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Biodegradation of Hydrocarbons under Nitrate and Sulfate Reducing Conditions

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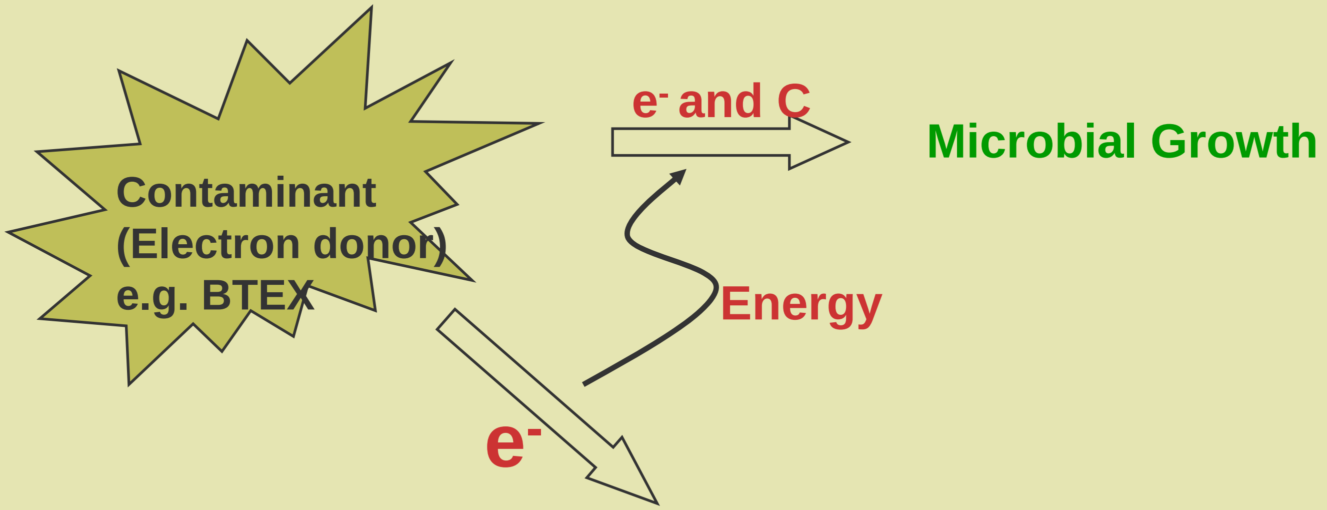
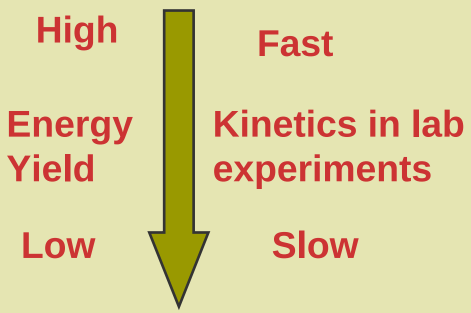
Hydrocarbon Biodegradation





	Electron Acceptors		Products
1.	Oxygen	>>>	Water, CO_2
2.	Nitrate	>>>	Nitrogen, CO_2
3.	Fe(III)	>>>	Fe(II), CO_2
4.	Mn(IV)	>>>	Mn(II), CO_2
5.	Sulfate	>>>	Sulfide, CO_2
6.	None (fermentation)	>>>	Methane, CO_2

Why Sulfate?

Electron Acceptor (EA)	Maximum Concentration (mg/L)	Mass of benzene degraded per unit mass of EA	Potential Benzene Degraded (mg/L)	Issues
Oxygen (in air)	9 - 10	0.33	3.0 – 3.3	•Limited solubility •Numerous oxygen sinks •Potential aquifer clogging •Biofouling near injection point
Pure Oxygen	60 - 70	0.33	19.8 – 23.1	
Sulfate	100 – 250*	0.22	22.0 – 55.0	•Hydrogen sulfide; never documented as an issue in the field •Secondary MCL for sulfate – 250 mg/L*
Nitrate	80 - 100	0.21	16.8 – 21.0	•DW concern •Primary MCL – 10 mg/L NO_3-N (45 mg/L NO_3)
Iron (III)	0 - 1	0.024	0 – 0.024	•Very low solubility •Aquifer clogging

Sulfate/Nitrate Advantages

- **Most HC plumes are anaerobic and depleted of soluble electron acceptors (nitrate and sulfate)**
- **Sulfate reducing bacteria are ubiquitous and rapidly grow in HC rich anaerobic conditions**
- **Nitrate may oxidize iron sulfides to sulfate and boost the total electron acceptor pool**
- **Suitable for a variety of hydrocarbons – gasoline, gas condensate, alkanes, PAH, diesel…**
- **Nitrate and sulfate salts are much more soluble than oxygen**
- **Lower cost alternative $ 19 to 150/t vs $16,500/ton for ORC**

