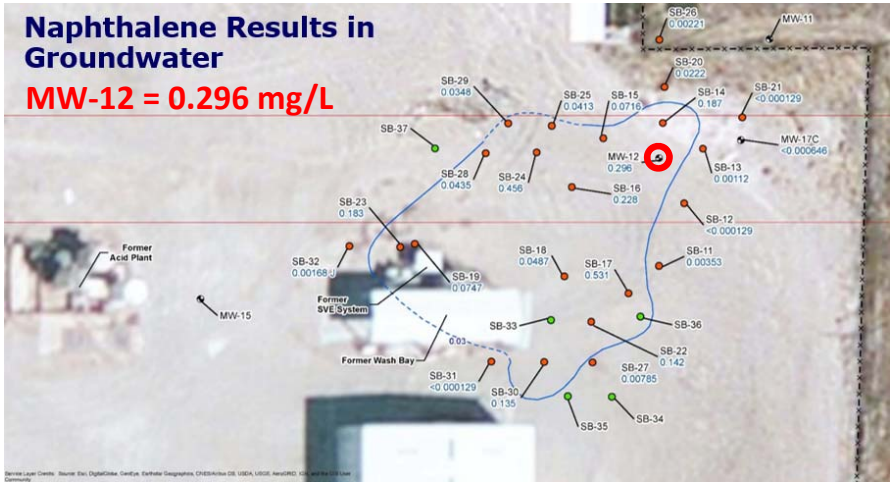
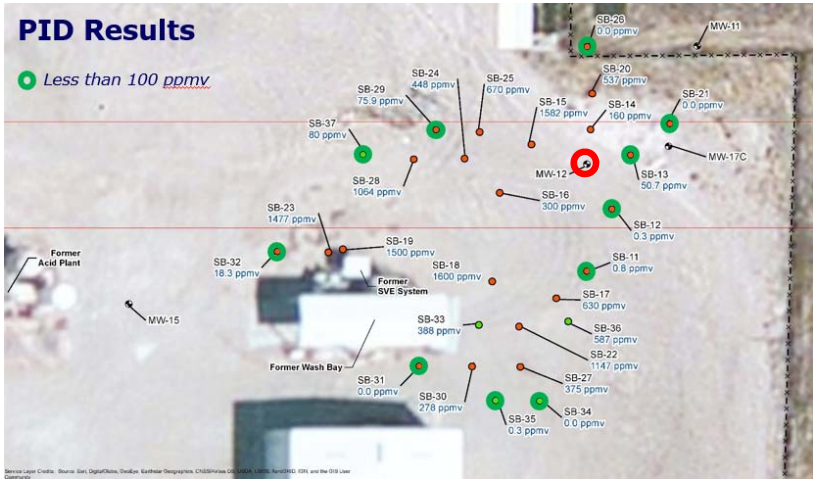
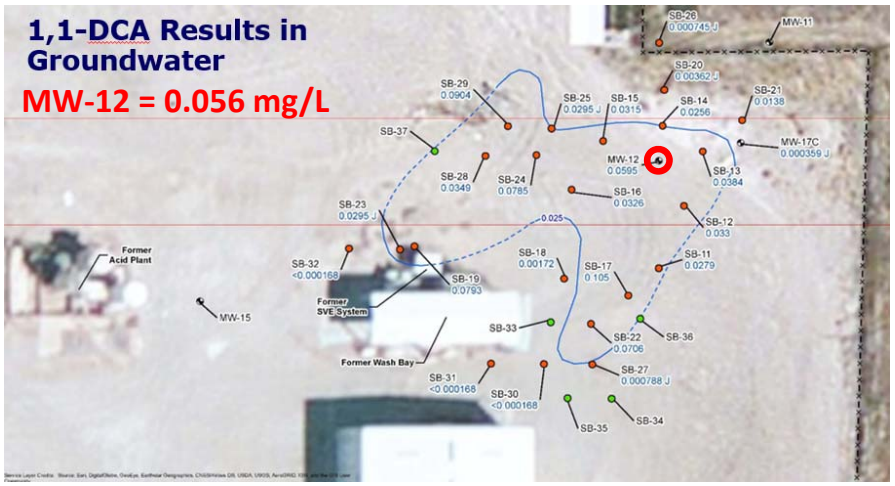
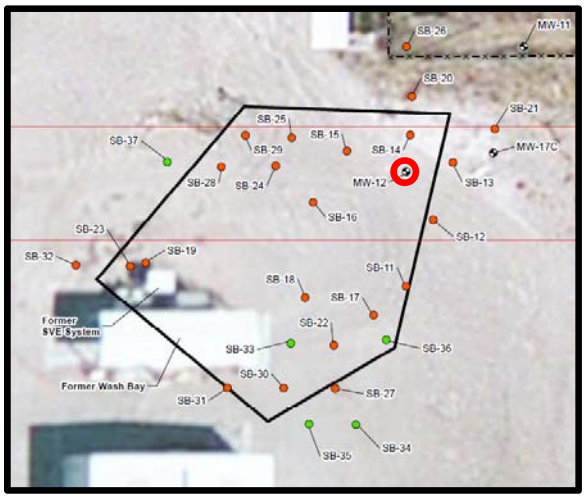
Investigation Outcome









