Sulfate-Enhanced Bioremediation of Petroleum Sites in Alaska

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Galena Site Summary

- Located in Alaska interior on Yukon River
- Former USAF Forward Operating Location
  - Base closed in 2008 – USAF responsible for cleanup
  - Currently home to a high school (boarding school) and airport
- Remote!
  - Accessible only by barge or air
  - No hotels, rental car agencies, restaurants; limited local support
  - Electric power generated on-site from fuel barged in each summer

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Galena Hydrology and Weather

- Aquifer consists of river deposits
  - ~ 0-5’ bgs – fill material
  - ~ 5’-15’ bgs – silt layer
  - >15’ bgs – gravels and sands, more gravel with depth
- Groundwater
  - Flows toward the river for most of the year
  - Flow reverses direction in spring when ice breaks on river
  - 20+ foot water table fluctuation
- Short field season (April – September)

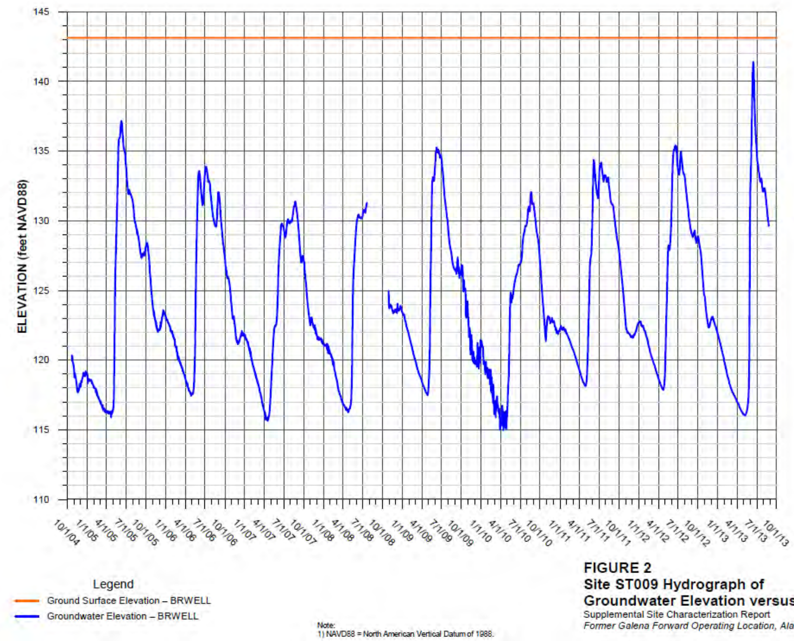

FIGURE 2
Site ST009 Hydrograph of Groundwater Elevation versus Time
Supplemental Site Characterization Report
Former Galena Forward Operating Location, Alaska