Installation Restoration Program (IRP) Site 25, 148th Fighter Wing (FW), Duluth, MN

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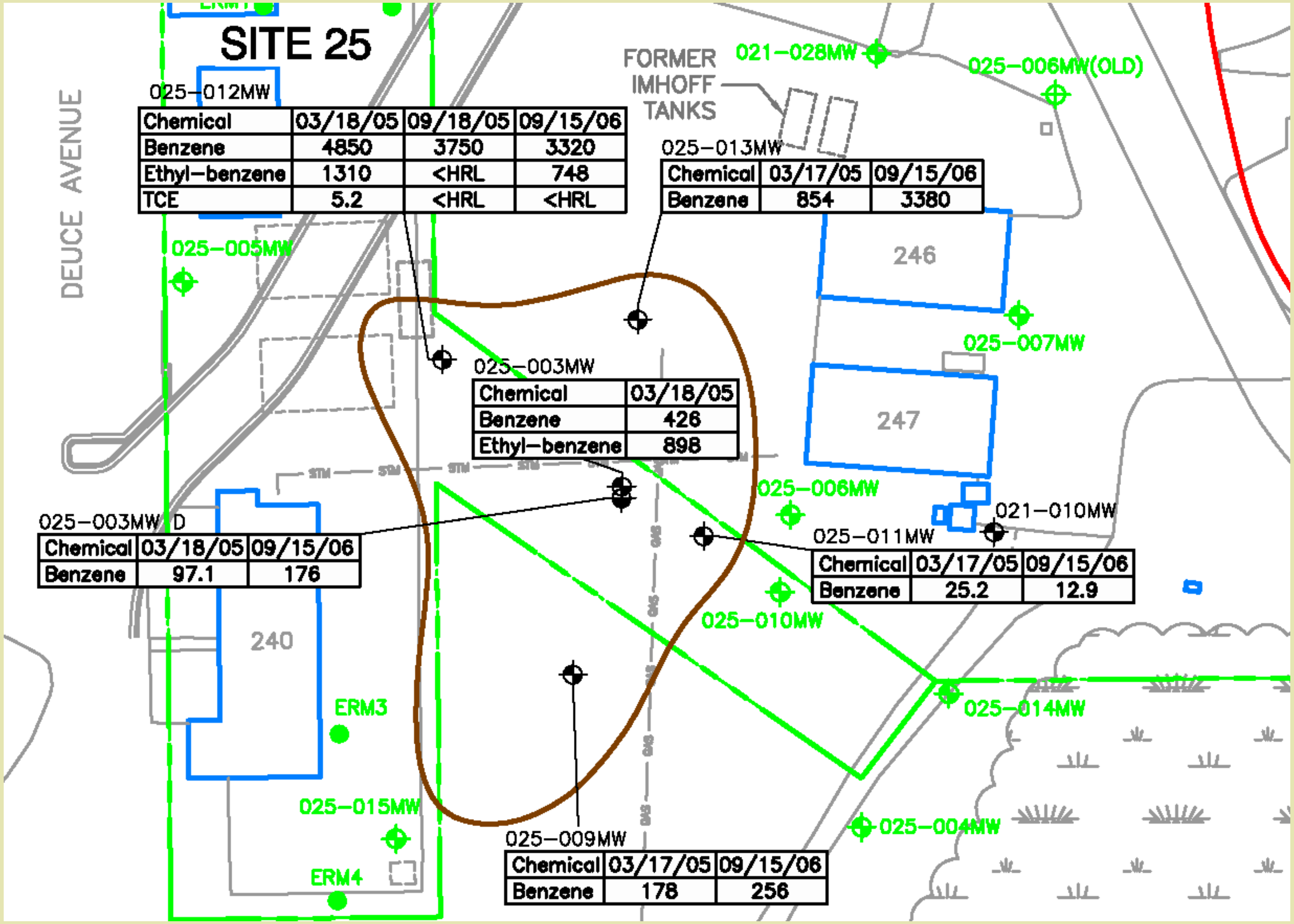
Site Background and Setting

- **Water table from 3 to 12 ft bgs, due to topographic slope**
- **Interbedded silts and clay to approximately 20 ft bgs**
- **Primary contaminant of concern: Benzene**
- **Abandoned upgradient UST source for BTEX, GRO and DRO**
- **Receptor of concern is a nearby wetland**

