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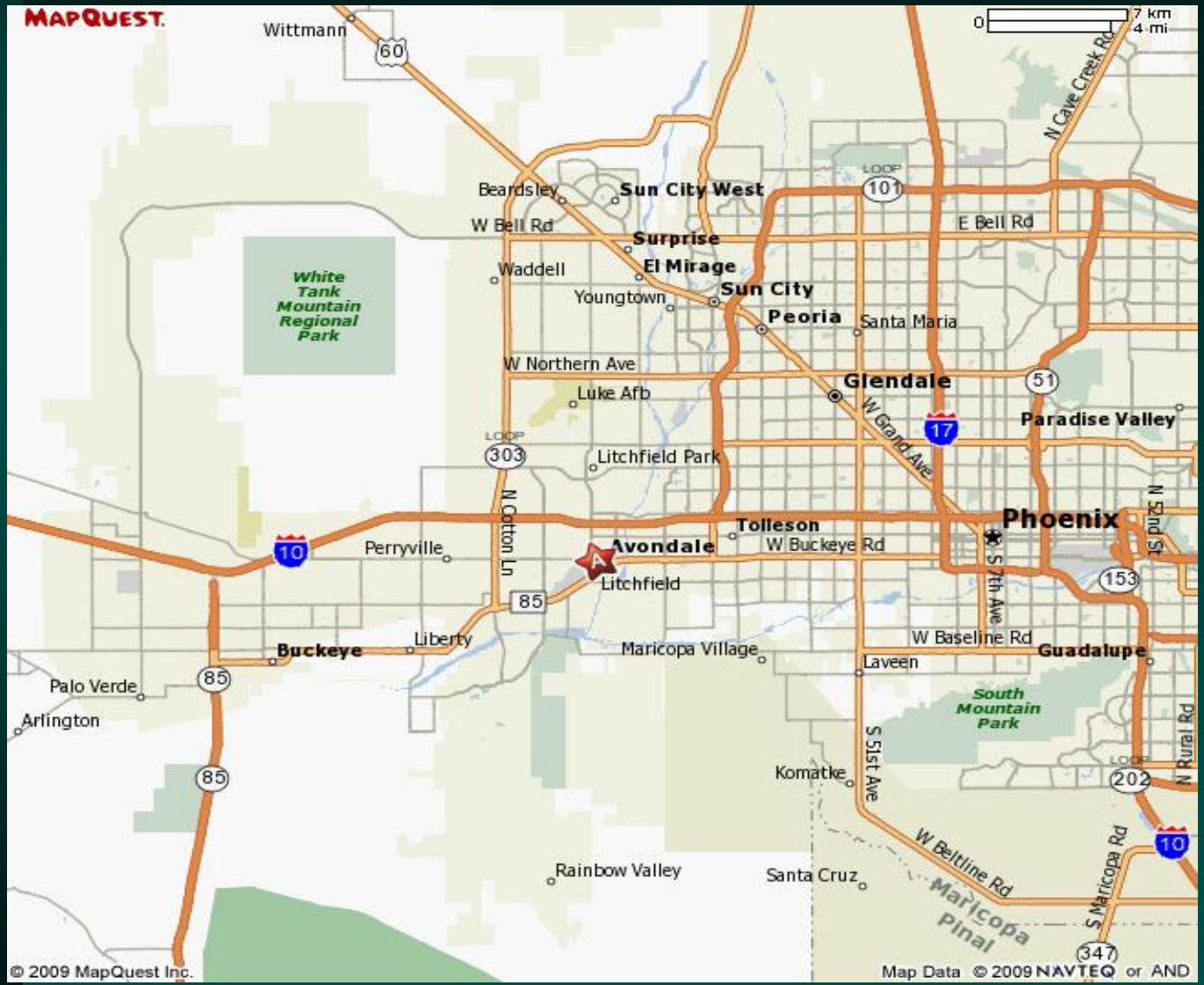
The Evolution of a Field Application of nano Scale Zero Valent Iron (nZVI) in a Deep Low Permeability Aquifer

Site Description

- Site is approximately 72 acres located in Goodyear, Arizona
- located in the western part of the Salt River Valley in the Sonoran Desert of central Arizona
- semi-arid climate, average rainfall 7.1 inches per year

Site Location Map



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Site History

- operated by Unidynamcis Phoenix Inc. from 1963 to 1993
- used for research, design, development, testing and manufacturing of ordnance components and related electromechanical devices used in defense and aerospace applications
- site utilized aprox. 180 different chemicals during its operation
- site consisted of 25 buildings, 10 – 750 gallon sedimentation tanks, 12 drywells, and 2 shallow oxidation ponds
- disposal of non explosive waste chemicals was done exclusively onsite through drywells, sedimentation tanks, and oxidation ponds
- Placed on NPL in late 1980s