- Groundwater plume delineated around MW-12
- Established target treatment zone around MW-12 to complete source remediation

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Remediation Strategy

- Goal is to obtain No Further Action (NFA) without long term monitoring
  - VOC concentrations in groundwater must be below respective state clean-up standards for eight consecutive quarters
- MW-12 area
  - **Status:** VOC concentrations are stable and above standards
  - **Strategy:** Use **ISCO** to address residual chlorinated ethene, chlorinated ethane, and petroleum hydrocarbon plume
- Downgradient plume
  - **Status:** Long-term VOC concentration trends are downward
  - **Strategy:** Optimize and continue operation of downgradient P&T and re-infiltration system

Why consider ISCO for MW-12?

- In situ thermal treatment and excavation not cost effective and too disruptive
- Air sparging ineffective in fine-grained materials
- Enhanced reductive dechlorination ineffective for petroleum compounds
- Could be paired with other technologies for polishing

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NOD Testing on Site Soil and Groundwater

- Sodium persulfate (SP) activation methods
  - Feasible
    - Iron-activated
    - Natural mineral activation (NMA)
  - Not feasible
    - Base – high demand and a clogging concern due to the carbonates in the formation
    - Peroxide – strong reaction with the natural iron the formation
    - Heat – not considered cost-effective
- Results
  - SP dose ~2 grams per kilogram (g/kg)
  - Both NMA and iron-activation tests treated the VOCs except for 1,1-DCA (max concentration = 100 µg/L), which does not respond to the iron-activation approach
    - Residual iron will support 1,1-DCA reduction
    - As necessary, a supplemental carbon substrate can be injected to further promote 1,1-DCA reduction and/or reduce any residual sulfate from the persulfate