Contaminant Concentrations



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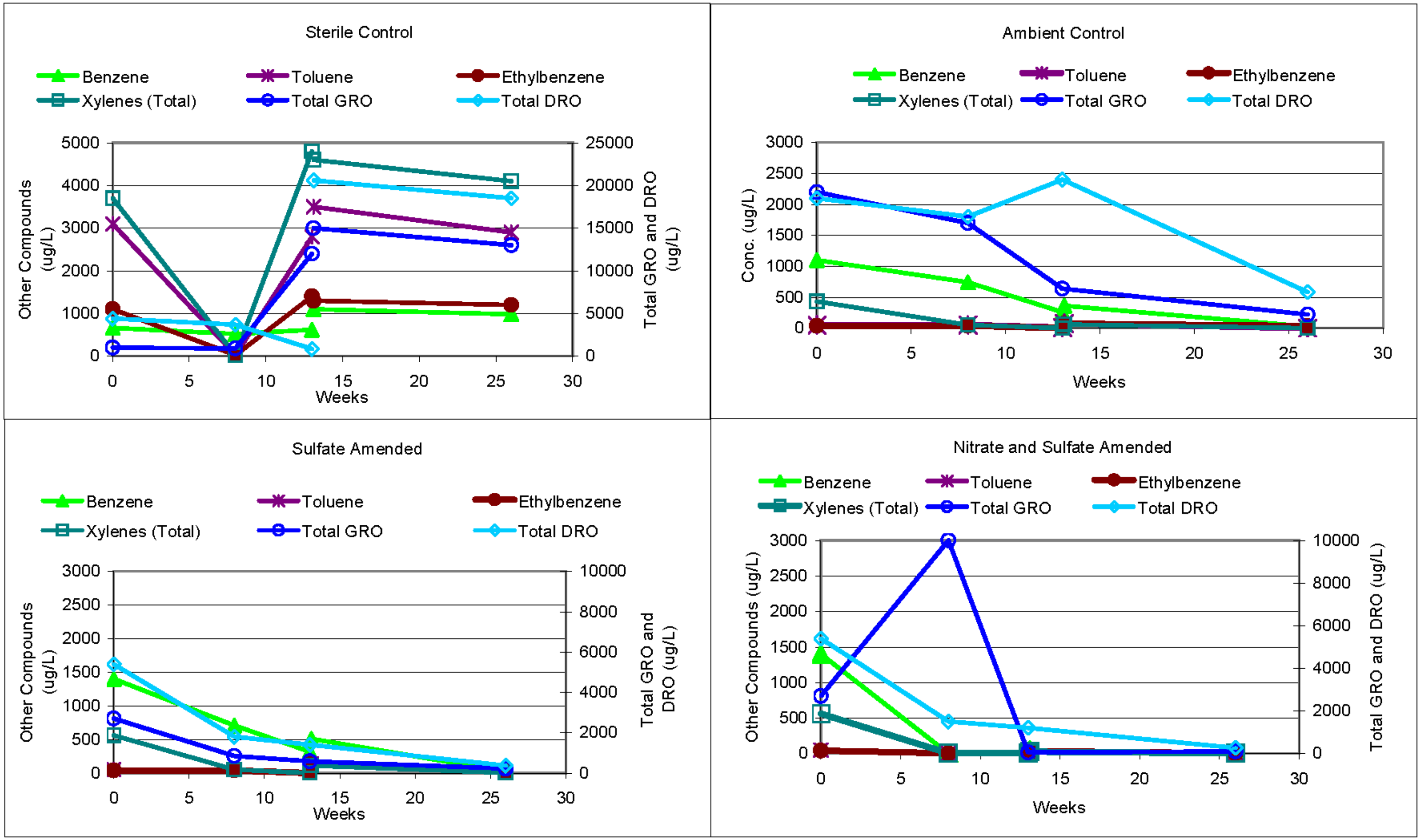
Treatability Study Set-up

- **Site groundwater and soil**
- **BTEX, GRO and DRO spiked at time zero**
- **Treatment Conditions:**
  - Sterile Groundwater Control – groundwater only
  - Ambient (Live) Control – groundwater and soil
  - Sulfate Amended – 400 to 1,000 mg/L
  - Sulfate and Nitrate Amended – 400 to 1,000 mg/L and 4 to 8 mg/L, respectively