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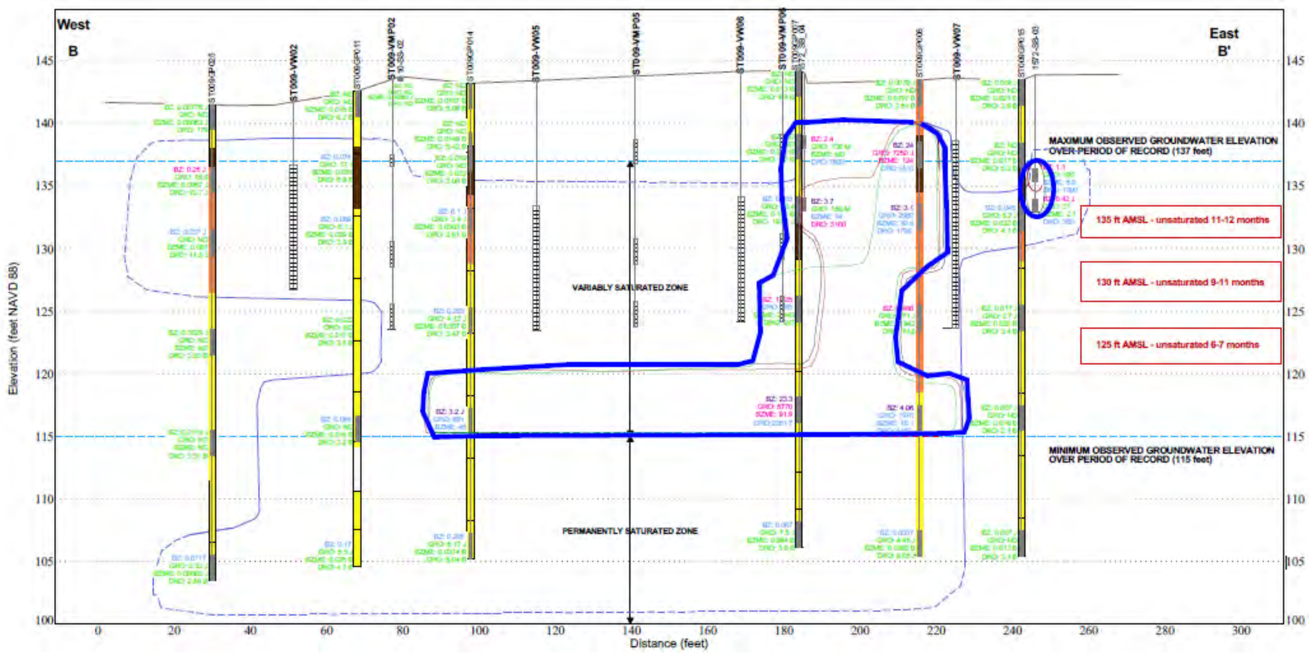
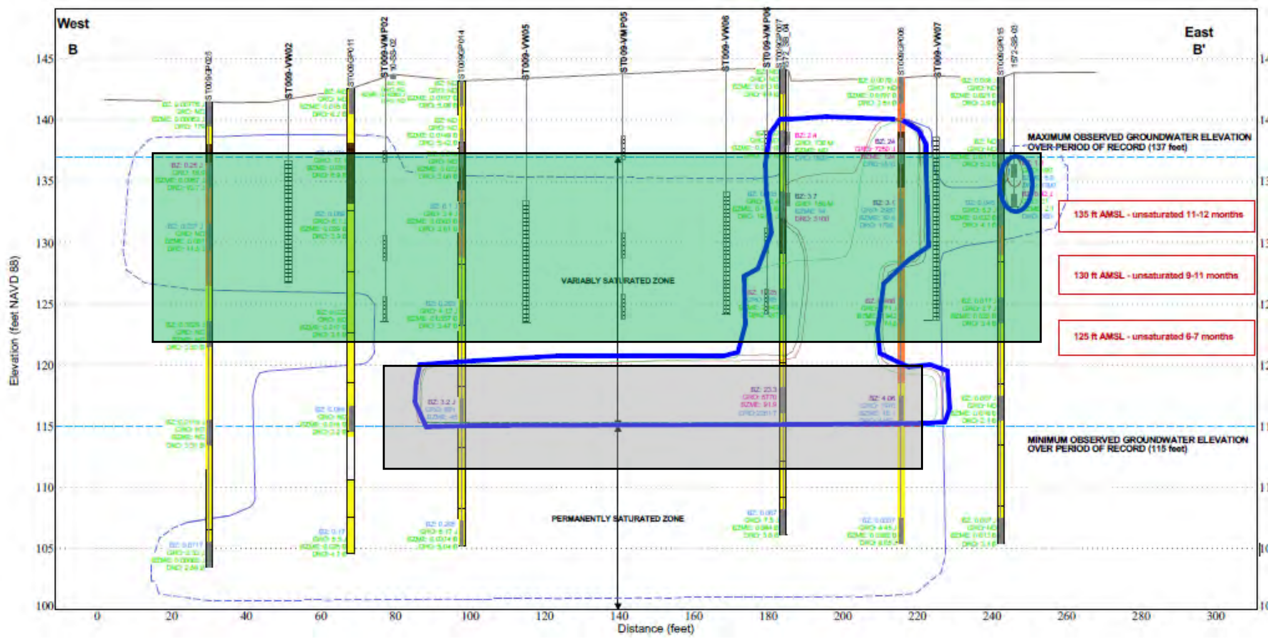
Galena Fuel Sites

- Fuel releases from pipelines and tanks
- Often Arctic diesel and usually heavily weathered (JP-4 at ST009)
- Residual NAPL-contaminated soil source area extends from bottom of vadose zone to top of permanently saturated zone (wider at top and bottom)



Fuel Sites Remedial Design

- SVE or Bioventing in NAPL source area at 5-15 ft (also excavation and landfarming)
- SVE or Bioventing in NAPL source area at 15-25 ft bgs
- Sulfate Enhanced Bioremediation in NAPL source area 25-35 ft bgs
- Monitored Natural Attenuation for downgradient plume



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Design -- Why Sulfate?