Regional Geology and Hydrogeology

- **site is located within the basin and range physiographic province, West Salt River Valley**
- **soils are primarily sandy loams, loams, and clay loams on alluvial fans and valley plains**
- **three hydrogeologic alluvial sub units:**

1. Upper Alluvial Unit (UAU) – gravel, sand and silt, mostly unconsolidated

2. Middle Alluvial Unit (MAU) – silt, siltstone, silty sand and gravel, weakly consolidated, moderately well cemented

3. Lower Alluvial Unit (LAU) – clays, silts, mudstone, evaporites, sandstone, gravel, conglomerate and andesitic basalt, moderately to well cemented, upper part of unit is weakly to well cemented and contains inter-bedded sand, gravel and conglomerate

Site Geology and Hydrogeology

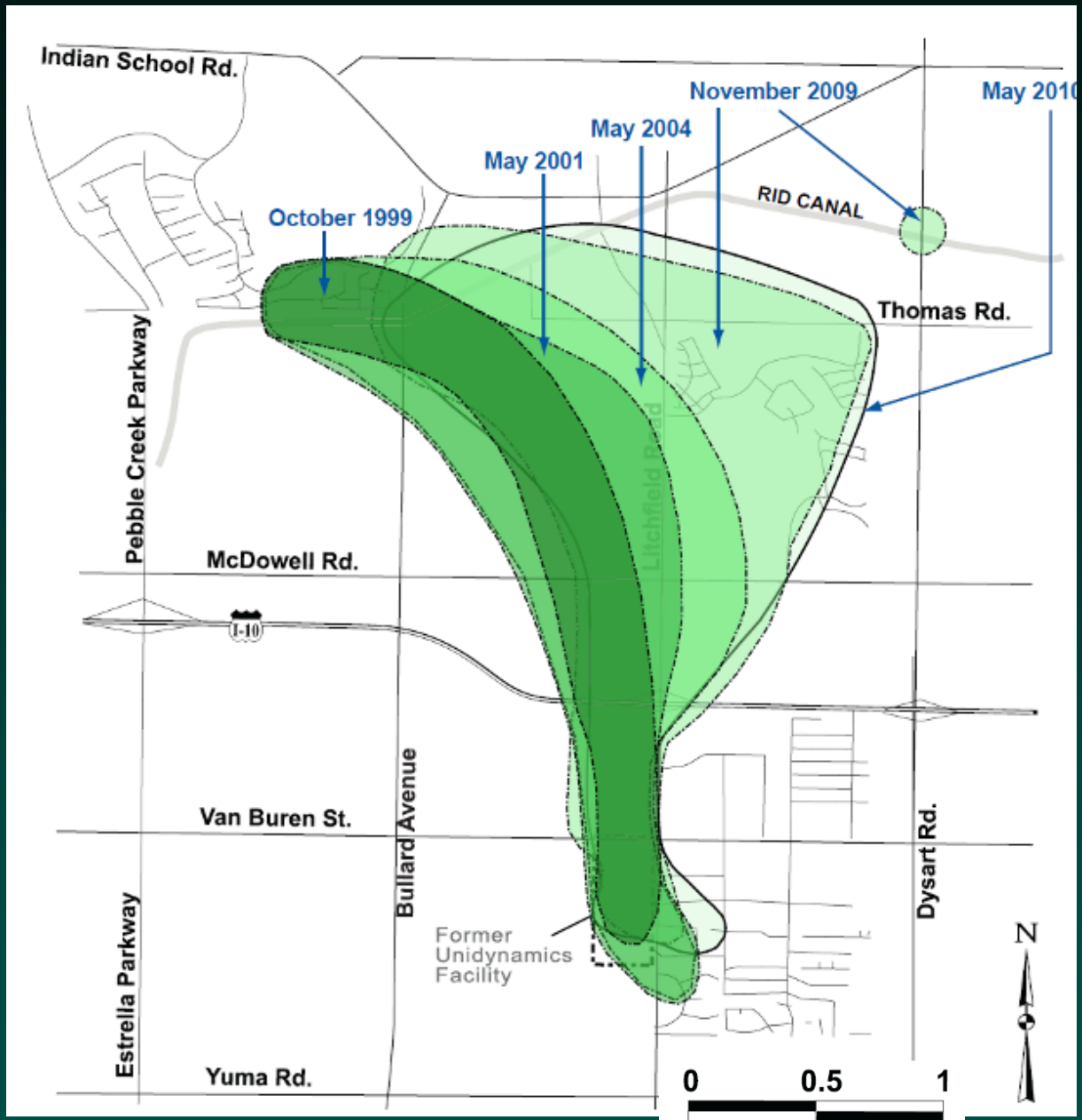
- site overlies the UAU
- 350 ft thick
- local stratigraphic sequence of UAU:

1. Subunit A – silty sands with thin lenses of gravel an fine grained soil, from surface to 160 ft bgs, 1/3 to ½ of lower portion saturated and considered an aquifer, depth to water 70 to 80 ft bgs, regional groundwater flow, north-northwest
2. Subunit B – sandy silts and/or clay, 50 to 70 feet thick, fully saturated, possibly discontinuous in north areas of the site
3. Subunit C – silty sands, sandy silts, gravely sands, 130 ft thick, fully saturated and considered an aquifer, local gradient west north-west

Contaminants of Concern

- Primary COCs identified at the site include
- TCE
- perchlorate
- found in all subunits
- highest soil concentrations to date found in the main dry wells area (5,585 ppm TCE, 41.5 ft bgs)
- highest GW concentrations to date located upgradient of the main drywells area (41,500 ug/L TCE, 110 ft bgs)

SubUnit A Plume Map



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Main Drywells Area

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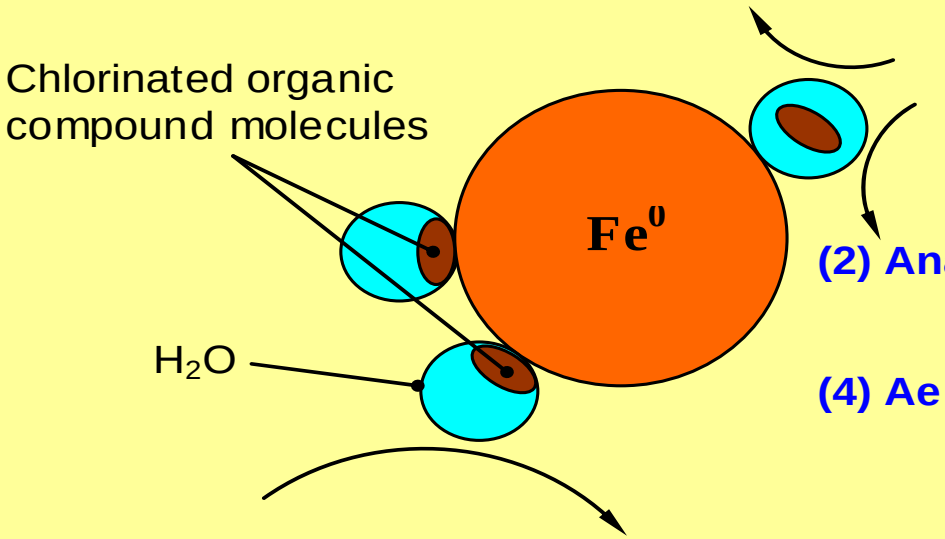
nZVI Chemistry

Zero-Valent Iron Reactions

(3) Reductive dehalogenation by hydrogen gas:

$H_2 + XCl + catalyst = XH + H^+ + Cl^-$



(2) Anaerobic iron corrosion:

$Fe^0 + 3H_2O = Fe^{2+} + 3OH^- + H_2 + H^+$

(4) Aerobic iron corrosion:

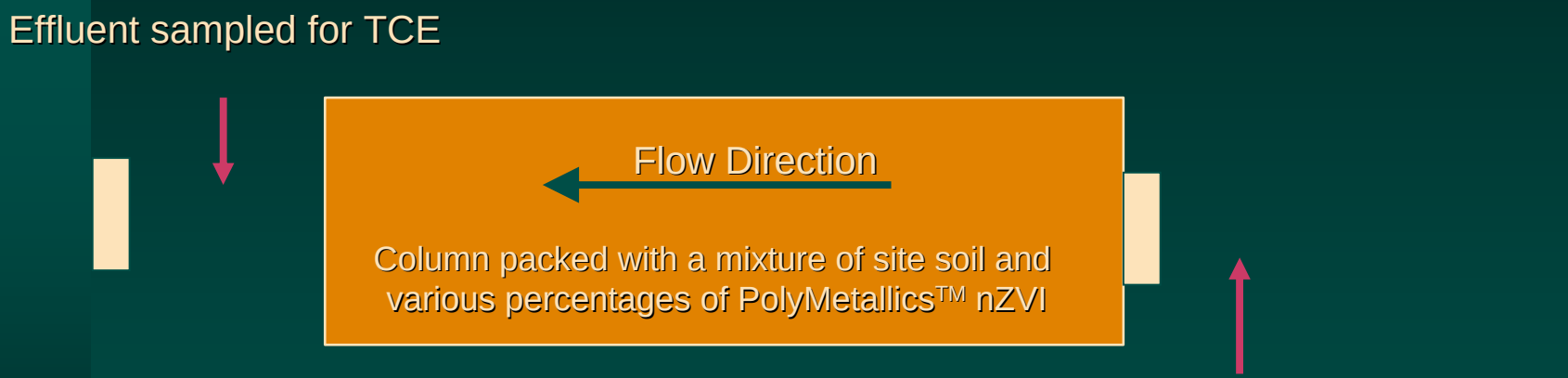
$2Fe^0 + O_2 + 2H_2O = 2Fe^{2+} + 4OH^-$

