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Remediation Technology Symposium (RemTech) 2012

In-Situ Chemical Oxidation (ISCO) Using Ozone Sparging for Treatment of Petroleum Hydrocarbon-Impacted Groundwater

October 19, 2012

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Presentation Overview

- Site Background
- Remedial Process Optimization
- Bench Scale Testing
- Capture Zone Analysis
- Pilot Test - In-Situ Chemical Oxidation (ISCO) Using Ozone

Site Background – Nature and Extent of Impacts

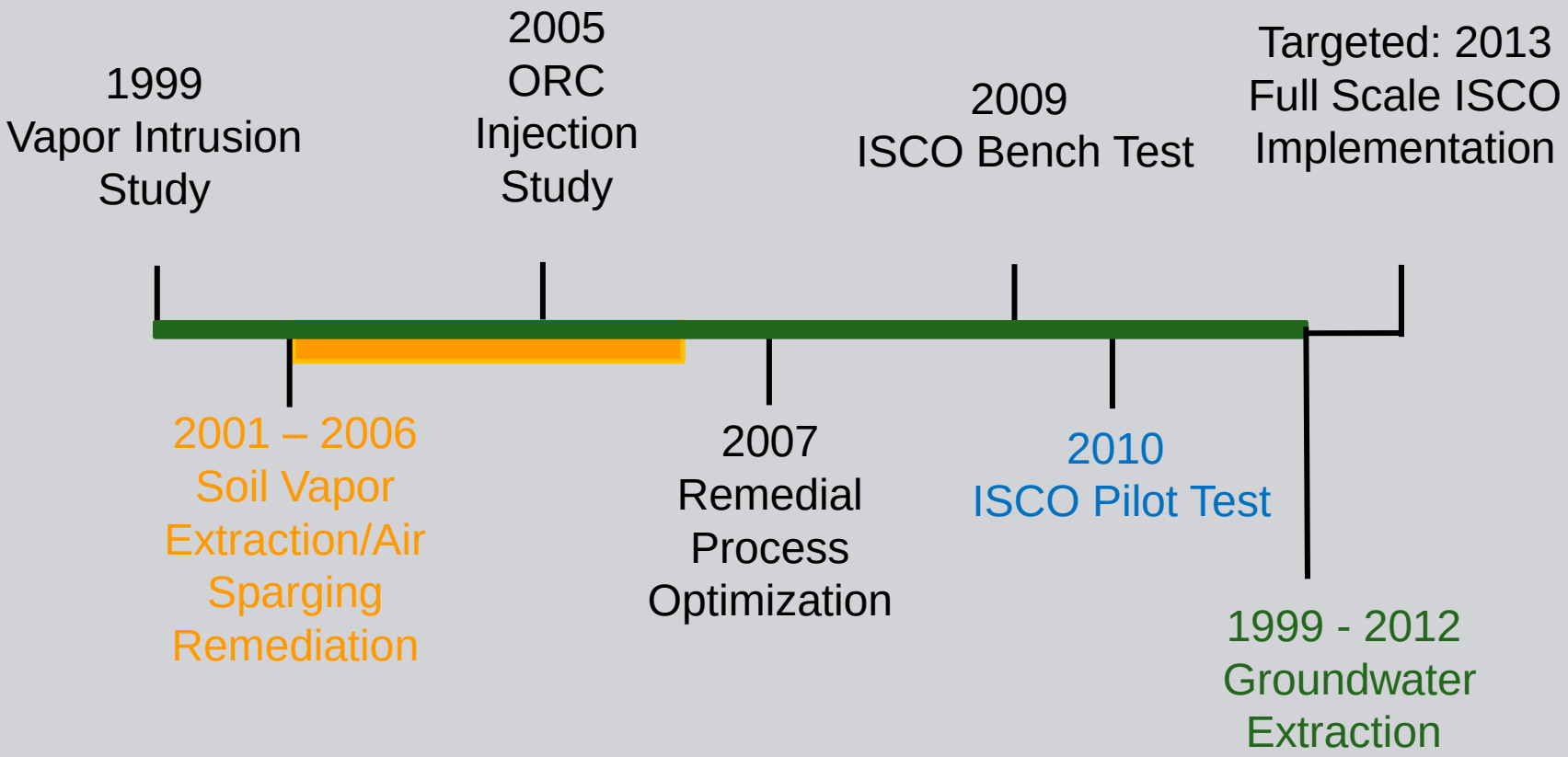
- Former Natural Gas processing station (1961 to late 1980's)

- Chemicals of Concern identified in saturated zone:
  - Gasoline Range Organics (GRO)
  - Diesel Range Organics (DRO)
  - Motor Oil Range Organics (ORO)
  - Benzene, toluene, ethylbenzene, and xylenes (BTEX)

Matrix	GRO	DRO	ORO	Benzene
Groundwater (µg/L)	1,600	5,000	770	25
Clean-up Levels (µg/L)	100	100	100	1

*Groundwater concentrations from 2011 Annual monitoring report.