Treatability Study Results



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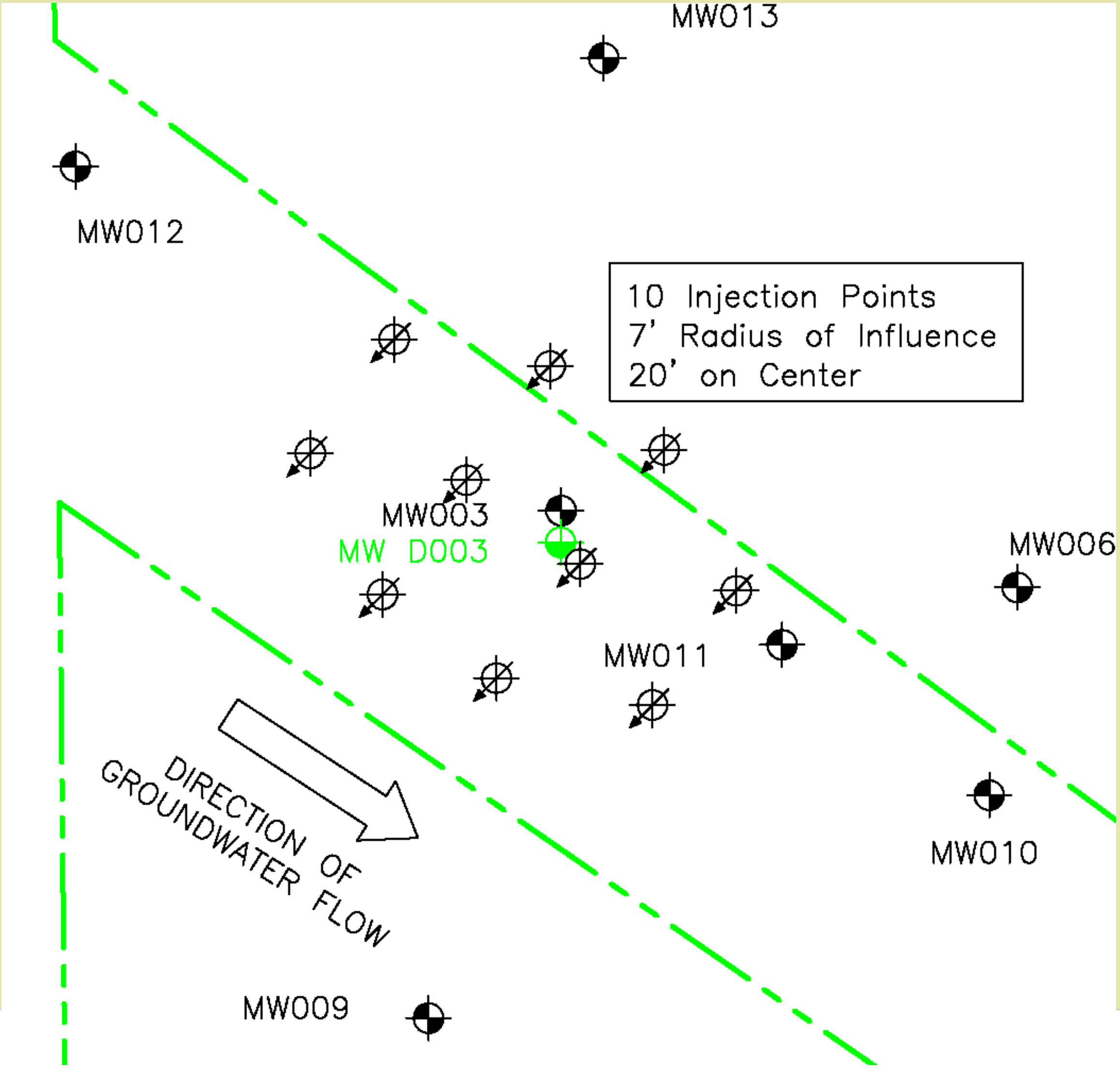
Treatability Results Summary

- **From 0 to 13 weeks, the nitrate+sulfate treatment show >98% decrease in Benzene, Toluene, Xylenes and GRO**
- **From 13 to 26 weeks the % change is almost equal in the ambient, sulfate and sulfate+nitrate treatments, indicating that the degradation rate caught up after the longer incubation period**
- **Soil GRO and DRO concentrations dropped significantly in all three treatments over the 26 week period**

Pilot Test Design

- Sulfate (Epsom Salt,$MgSO_4$, 400 mg/L) Nitrate (as KNO_3, 4 mg/L) and dosages from treatability test
- 850 lb of of 40% $MgSO_4$
- 6 lb of 62% KNO_3
- 4,650 gal GAC filters tap water used to batch-mix injection solutions
- ROI of 20 ft, targeted top 12 feet below water table
- Injection grid of 10 points
- Distribution testing at 5, 10 and 15 ft from two injection points

Pilot Test Design



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Ideal Field Conditions vs. Reality - a Difference of 40 Degrees