(1) Direct reduction on metal surface:

$Fe^0 + H_2O + XCl = Fe^{2+} + OH^- + XH + Cl^-$

Bench Test Column

- 4 columns were tested
- 3 with 2%, 1%, 0.5% nZVI,
- one with 0.5% palladium coated nZVI



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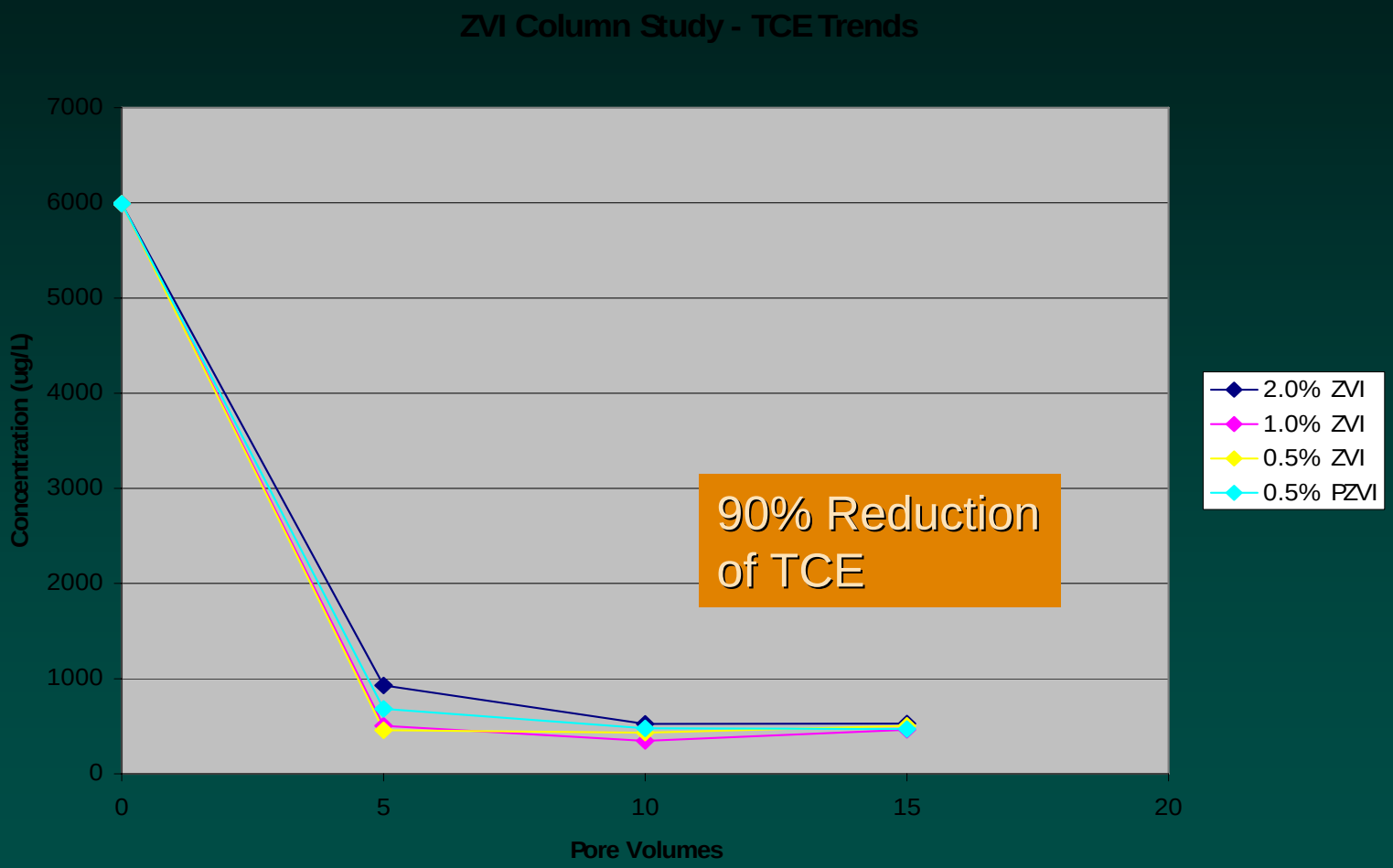
Results of Column Test



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Lessons Learned from Column Test

- column test proved concept, nZVI will reduce TCE
- column test must approximate site conditions as closely as possible, no ZVI was injected through the site material in the column
- kinetics testing was not completed, should be completed for all technologies with reaction rates

Field Pilot Test

- nZVI was shipped in 50 gallon drums in a water slurry
- drums were onsite several weeks prior to injection
- slurry was measured and mixed with potable water to produce a 20% nZVI injectate mixture
- mixing was done in a 500 gallon polytank through recirculation
- recirculation hose clogged, so material was mixed with a mechanical mixer prior to addition to the polytank
- mixing was completed for 30 to 45 minutes prior to injection