Site Background – Previous Relevant Activities



Remedial Process Optimization – Recommendations

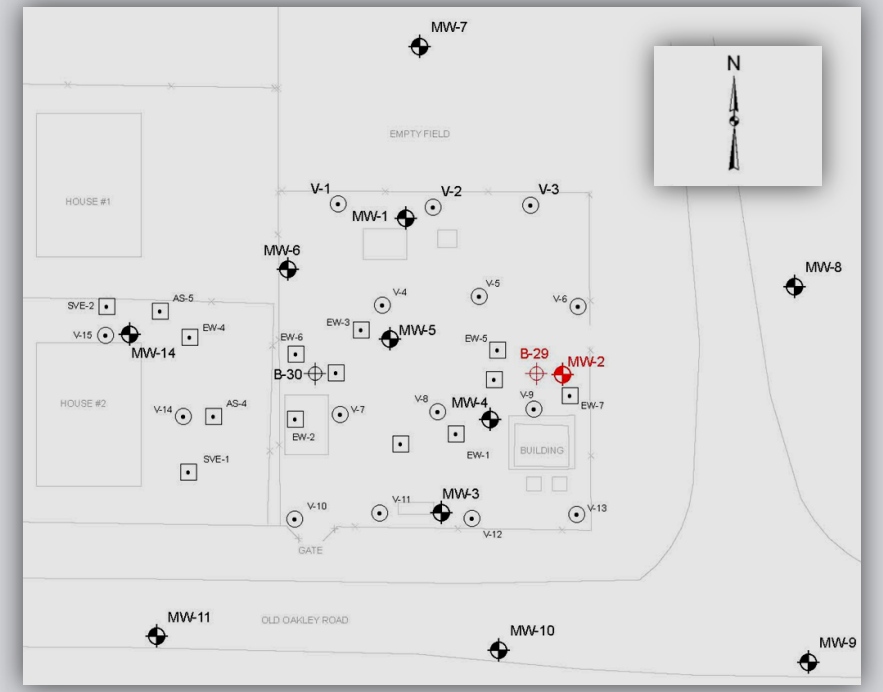
- Both the AS/SVE system and the groundwater extraction system have reached the practical limits of COC mass removal and COC concentration reduction and will not produce significant additional COC mass removal.
- Shut down the groundwater extraction system
- Monitor the off-site groundwater concentrations
- Conduct an in-situ chemical oxidation (ISCO) Pilot Study - Study onsite conditions to evaluate the best ISCO product and approach (potassium permanganate, persulfate, ozone, etc.)

Bench Test


MULTI-MAGNESTIR
ON
OFF
SPEED


CAUTION
FLAMMABLE
KEEP FIRE AWAY

Bench Test Activities



- Collected soil from 12 to 26 feet bgs (8 kg total) in boring B-29
- Collected groundwater from MW-2 (24 L total)
- Homogenized samples
- Established six reactor studies to evaluate COC degradation, secondary impacts, and ozone demand