- Role of sulfate in hydrocarbon degradation
  - 97% of petroleum hydrocarbon biodegradation (via natural attention) is through anaerobic processes
  - Nearly 75% of petroleum hydrocarbons are degraded through reduction of sulfate if sulfate concentrations ≥ 200 mg/L
- Parsons "NAPL Away" US Patent 8,679,340 B1 (March 25, 2014)
  - Enhanced anaerobic bioremediation for LNAPL source zones / residual saturation
  - Amendments, specifically including sulfate, may be added as dissolved phase or slow-release minerals (e.g., gypsum)
- Conditions at Galena sites amenable for sulfate-enhanced bioremediation
- Specific Galena advantages of sulfate over air sparge

Technology Application at Galena

Redox Conditions Before Sulfate Injection

Constituent	Upgradient	ST009 Source Area	ST009 Plume	ST009 Downgradient	SS014 Downgradient
	06-MW-01 4/22/12	1572-MW-03 9/2/13	1572-MW-04 9/2/13	10-MW-05 9/3/13	SS014-MW004 9/13/13
Benzene (μg/L)	0.601 J	3200	460	98	18
DRO (μg/L)	33.2 U	5900	8600	250 J	6800
Dissolved Oxygen (mg/L)	0.65	0.41	0.35	0.16	0.21
Iron (Dissolved) (mg/L)	0.022 U	109	36.4	76.5	96.8
Sulfate (mg/L)	34.7	0.18J	10.3	0.449 J	0.462 J
Methane (μg/L)	54	2400	2700 J	3000	5100
ORP (mV)	93.4	-66.2	-26.9	-41	-75

- Moderate natural levels of sulfate depleted (methanogenic in source areas)
- High dissolved iron concentrations (potential to precipitate sulfide)

Comparison of Air Sparging and Sulfate-Enhanced Bioremediation

	Air Sparging	Sulfate-Enhanced Bioremediation
Treatment Mechanisms	Volatilization /Stripping – VOCs only Aerobic Biodegradation	Anaerobic Biodegradation
Electron acceptor	O_2	SO_4^{2-}
Solubility	8 mg/L (air)	1400 mg/L (gypsum)
Mass hydrocarbon mineralized / mass of electron acceptor	0.35 g benzene / g O_2 0.294 g $C_{12}H_{23}$ / g O_2	0.233 g benzene / g SO_4^{2-} 0.196 g $C_{12}H_{23}$ / g SO_4^{2-}
Mass of hydrocarbon mineralized per 1000 liters of water at solubility	2.8 g benzene 2.35 g $C_{12}H_{23}$	327 g benzene 274 g $C_{12}H_{23}$
Electron acceptor priority	**O_2** > NO_3^- > Fe/Mn > SO_4^{2-} > CO_2	O_2 > NO_3^- > Fe/Mn > **SO_4^{2-}** > CO_2
Percent operational	50%	100%
Infrastructure	Blowers, sparge wells and manifolds	No permanent infrastructure
Energy requirements	High pressure blowers	None
Materials to be transported to Galena	Equipment; Fuel for increased energy demand; Electricity costs $0.67/kWh	Sulfate amendments
O&M	Maintain blower operations, groundwater monitoring	Groundwater monitoring

Design Considerations

- Emplace gypsum ($CaSO_4 \cdot 2H_2O$) to slowly dissolve over time in “lower pancake” NAPL source area
  - Inspired by PRB concept – emplace gypsum in “injection zones” near upgradient end of source area and allow groundwater to distribute dissolved sulfate across source area
- “Injection zone” thickness – designed to supply sulfate for five years
  - Thickness of injection zone = Design time for gypsum dissolution x groundwater flux x gypsum solubility / (porosity x gypsum concentration in slurry)
- Spacing between “injection zones” designed based on groundwater velocity and estimated sulfate utilization rate
- Do not fill the entire pore space – keep groundwater flowing through (not around) injection zone
  - Injection slurry originally designed for 7.7% solids (later increased to 10.4%)
  - Did not design monolithic “injection zone” – dispersed injection points to ensure water could flow between points