Field Pilot Test

- nZVI slurry was injected under pressure (50 psi) into well IW-01
- immediate back pressure resulted in reduction of injection pressures
- refusal of nZVI slurry occurred, moved to injection well IW-02
- same injection refusal occurred
- 50 lbs of nZVI were injected
- projected volume was to be 1000 lbs

Lessons Learned from Pilot Test Phase I

- material properties are very critical to delivery (ie. particle size and age)
- chemical properties including pH, ionic strength and surface chemistry (coatings) have the potential to influence mobility
- agglomeration is a persistent problem with nZVI and can be caused by material age, shipping conditions and groundwater chemistry
- agglomeration is irreversible, additional mixing will not sufficiently reduce agglomerated particle size
- site specific chemistry must be considered
- mixing and injection techniques should be tested at the bench scale to the extent practicable
- information on kinetics of material are required

Post Injection Testing

- **Falling Head Tests**
  - Performed on both Injection Wells
  - Pre-Injection Recovery ~ 15 minutes
  - Post-Injection Recovery ~ 4 – 5 hours

Phase II Pilot Test

- bench testing for batch kinetics on raw nZVI and nZVI amended with dispersant solution were completed prior to Phase II test
- 2 additional injection wells were installed in June 2007
- Phase II field injections were completed summer 2007

Injection System Layout

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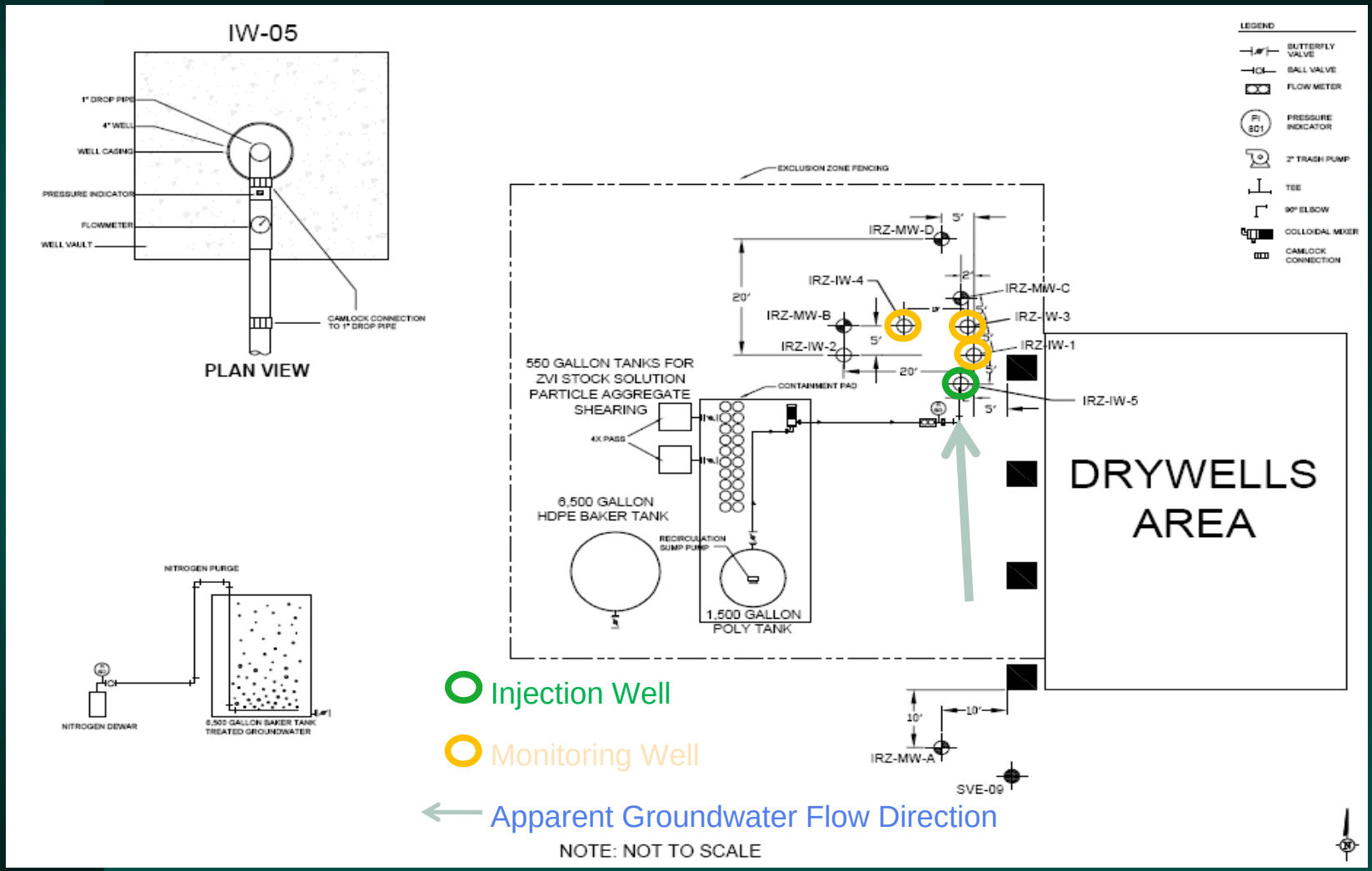
Injection System Layout