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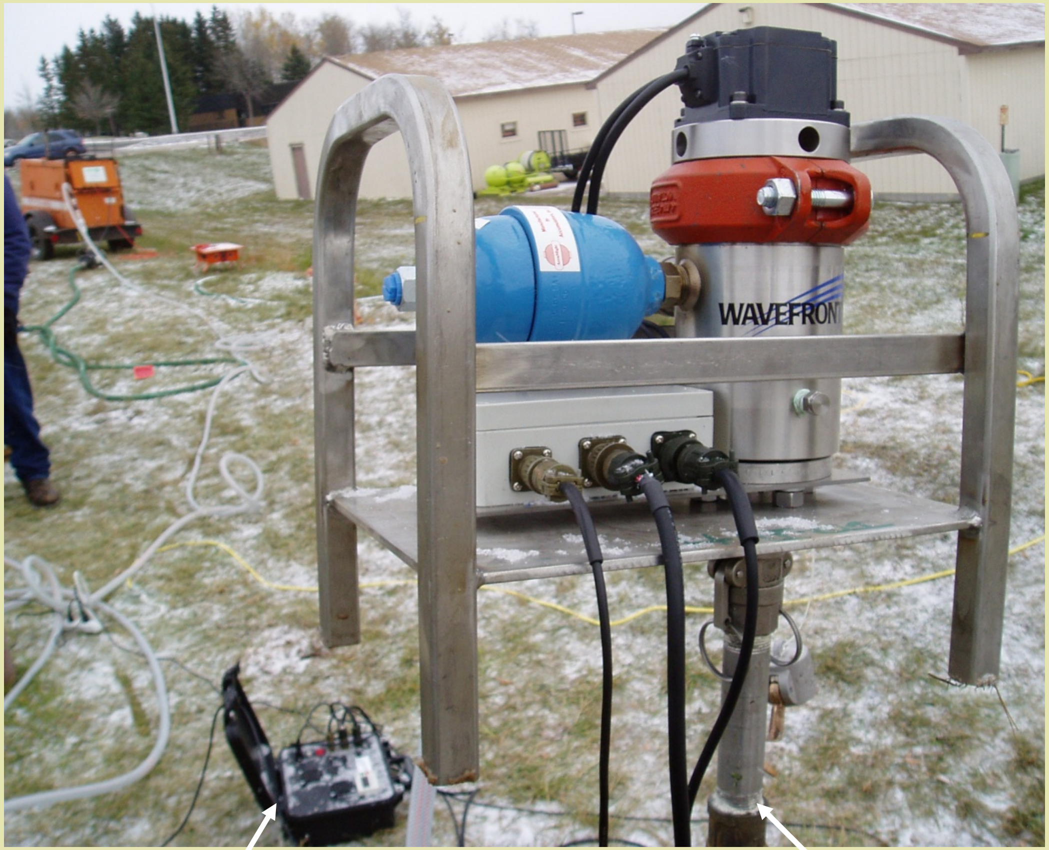
Field Set-up

Pressure Pulse Injection – Wavefront™

- Pressure wave induces pore throat dilation
- Hornet – Model Name
- Injections were performed with and without the pressure pulse
- The unit is pressure sensitive – needs a minimum pressure (can be set by manufacturer)
- Affects ability to valve down injection pressures/rates