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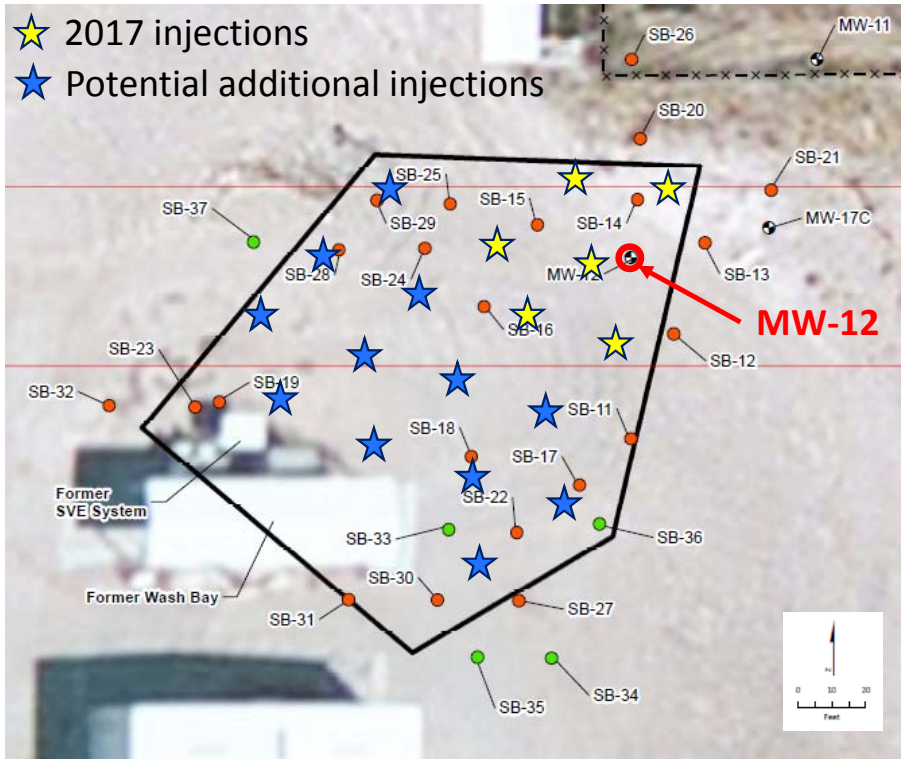
Field Approach – Injection Locations and Delivery

- Hydraulically fracture and inject a mix of reagents into the low permeability clay interval within the target treatment area
- Six injection locations completed in 2017 as pilot-scale study
  - More may be added pending pilot-scale sampling results
- Reagents injected via four fractures in boreholes advanced via a direct push technology (DPT) rig
  - **Treatment depth:** 15 to 25 feet bgs
  - **Injection spacing:** 20-foot centers
  - **Fracture intervals:** 15, 18, 21, and 24 feet bgs



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Field Approach - Reagents

Material	Basis/Purpose	Average per Fracture
Sodium persulfate (Klozur SP)	Kick-starts the oxidation process	75 pounds
Potassium persulfate (Klozur KP)	Less reactive but lasts longer than the Klozur SP; best for addressing the VOCs as they diffuse/desorb from the clay	375 pounds
Chelated iron (Dissolvine)	Activated the persulfate and provide residual iron to support 1,1-DCA reduction	2.3 pounds
Carrier fluid (bentonite powder and water)	Support fracture propagation and reagent distribution	40 gallons
Chase water	Prevent system clogging	30 gallons

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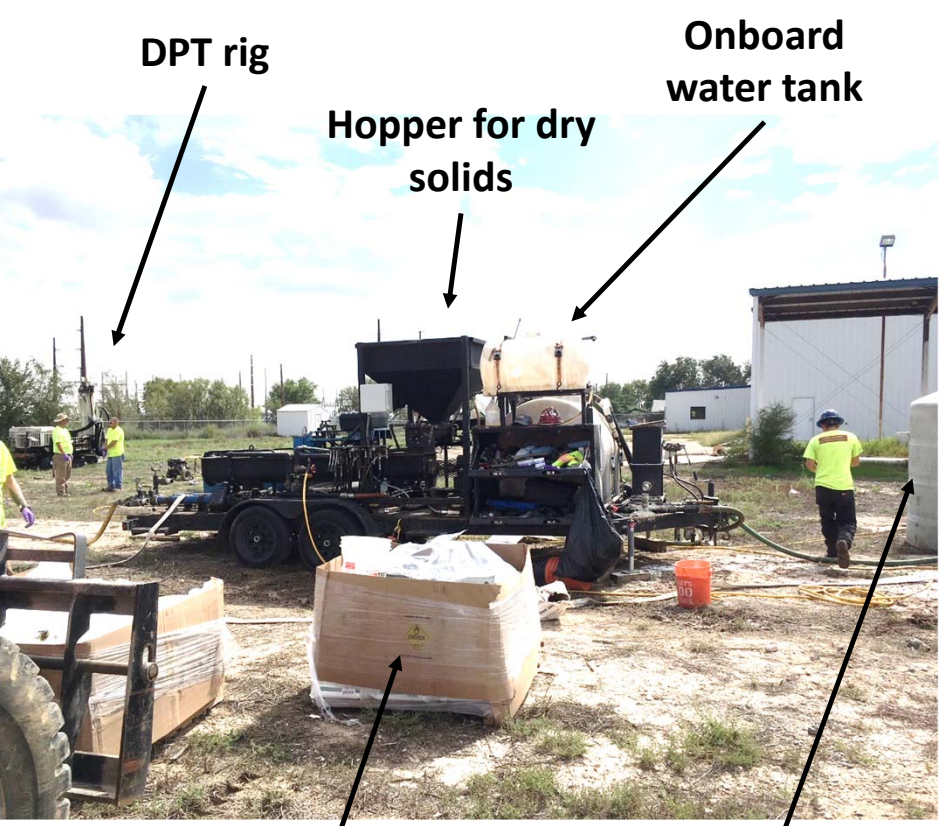
Field Approach - Photographs