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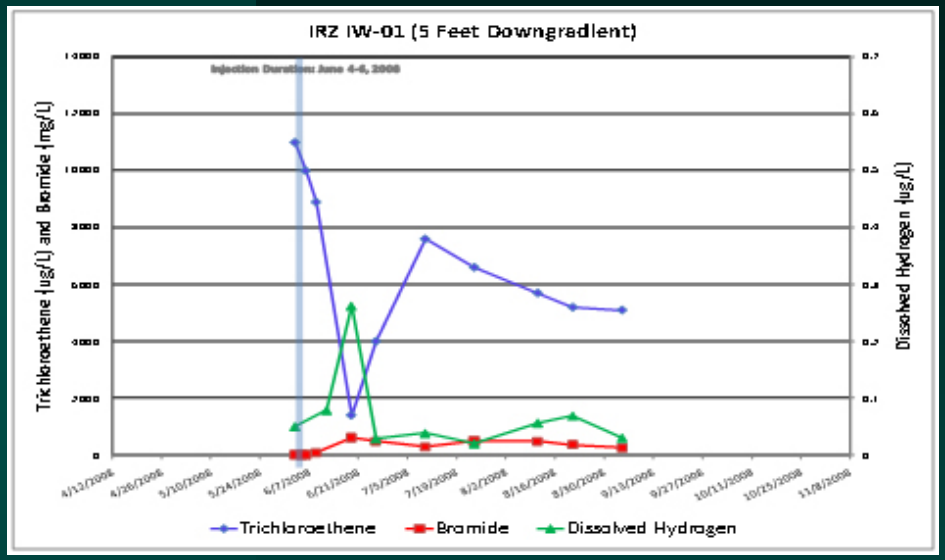
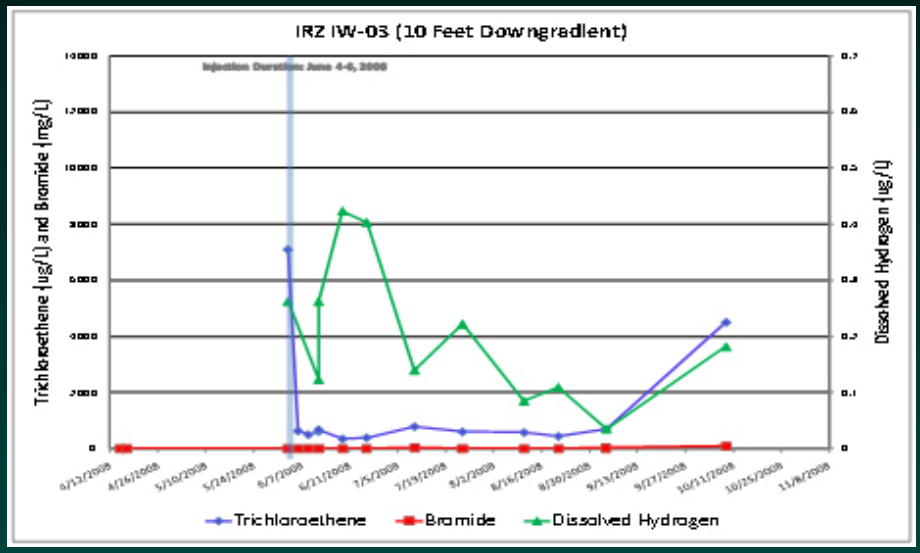
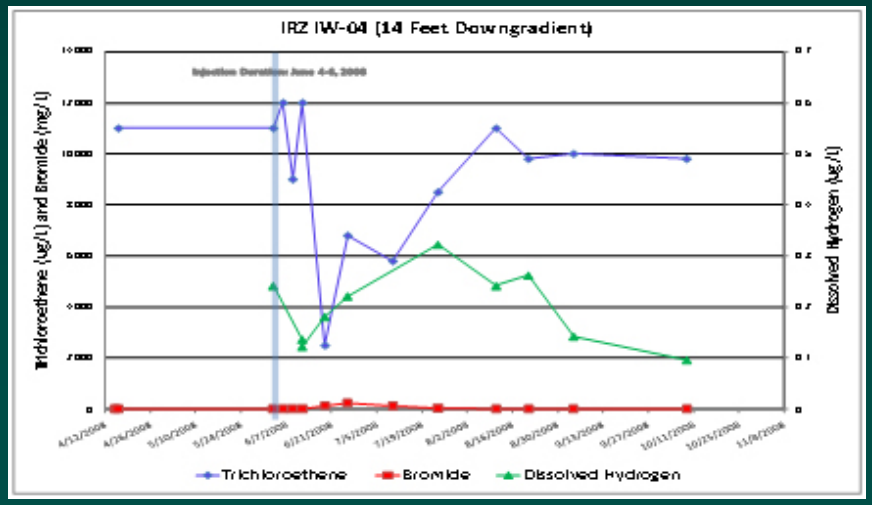
Phase II Injection Results