Control Box

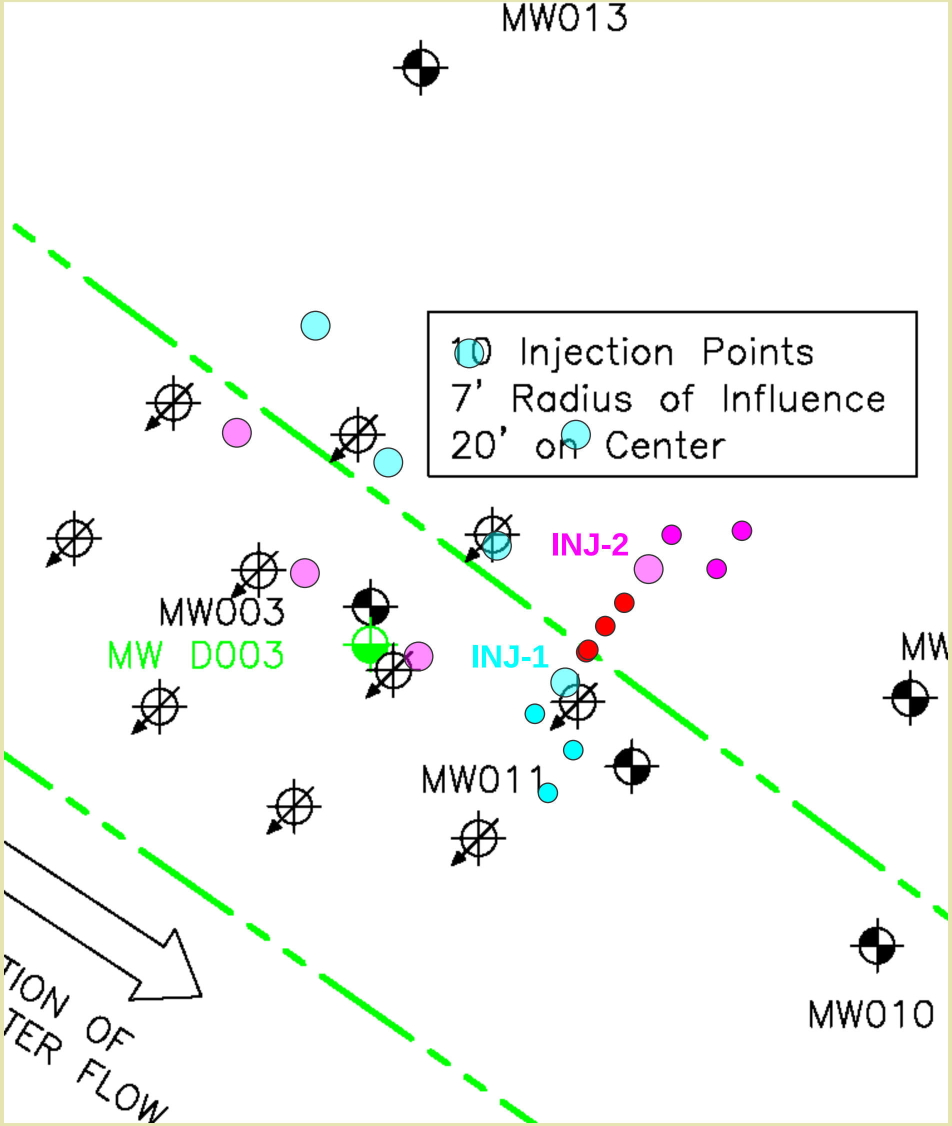
Injection Point Rod

ROI Confirmation Sampling

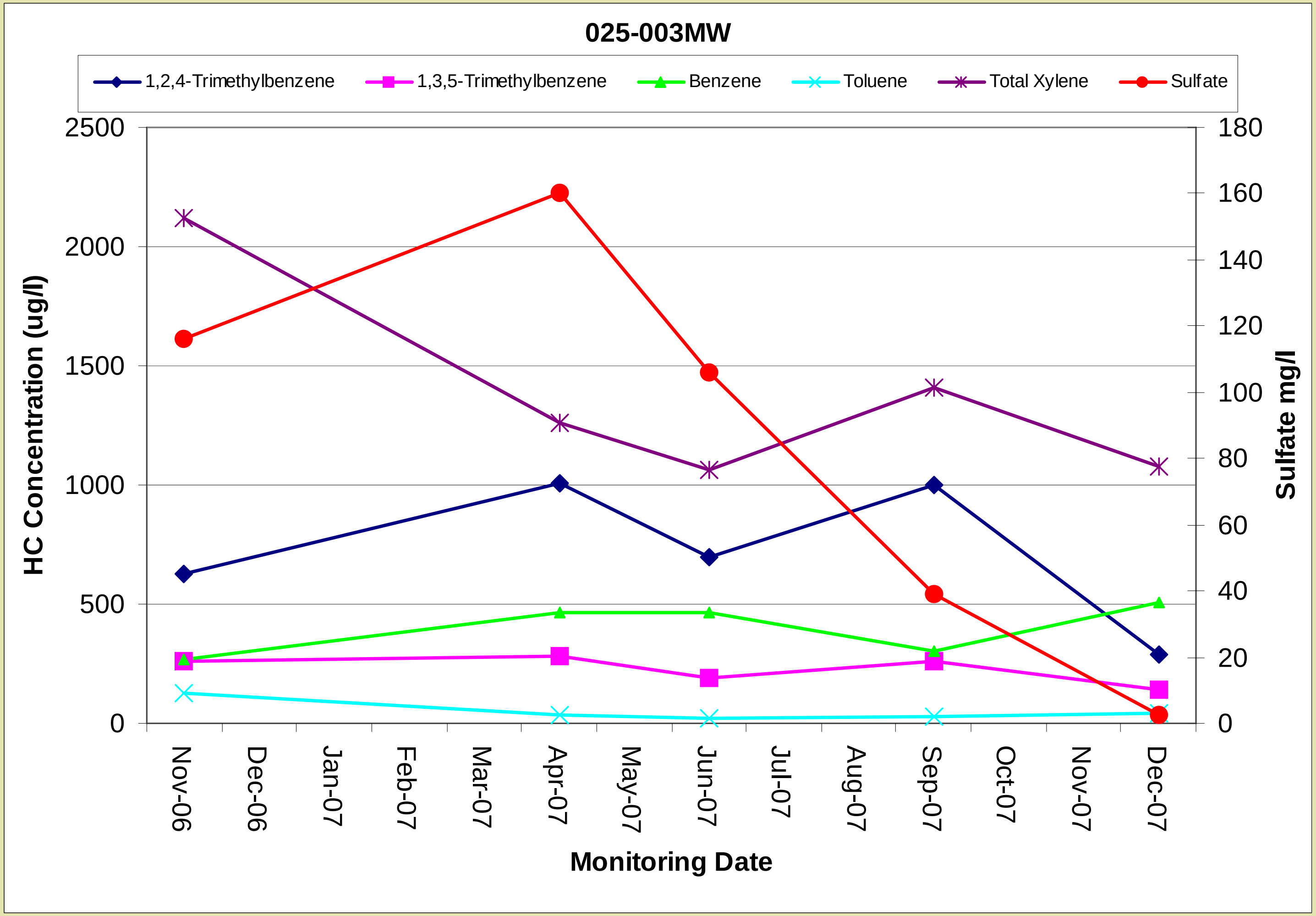
- Injections were performed downgradient to upgradient
- 6 of the 10 injection points used Wavefront
- Groundwater samples were collected a radia distances from injection points at 5, 10, and 15 feet
- Analyzed using a LaMotte Field Test Kit for Sulfate, range 0 – 200 ppm