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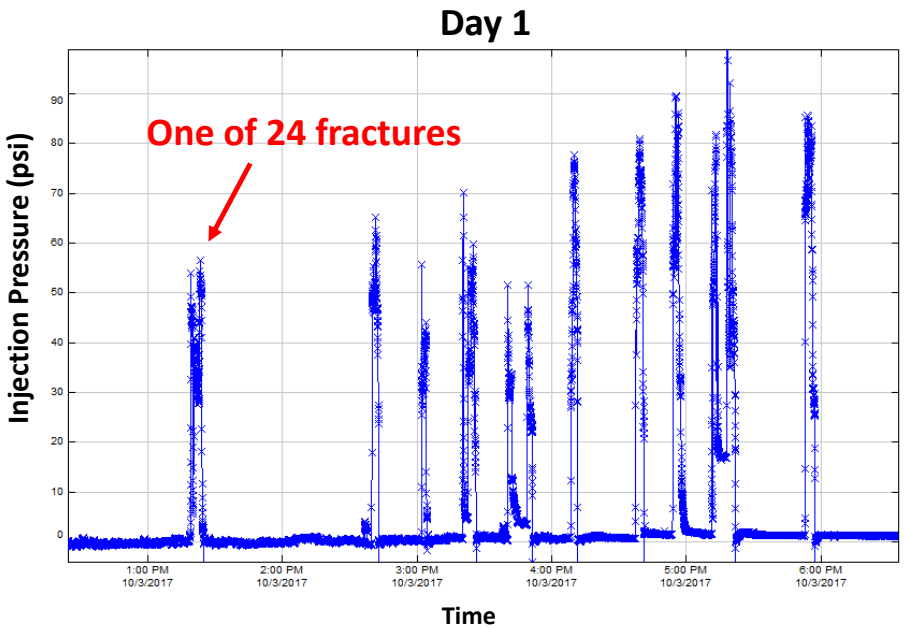
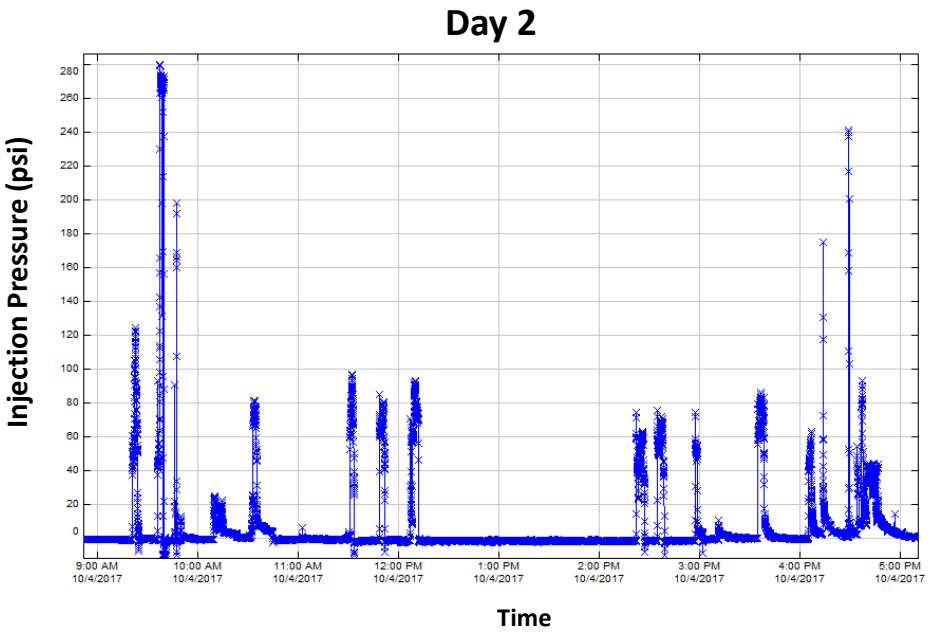
Field Approach – Fracture and Injection Statistics