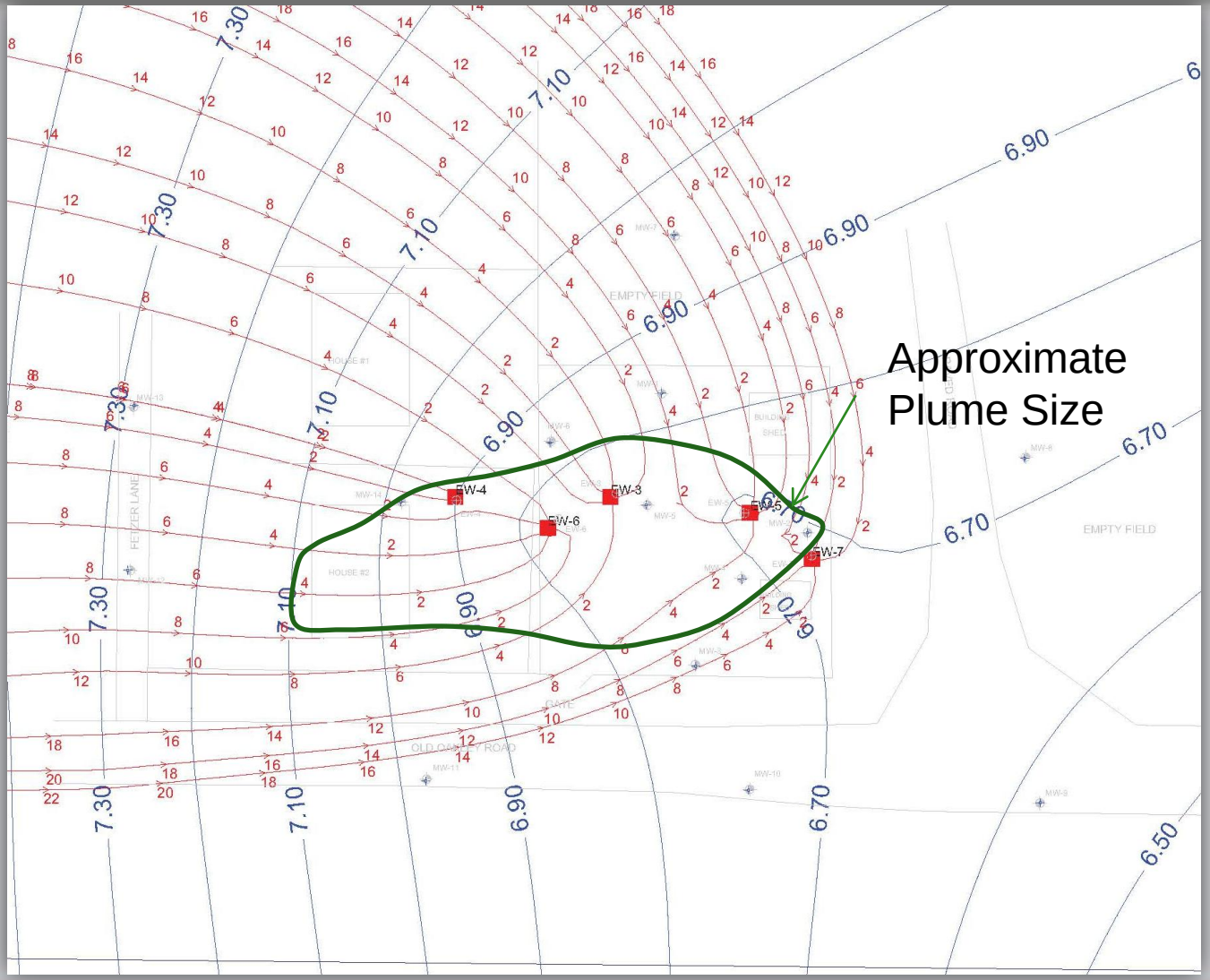
Bench Scale Test - Conclusions

- Ozone effective in removing DRO (primary COC) in impacted groundwater
- DRO removal in saturated soil appeared to be desorption/dissolution limited
- Ozone off-gas ~ 21 mg/L (a 30% ozone consumption within the reactors)
- Ozone demand of 8 to 12 mg ozone/ mg TPH
- Secondary by-products identified as hexavalent chromium, nitrate, bromate

Bench Scale Test - Recommendations

- Conduct pilot test to determine operating pressure and flow rate and estimate radius of influence (ROI) of ozone sparging system
- Ozone sparging should be pulsed to maximize ROI, minimize off-gassing, and maximize the use of ozone since COC removal in saturated soil appears to be desorption/dissolution limited
- Monitor attenuation of identified secondary COCs

Capture Zone Analysis



LEGEND:

6 — Flowline Captured by Extraction Well (Travel Time = 6 months)