ROI Monitoring

Location	Sulfate (mg/L)	Wavefront
I1-5	160-200	Y
I1-10	160-200	Y
I1-15	50-80	Y
I2-5	160-200	NA
I2-10	160-200	NA
I2-15	160-200	NA
I2-5	>200	N
I2-10	>200	N
I2-15	80-120	N



Results – Test Area Shallow Well



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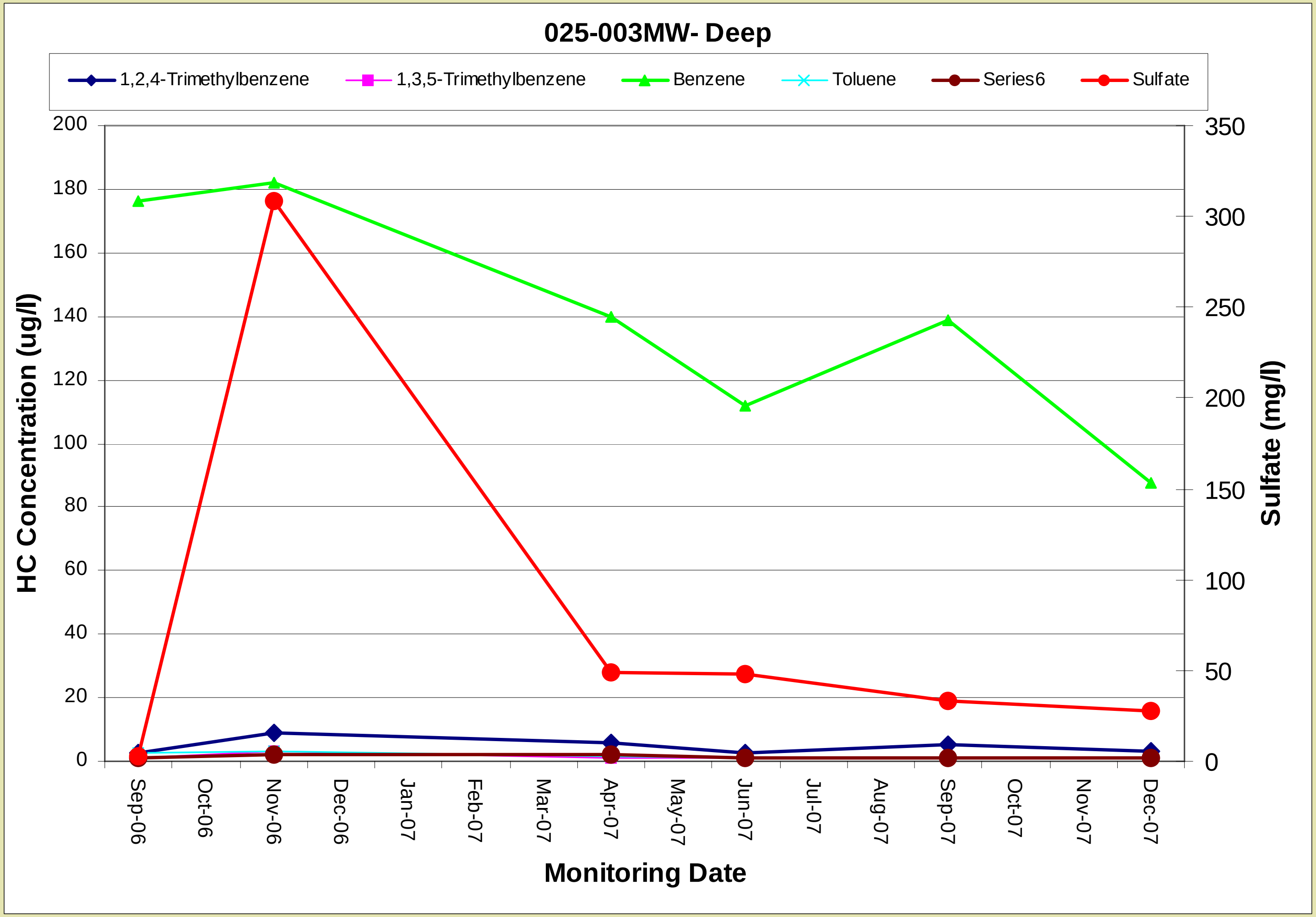
Results – Test Area Deep Well