- Fracture and injection durations: ~5 to 7 minutes
- Fracture pressure: typically 50 to 100 pounds per square inch (psi) with a maximum of 280 psi
- Average injection rate: 15 gallons per minute (gpm)
- Groundwater geochemistry in monitoring wells used to assess influence of injections

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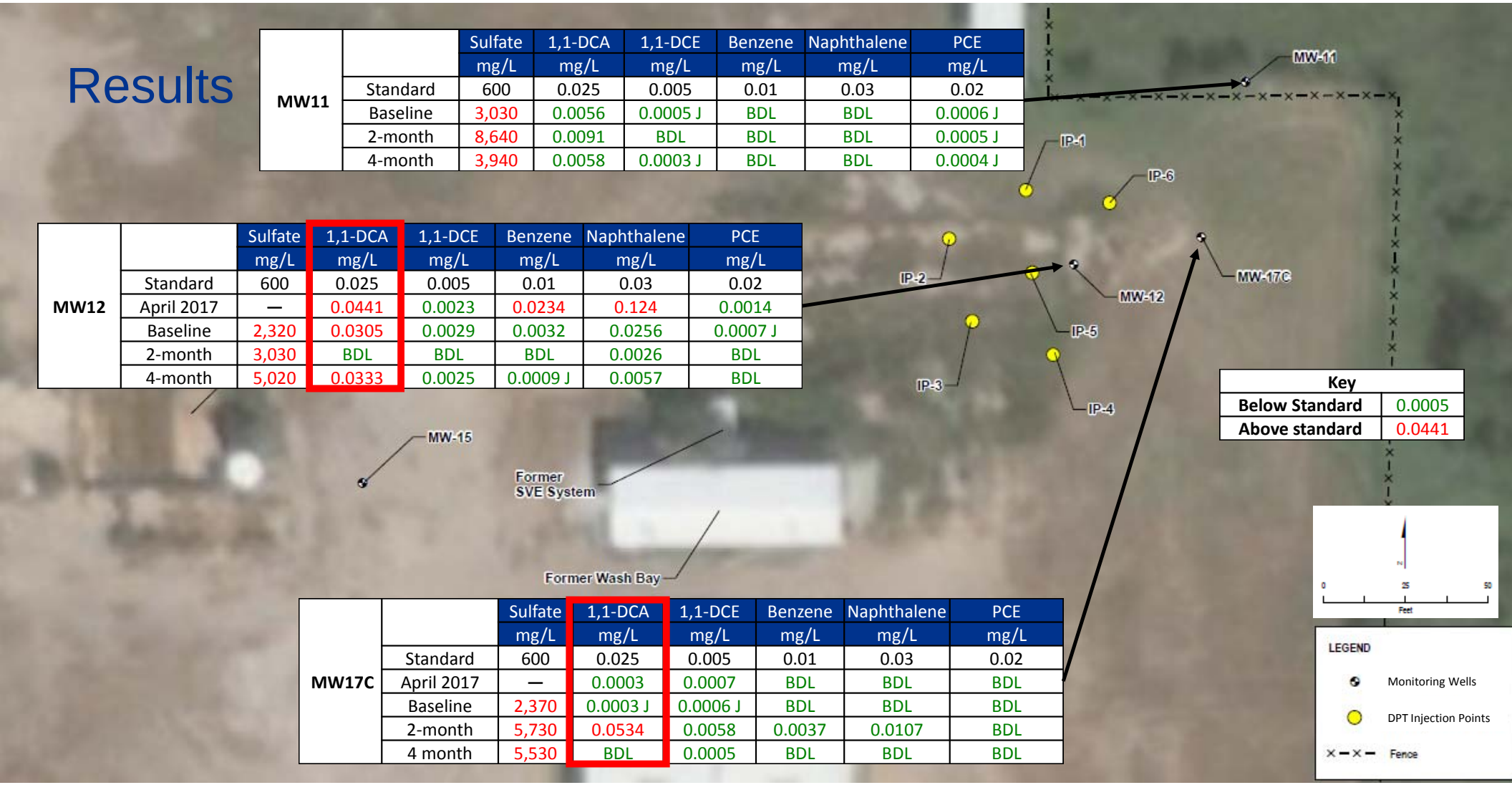
Results