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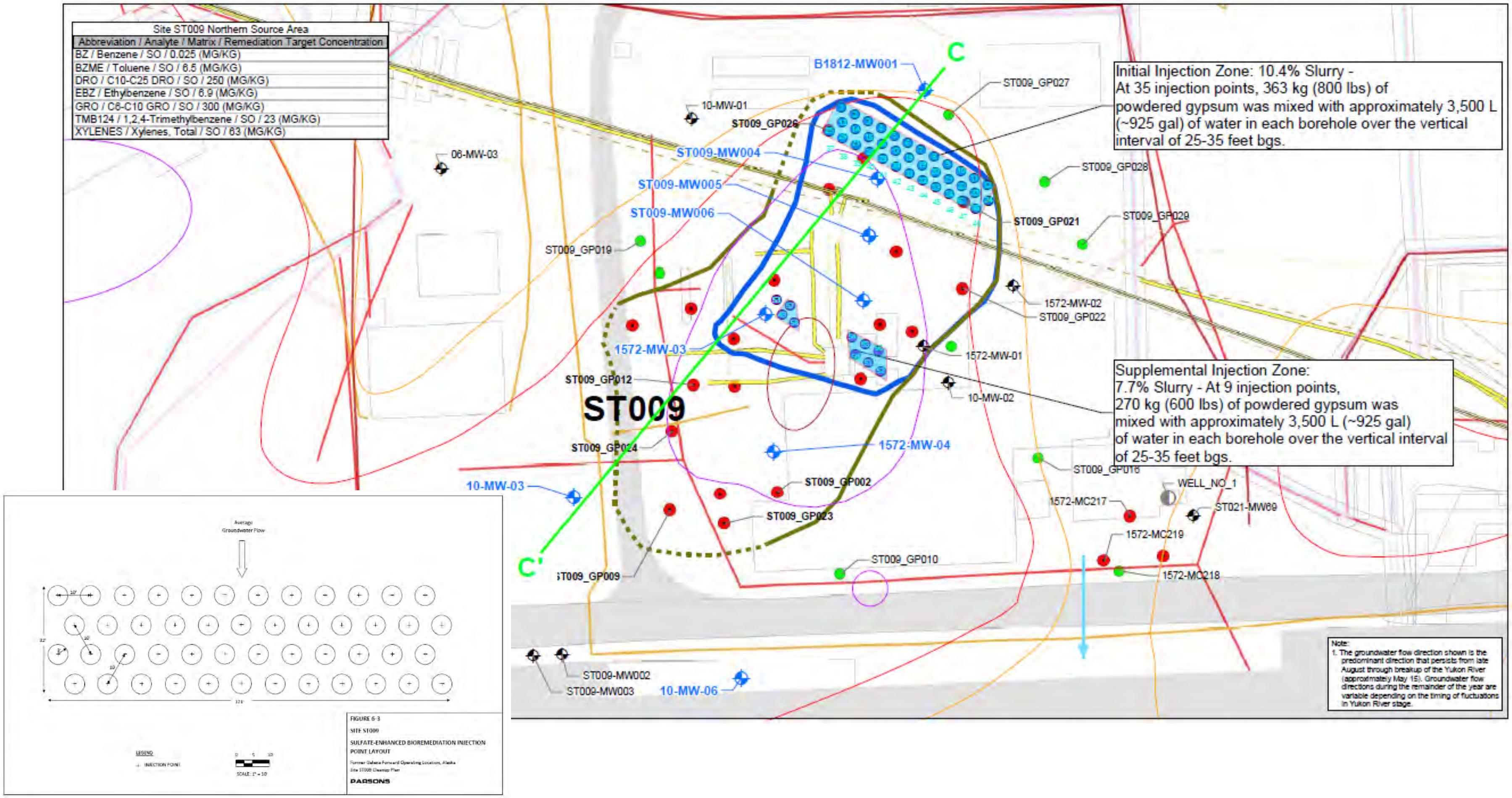