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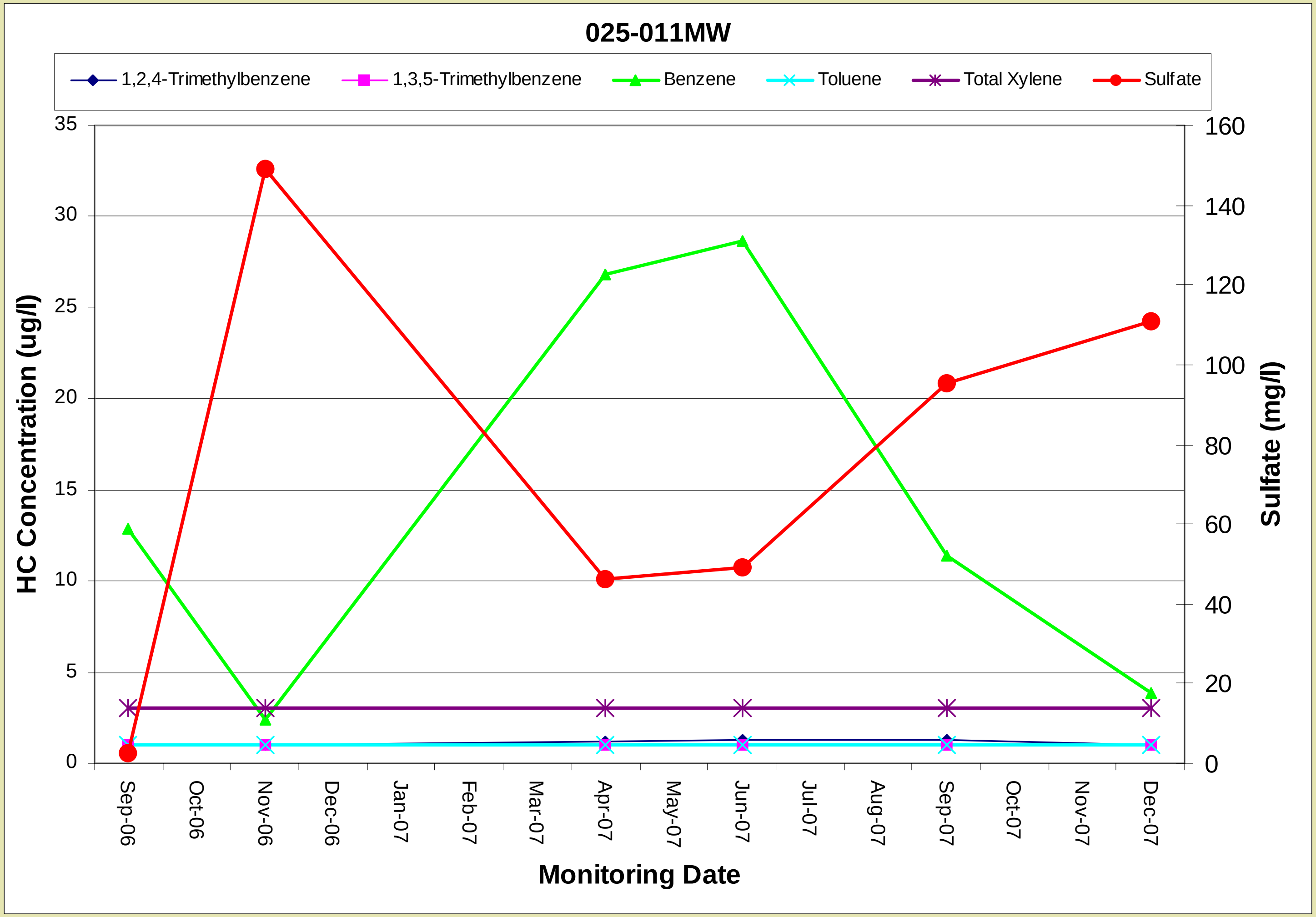
Results – Down Gradient Shallow Well



Pilot Test Conclusions

- **Sulfate/nitrate reduction is an effective tool for accelerating natural attenuation of HCs in groundwater**
- **Removal of free-phase hydrocarbons is necessary for successful application sulfate reduction**
- **Based on the rapid consumption rates, high sulfate/nitrate dosing will likely not result in groundwater exceeding secondary standards**

Future Site Work

- **High Vacuum Extraction for source area separate phase HC removal**
- **Sulfate/Nitrate amendments to address residual dissolved phase HC remediation**
- **Monitored Natural Attenuation as final polishing step**

Questions