MW11		Sulfate	1,1-DCA	1,1-DCE	Benzene	Naphthalene	PCE
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	Standard	600	0.025	0.005	0.01	0.03	0.02
	Baseline	3,030	0.0056	0.0005 J	BDL	BDL	0.0006 J
	2-month	8,640	0.0091	BDL	BDL	BDL	0.0005 J
	4-month	3,940	0.0058	0.0003 J	BDL	BDL	0.0004 J

MW12		Sulfate	1,1-DCA	1,1-DCE	Benzene	Naphthalene	PCE
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	Standard	600	0.025	0.005	0.01	0.03	0.02
	April 2017	—	0.0441	0.0023	0.0234	0.124	0.0014
	Baseline	2,320	0.0305	0.0029	0.0032	0.0256	0.0007 J
	2-month	3,030	BDL	BDL	BDL	0.0026	BDL
	4-month	5,020	0.0333	0.0025	0.0009 J	0.0057	BDL

MW17C		Sulfate	1,1-DCA	1,1-DCE	Benzene	Naphthalene	PCE
		mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
	Standard	600	0.025	0.005	0.01	0.03	0.02
	April 2017	—	0.0003	0.0007	BDL	BDL	BDL
	Baseline	2,370	0.0003 J	0.0006 J	BDL	BDL	BDL
	2-month	5,730	0.0534	0.0058	0.0037	0.0107	BDL
	4 month	5,530	BDL	0.0005	BDL	BDL	BDL



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Summary and Conclusions

- Delivery was relatively fast (2 days to do 24 fractures)
- Sulfate increases within and downgradient of injection area indicate persulfate influence
- VOCs after two months
  - No exceedances at MW-12
  - 1,1-DCA increased at downgradient monitoring well (MW-17C) likely due to it position just downgradient of the high-pressure ISCO application
- VOCs after four months
  - Only 1,1-DCA exceeded its goal at MW-12
  - No exceedances at MW-17C
- Pending further sampling results
  - Additional injections to expand treatment area
  - Necessity of carbon substrate supplement to address sulfate and 1,1-DCA

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Subcontractors and Costs

- Subcontractors
  - Ground Penetrating Radar Systems, LLC (utility surveying)
  - Earth Worx Environmental Services, LLC and Talon/LPE (DPT – investigation)
  - PeroxyChem (oxidants)
  - Drilling Engineers, Inc. (DPT - injections)
  - FRx (hydraulic fracturing)
- Costs
  - Hydraulic fracturing = $80,000
  - Reagents = $25,000
  - Oversight = $5,000
  - **TOTAL** = $110,000 or about $20,000 per boring or $2,000 per vertical foot

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Thank you!

Mike Perlmutter, PE

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