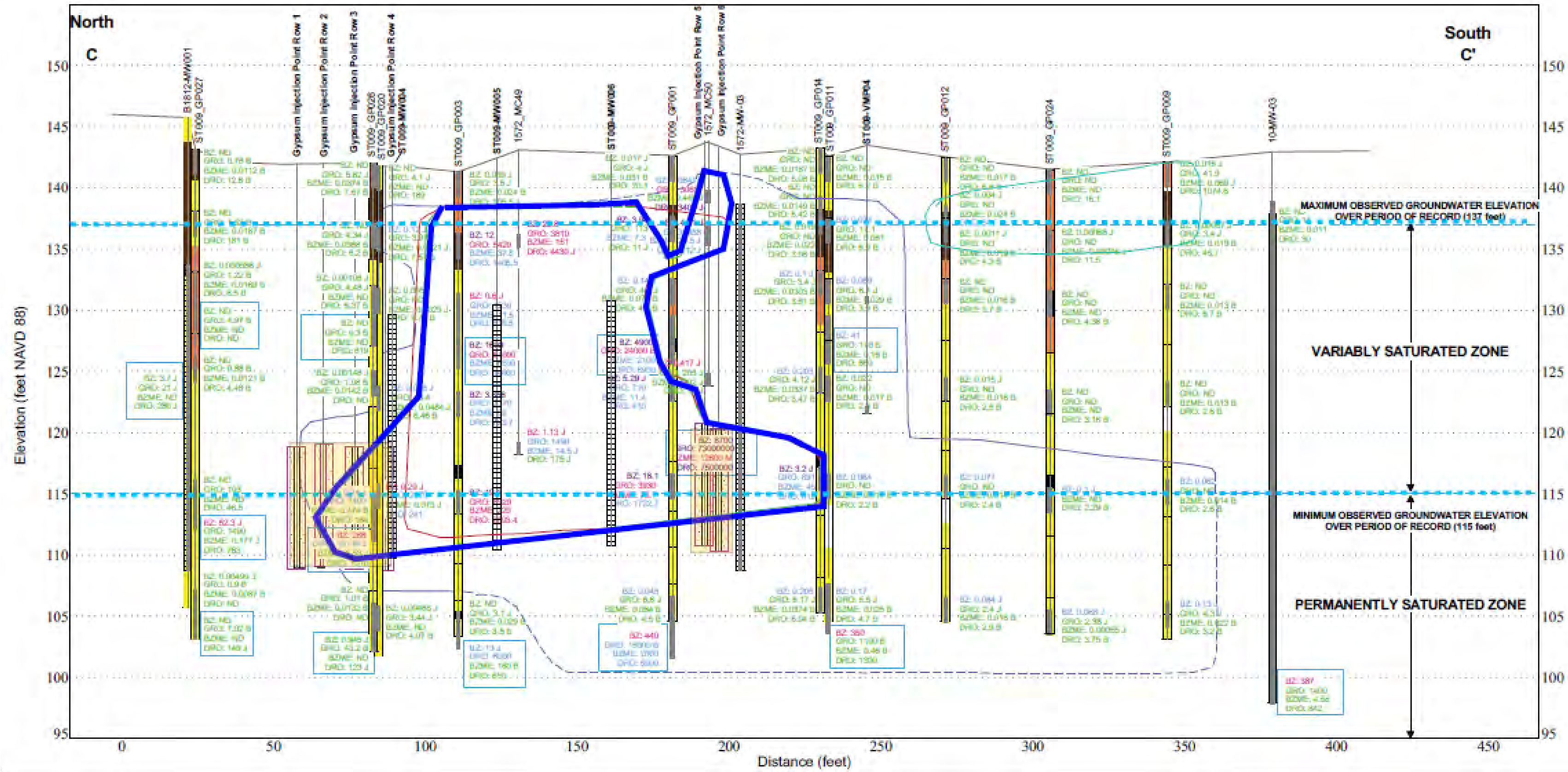
Sulfate Injection Zones – Plan View