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Summary of Field Pilot Testing Phase II

- Injected 2,700 gallons of nZVI solution (~50 lbs) over three days
- nZVI distribution was likely limited to the immediate screen area
- Preliminary data indicate rapid decline in TCE concentrations in wells near the injection location, but rebound was prevalent
- injection wells are not re-usable

Phase III - Pilot Test

- injection under pressure
- nZVI solution increased to 21 g/L
- nZVI preparation remained the same
- goal to inject 8000 gallons over 4 fractures
- 350 lbs nZVI per fracture
- Completed February 2010

Injection Technique

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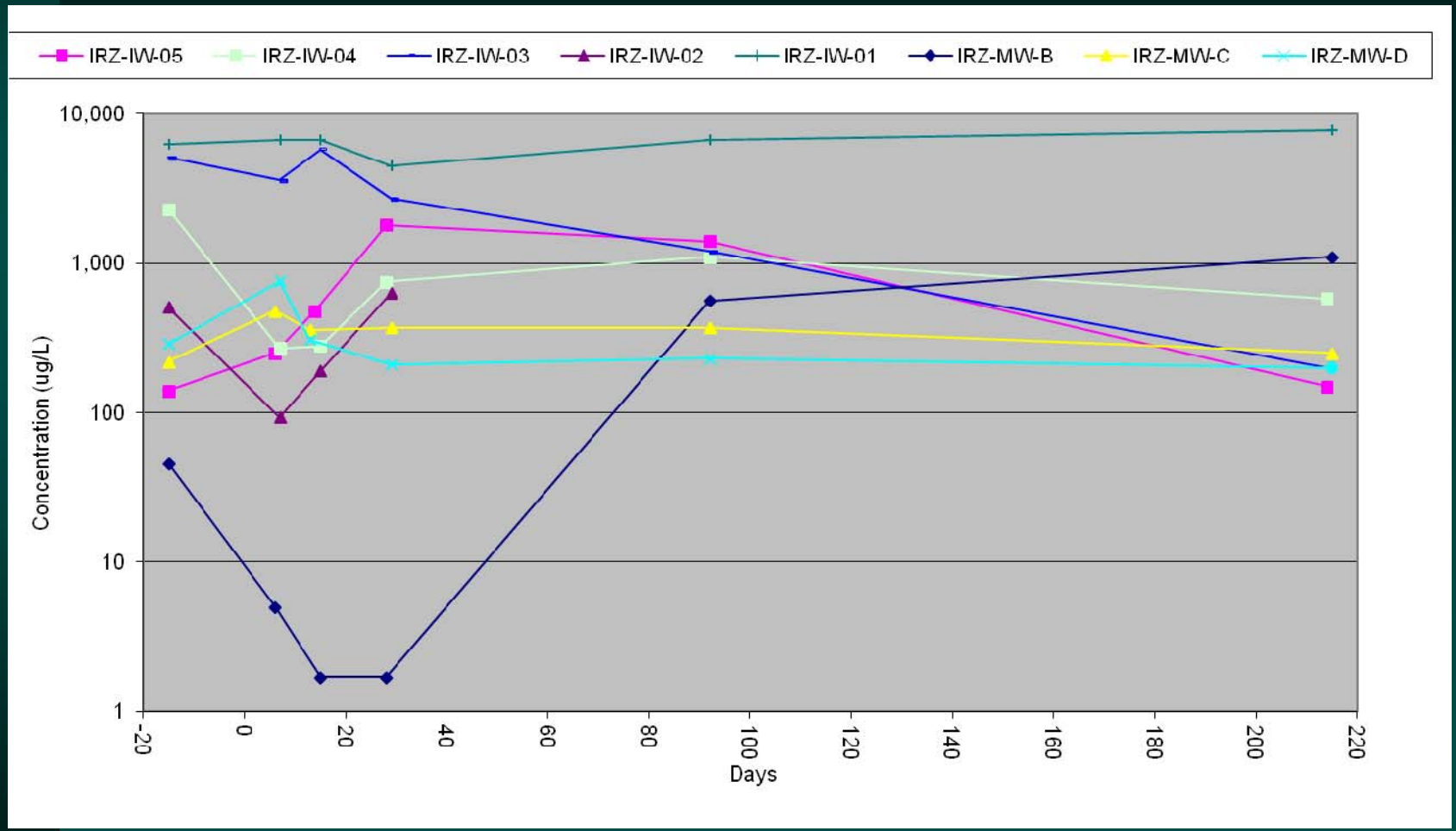
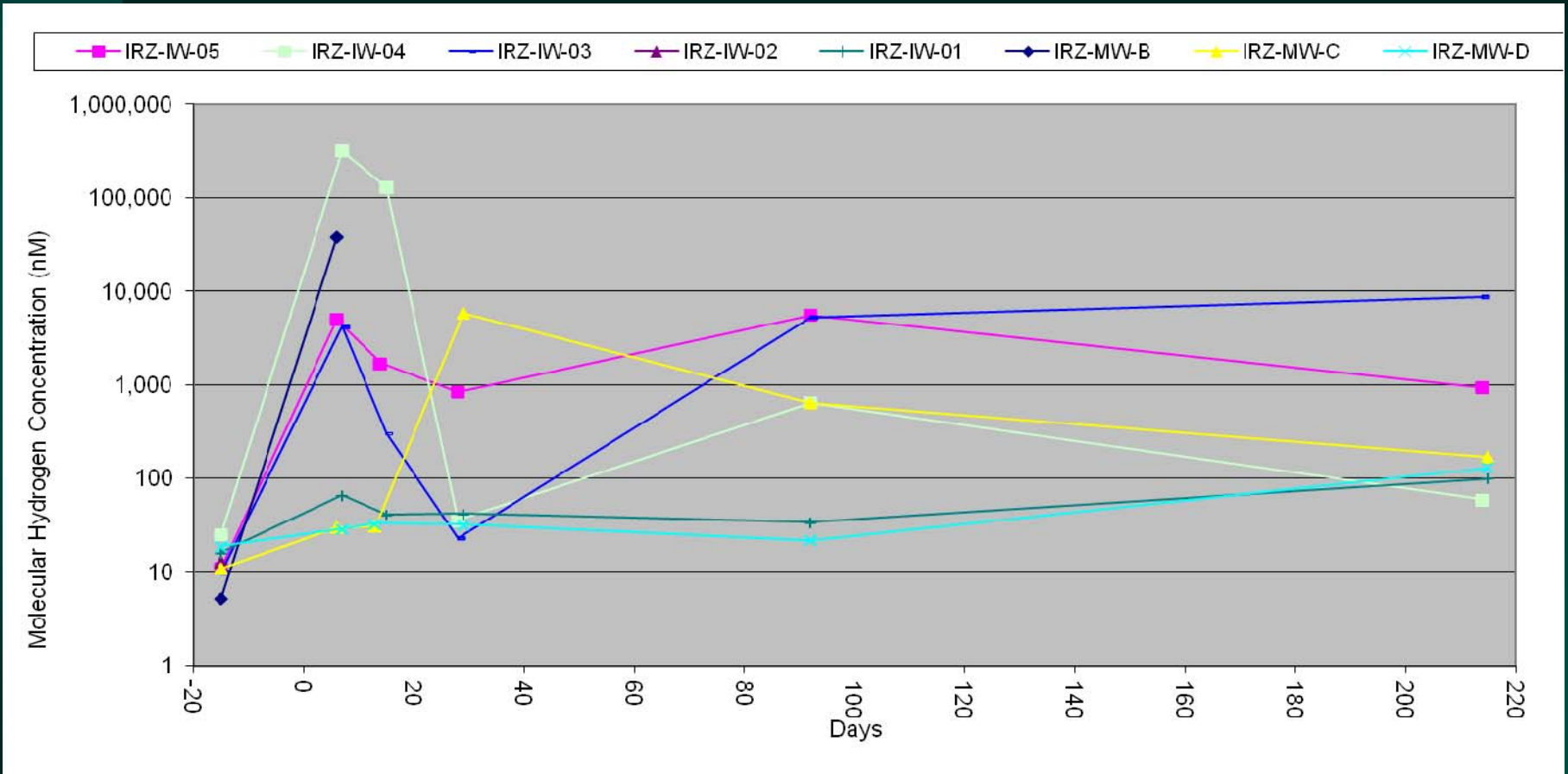
TCE Results


IRZ-IW-05
IRZ-IW-04
IRZ-IW-03
IRZ-IW-02
IRZ-IW-01
IRZ-MW-B
IRZ-MW-C
IRZ-MW-D
10,000
1,000
100
10
1
Concentration (ug/L)
-20
0
20
40
60
80
100
120
140
160
180
200
220
Days

Hydrogen Results



Conclusions

- Pressure injection method was successful in delivering the calculated volumes of nZVI
- Radius of influence was estimated at 20 feet from injection point
- Future applications are under discussion
- Method may be cost prohibitive based on use of nZVI, injection method with more cost effective injectate will be necessary to ensure delivery of amendment

Acknowledgements

CRANE POLYFLON

A Crane Co. Company

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Questions?

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