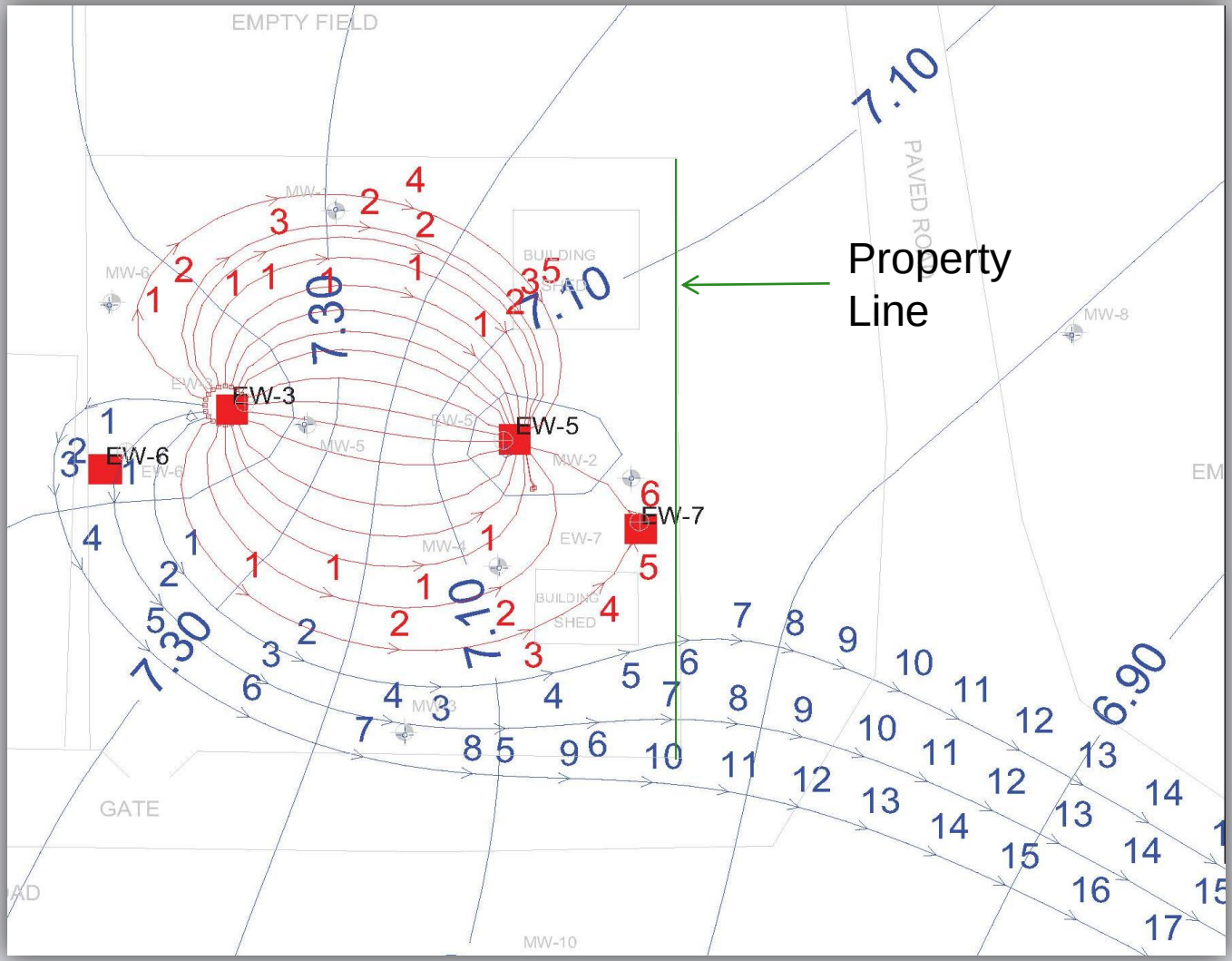
6.90 — Simulated Water Contour Level

N

0 25 50 Feet

Approximate Scale

Capture Zone Analysis



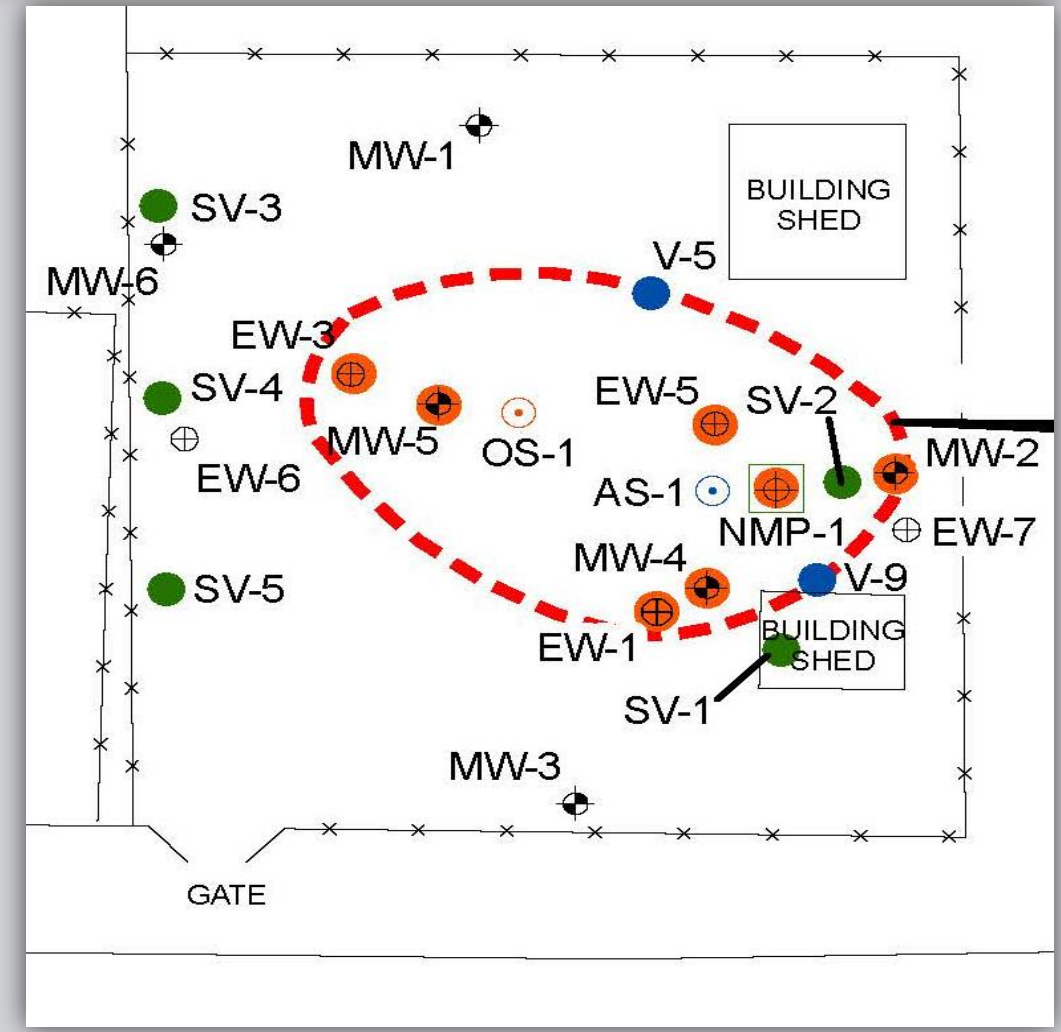
ISCO Pilot Test

ISCO Ozone Pilot Test Approach

- Short-Term Ozone Sparge Test – determine appropriate injection pressure and flow rate, estimate injection pulse frequency and ROI
- Long-Term Ozone Sparging Test – evaluate the COC removal efficiency, secondary groundwater impacts, and off-gas emissions
- Post Sparging Monitoring – evaluate the COC rebound and attenuation of secondary groundwater impacts