Sulfate Injection Zones – Profile View



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Implementation and Monitoring

- Gypsum “injection zones” emplaced during 2017 field season
  - Injected 196,000 lbs of gypsum in 340 boreholes at 3 sites
- Annual groundwater monitoring
  - GRO/DRO/RRO, VOCs, Methane, Sulfate

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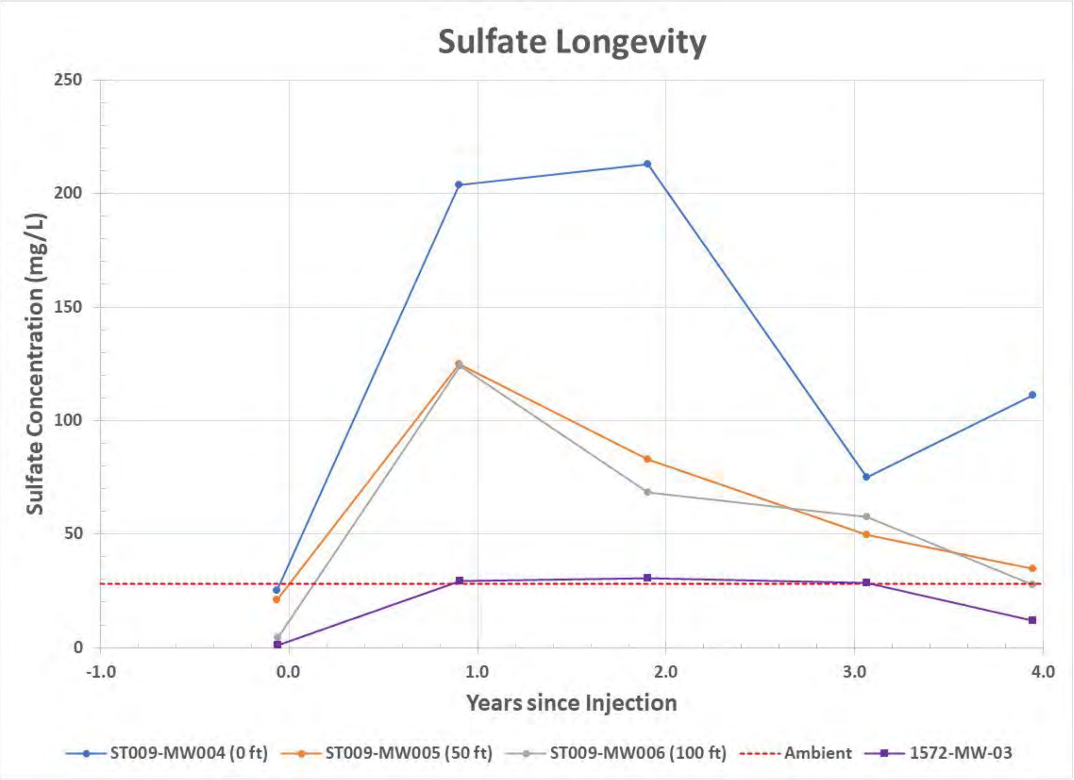
Injection Zone Longevity

- Design life = 5 years
- Sulfate source on track to be depleted within 4 years
- Groundwater flux likely greater than estimated in design
- Wells:
  - MW004 = at injection zone
  - MW005 = 50 feet downgradient of injection zone
  - MW006 = 100 feet downgradient of injection zone
  - MW-03 = downgradient of supplementary injection zone



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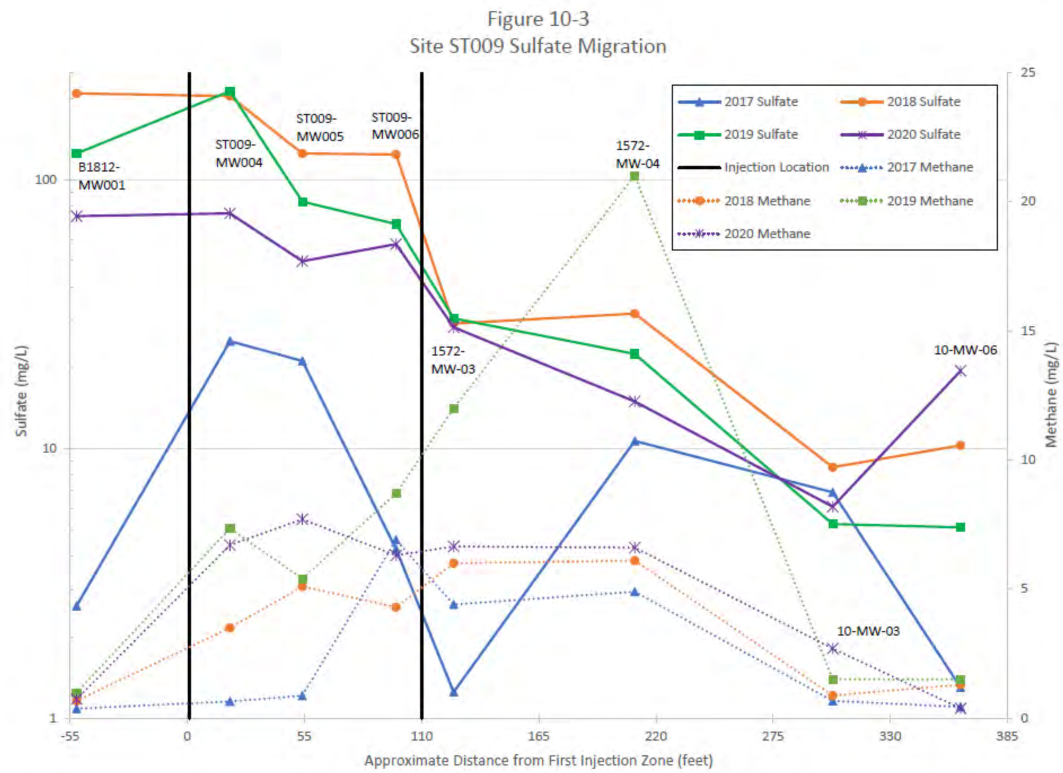
Sulfate Utilization and Indication of Biological Activity

- Sulfate travels ~ 125 feet downgradient of first injection zone before reaching ambient levels
- Increased methane in source area and downgradient indicates biological activity



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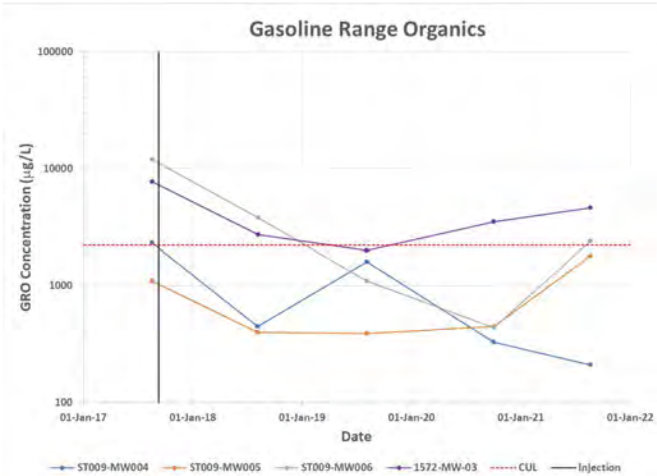
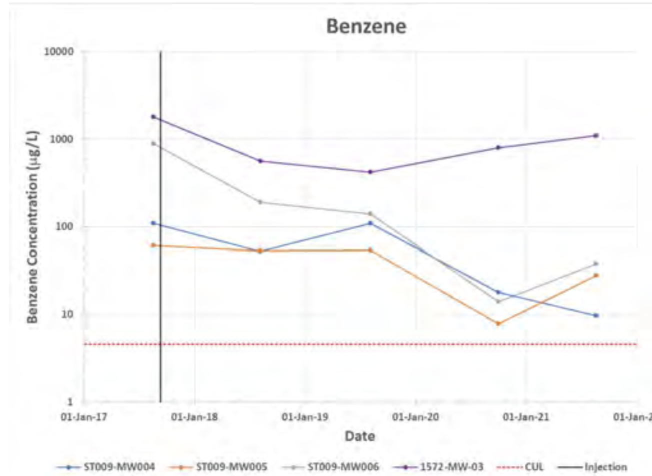
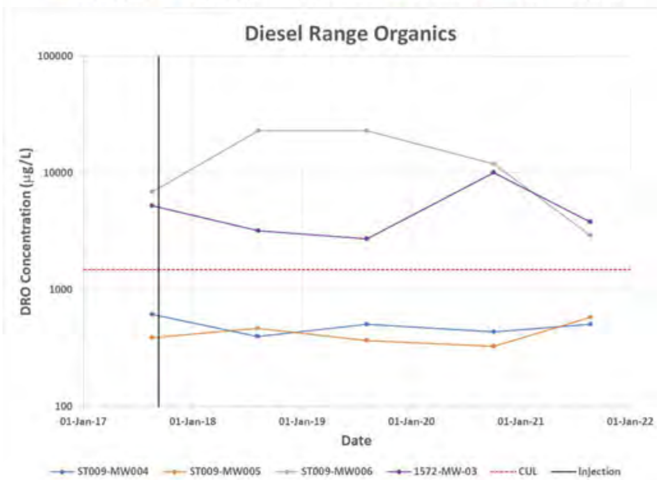
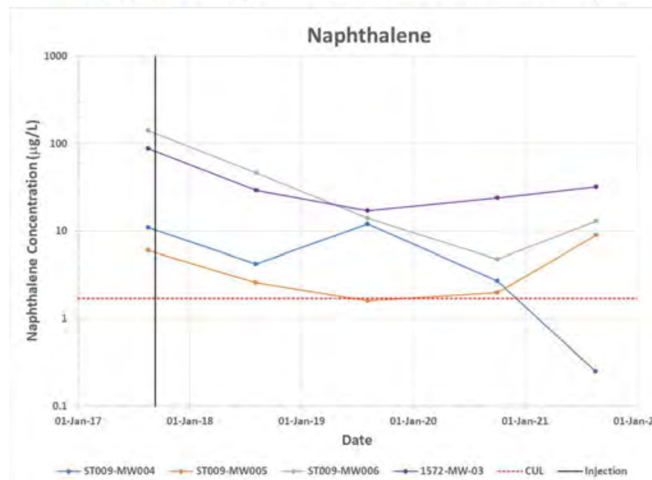
Impact on Groundwater