Treatment Zone Monitoring Well Network

Well ID	Media Monitored
EW-1	Groundwater – Performance
EW-3	Groundwater – Performance
EW-5	Groundwater – Performance
MW-2	Groundwater – Performance
MW-4	Groundwater – Performance
MW-5	Groundwater – Performance
NMP-1-W	Groundwater – Performance
SV-1	Soil Vapor - Performance
SV-2	Soil Vapor - Performance
SV-3	Soil Vapor - Compliance
SV-4	Soil Vapor - Compliance
SV-5	Soil Vapor - Compliance
NMP-1-S	Soil Vapor - Performance
V-5	Soil Vapor - Performance
V-9	Soil Vapor - Performance
NMP-1-D	Soil Vapor - Performance



Short Term Ozone Sparge Test

Well	Injection Time (hours)	% Ozone by weight	Pressure (psi)	Flow Rate (cfm)	Concentration (g/m^3)	Ozone Delivered (lbs/day)
AS-1	8	0.56	4.5-5.5	2.5	7.2	1.62
OS-1	7	0.55	6.0-6.5	2.5-3.0	6.8	1.50

Monitoring Specifics

- Four rounds soil gas
  - O_3, VOCs, O_2, CO_2, CH_4
- Three rounds groundwater
  - DO, dissolved O_3, ORP, pH, temperature, well head pressure, depth to water

Ozone Sparging Test

Long-Term Injection Specifics

- 2 months of injection
  - ~12.8 g/m^3
  - 5.5 to 6.0 psi
  - 3.5 cfm
  - Equivalent to ~ 4 lb O_3/day (2 lb O_3/day to each injection well)
  - ROI ~20 ft
  - Alternating pulse period 60 minutes