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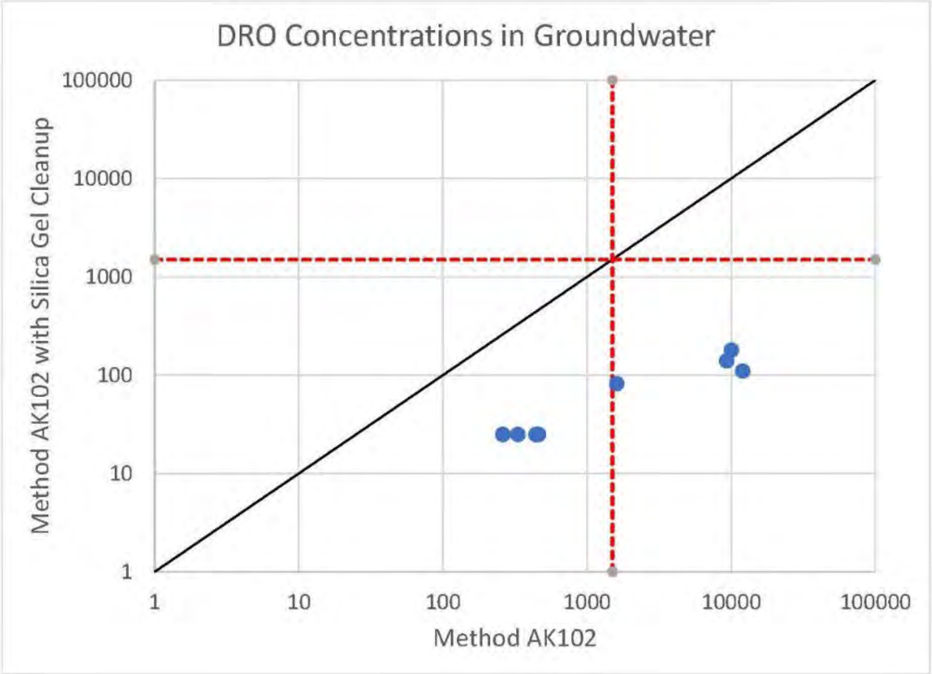
Impact on Groundwater -- DRO

- Total DRO concentrations detected by Method AK102 initially increased
- Silica Gel cleanup shows < 5% of Method AK102 detection are non-polar compounds
- Most of Method AK102 result are partially degraded polar by-products
  - Acids, alcohols, ketones, esters and phenols have higher solubility than aromatic and aliphatic hydrocarbons



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Summary

- Sulfate enhanced-bioremediation designed/installed as “green” remedies to address residual petroleum source areas for three sites at Galena
  - Systems generally working as designed
  - Gypsum depleted somewhat faster than designed – groundwater flux likely greater than estimated
- Fuel contaminant concentrations decreasing in groundwater
  - Sulfate responsible for ~ 7% of total mass removal at Site ST009

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