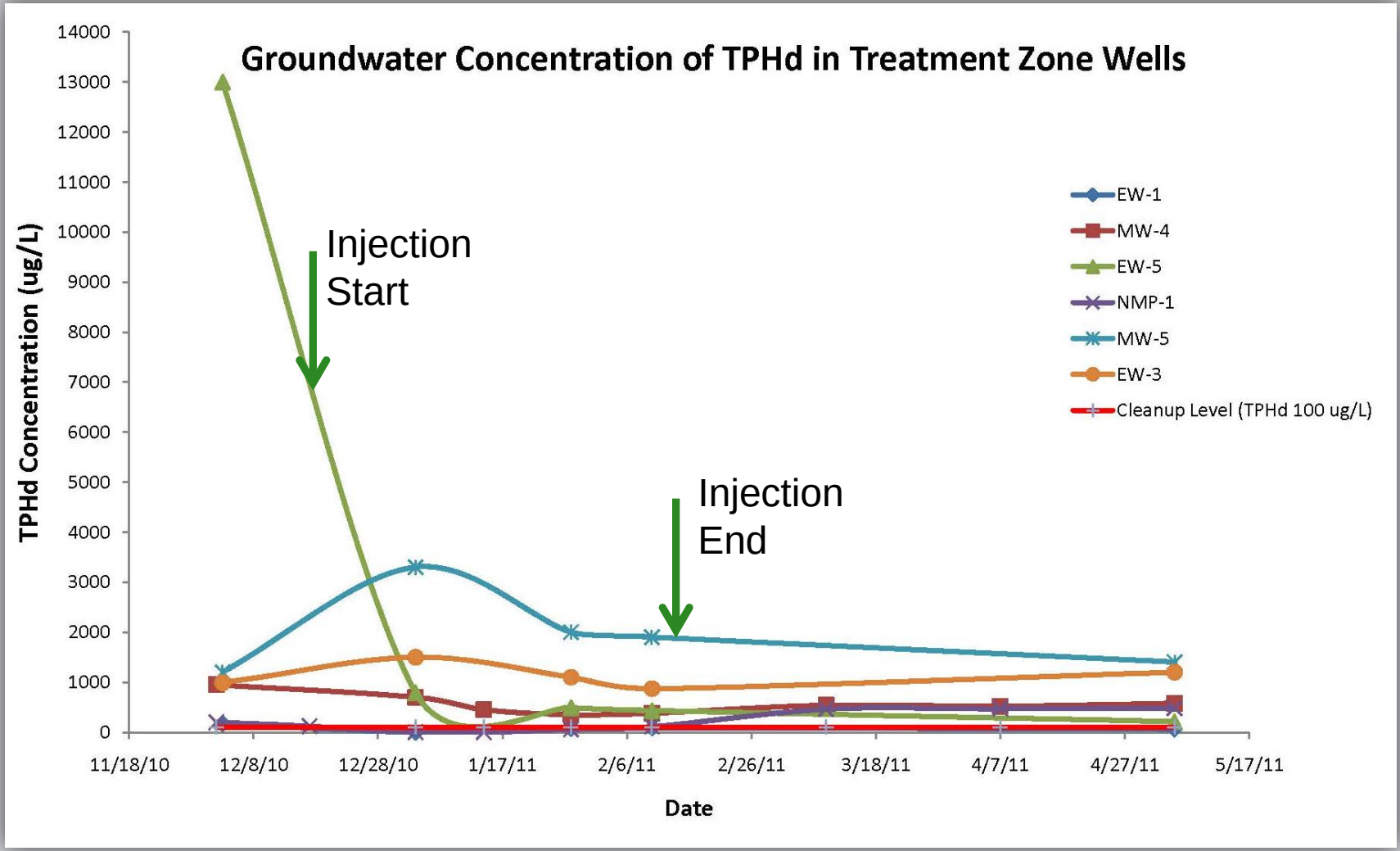
Monitoring Specifics

- O&M site visits – two times a week
- GW and SG monitoring
- Inspected for leaks, proper injection parameters, fugitive emission monitoring

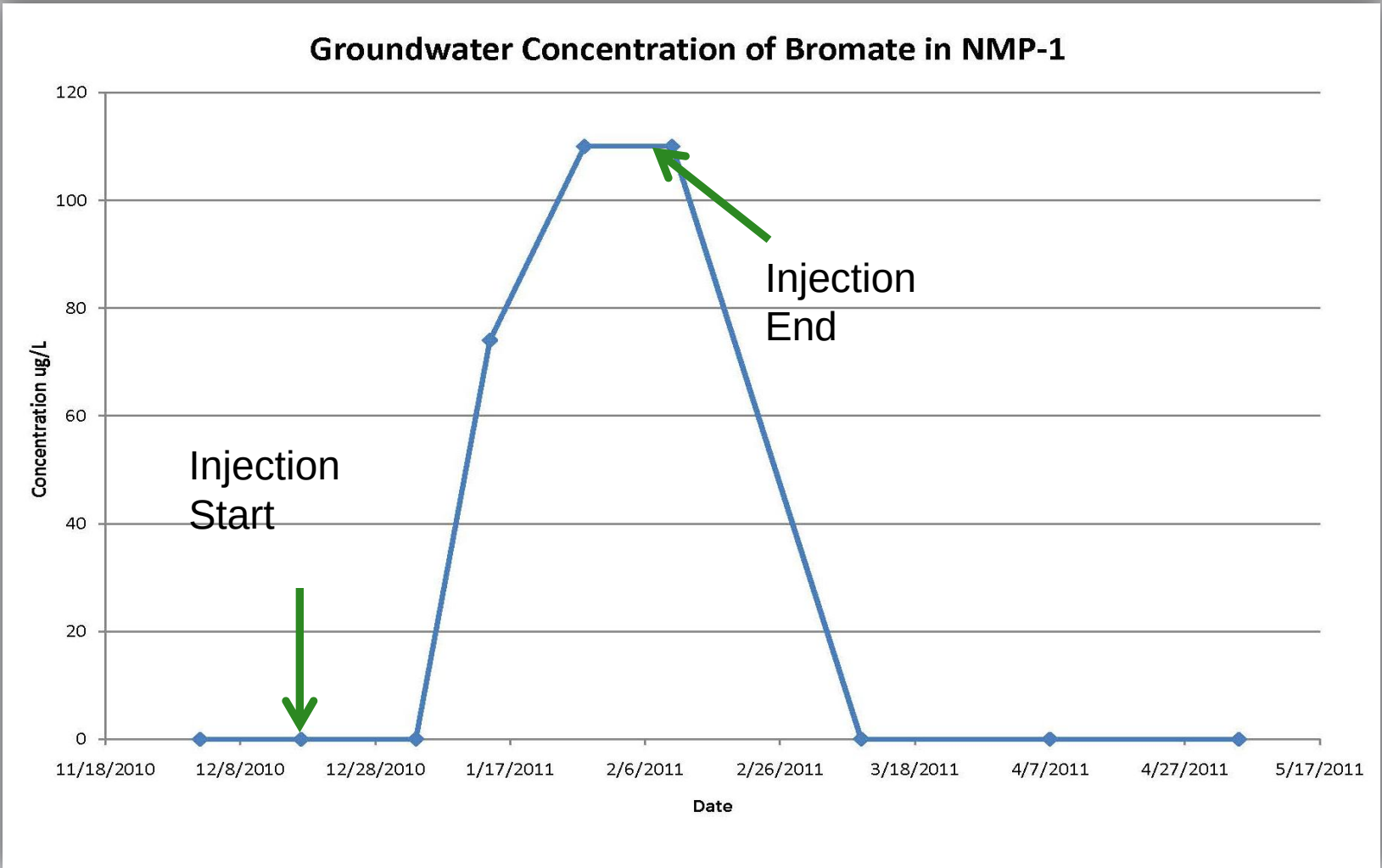
Long-Term Ozone Sparging Test - Results

- Concentrations of GRO and BTEX inside treatment zone typically non-detect;
- Concentrations of DRO had a decreasing trend with notable decreases;
- Concentrations of secondary impacts increased in the treatment zone to above water quality objectives
  - Hexavalent chromium as high as 44 µg/L (WQO 2 µg/L)
  - Bromate as high as 110 µg/L (WQO 10 µg/L)
- Increasing trends of ORP and DO in field measurements in the treatment zone during injection indicates an increased state of oxidation during injection.

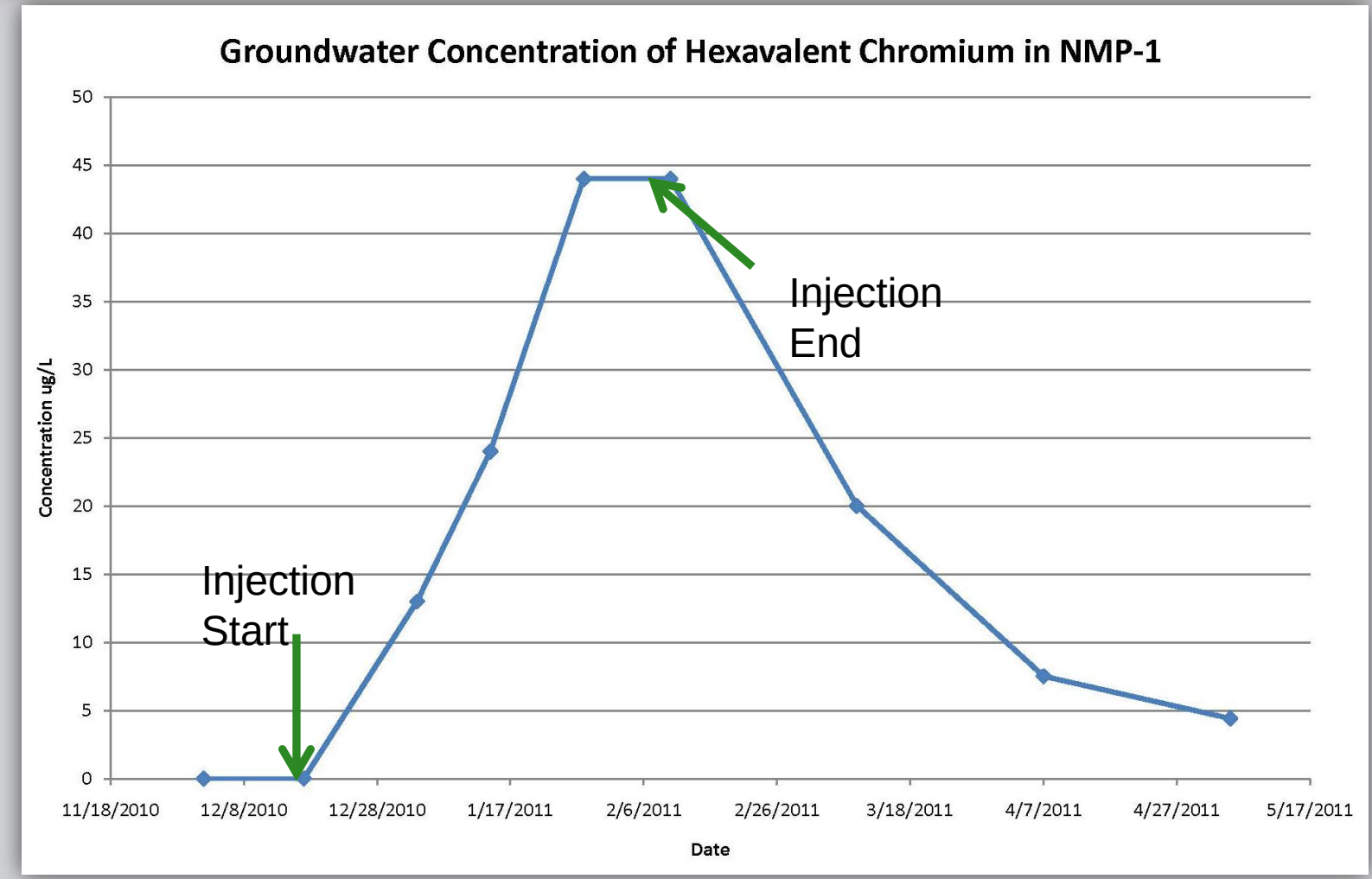
Pilot Test Results - Groundwater COCs



Pilot Test Results - Secondary Impacts: Bromate



Pilot Test Results - Secondary Impacts: Cr^{+6}



Pilot Test Results – Soil Sampling

Pre-Pilot and Post-Pilot Soil Concentrations

Location	Depth (ft bgs)	Date	GRO (mg/kg)	DRO (mg/kg)
OS-1	17	9/1/2010	340	1000
		2/23/2011	ND	26
NMP-1	15.5	9/2/2010	ND	26
		2/23/2011	ND	6.7
NMP-1	20	9/2/2010	ND	6.5
		2/23/2011	ND	ND

COC Removal and Rebound

- Concentrations of GRO and BTEX inside treatment zone typically non-detect.
- Concentrations of DRO had a decreasing trend with notable decreases.

Well	Baseline (µg/L)	Post-Injection (µg/L)	Rebound (µg/L)
NMP-1	200	ND	460
EW-1	170	ND	88
EW-5	13,000	430	490

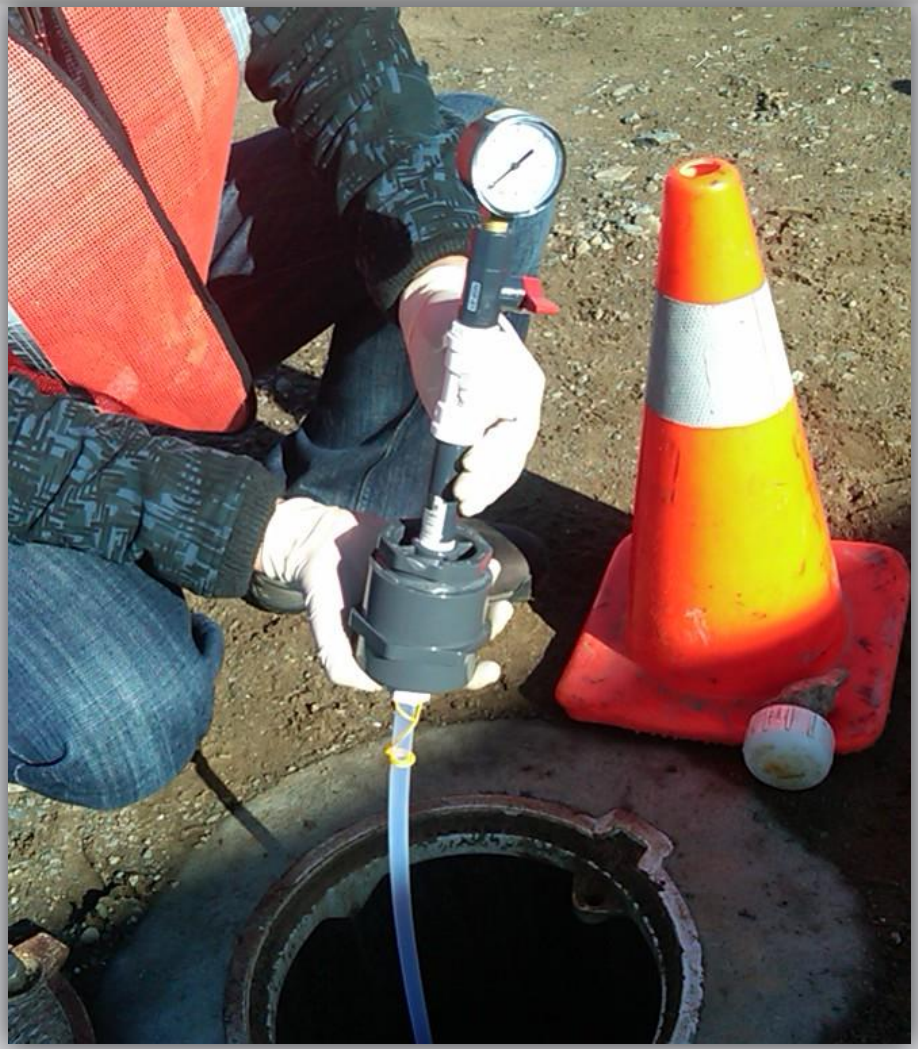
Secondary Contaminants

- Hexavalent Chromium and bromate detected in only NMP-1.
  - Increased above water quality objectives of 2 µg/L and 10 µg/L respectively
- Hexavalent Chromium decreased more than 50% the first month and each month thereafter to reach baseline levels in three months
- Bromate decreased more rapidly and was near baseline levels in one month

Conclusions – Overall

- ISCO using ozone successfully destroys COCs in saturated zone.
- Ozone injection should be targeted to areas that experience large rebound.
- Groundwater secondary impacts attenuated to their background levels without any secondary treatment.
- Ozone/VOCs did not impact offsite residence and can be contained within treatment zone by controlling injection rate without initiating a mobile SVE system.
- This technology is fit for this site and can be scaled up.
- Materials selection is very important!

Injection Location



Injection Locations (View to the SE)

Injection Locations (View to the NW)

Questions

Thank You