Federal Remediation Technologies Roundtable

Source Removal of VOC Contaminants in Bedrock

Letterkenny Army Depot
Chambersburg, Pennsylvania

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Special Thanks

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- Mike West
- Ed Kellar
- Mark Tucker

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Site Information and Background/Pilots

- LEAD has Two (2) NPL sites
- SE (Southeast Area)
- PDO (Property Disposal Office Area)

- SE OU 3A DA Pilot Study - In-Situ Chemical Oxidation (Fenton's). SE OU 3A Currently in PP Stage

SE Pilots (cont)

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- SE OU 11 In-Situ – Peroxone Pilot Study (Lagoon Area) Currently in PP Stage

  SE OUs 3A and 11 discharge to SE OU Six (Offpost groundwater) PP

- SE OU 10 SSIA Contaminated Groundwater (VOCs and BTEX); Enhanced Bio Currently in RAO

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SE OU 3A, 10 & 11 Site History

- Sources of Volatile Organic Compounds (VOCs) contamination in SE 11: former leaking industrial wastewater sewers, former Industrial Waste Treatment Plant (IWTP) lagoons .

- Sources of VOC contamination in Disposal Area (DA): former waste solvent disposal lagoons (Area K-1), and spill area (Area A).

- VOC contamination in SE OU 10 leaking industrial wastewater sewers

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Oxidizer Strength

Substance	Volts	ISCO
Fluorine	3.0	No
Hydroxyl Radical	2.8	Yes
Ozone	2.1	Yes
H_2O_2	1.8	Yes
2 KMnO4	1.7	Yes

Study Areas

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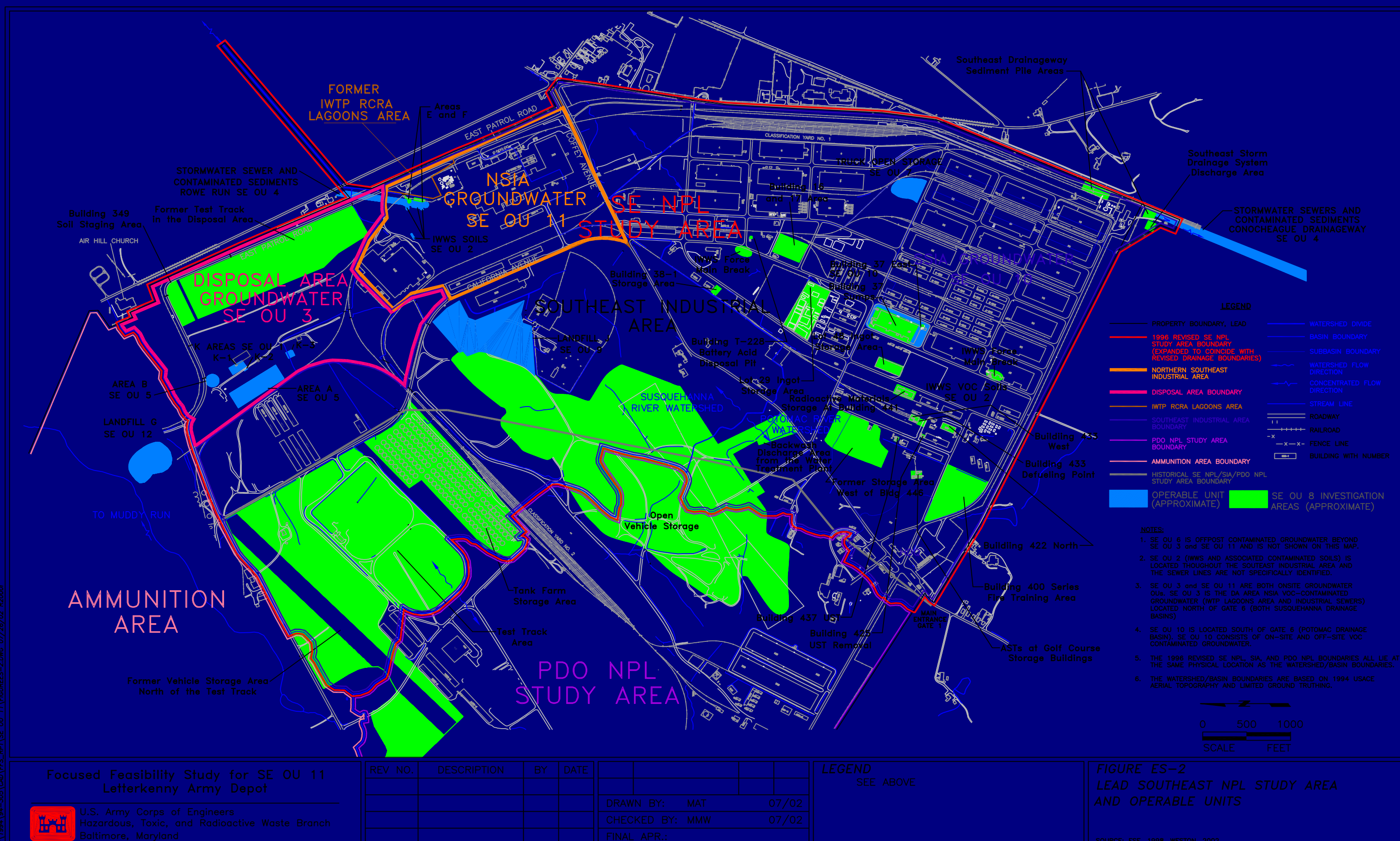

In Situ Chemical Oxidation Pilot Study of a DNAPL Source Area Within the SE OU 3A Karst Bedrock Aquifer

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K-1 Area Site History

- Former waste solvent disposal lagoon (10^6 gallons)
- Source removal no effect on groundwater quality treated using LT^3
- VOC-impacted groundwater sources/plume delineated in DA

Geology

- St. Paul formation (ordovician limestone)
- Karst features present (solutioning)

Hydrogeology

- Generally high flow/permeability 20+ gpm yields
- Water table ranges from ~5 ft. to >30 ft. bgs

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Characterization of Source Area

- Review historical groundwater data, dye study data, and pumping test results
- Bench-scale study
  - Evaluate reactivity between limestone bedrock and acidic injection fluids
  - Determine optimal mixture of injection fluids for most effective VOC reductions
- Conduct baseline groundwater sampling
- Geophysical logging/downhole video
- Packer Testing

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Bench Study Results

- pH of injection fluid (3) not effected by dissolved carbonates in groundwater
- Any reaction with bedrock was over within 2 hours.
- Bedrock surface covered with precipated iron which protected rock surface.
- No reaction between bedrock and H_2O_2
- Change of injection fluid pH (from 3 to 5) had no noticable effect on OH. Generation

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Bench Study Results (cont)

- Oxidation efficiency was only mildly influenced by hydrogen peroxide concentration.
- 50% hydrogen peroxide solution resulted in a slightly lower oxidation efficiency relative to 25%, 12.5%, and 6.25% solutions.
- Most likely due to vigorous iron oxidation and precipitation in the 50% solution experiments.

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Groundwater Contamination Summary

- VOC-impacted groundwater plume contains over 94% Chlorinated VOCs
- Chlorinated VOCs consist mainly of 1,2-DCE (61%), TCE (20%), Vinyl Chloride (10.5%), and PCE (3%)
- Maximum Total and Chlorinated VOCs = 114, 242 μg/L (PW-6)

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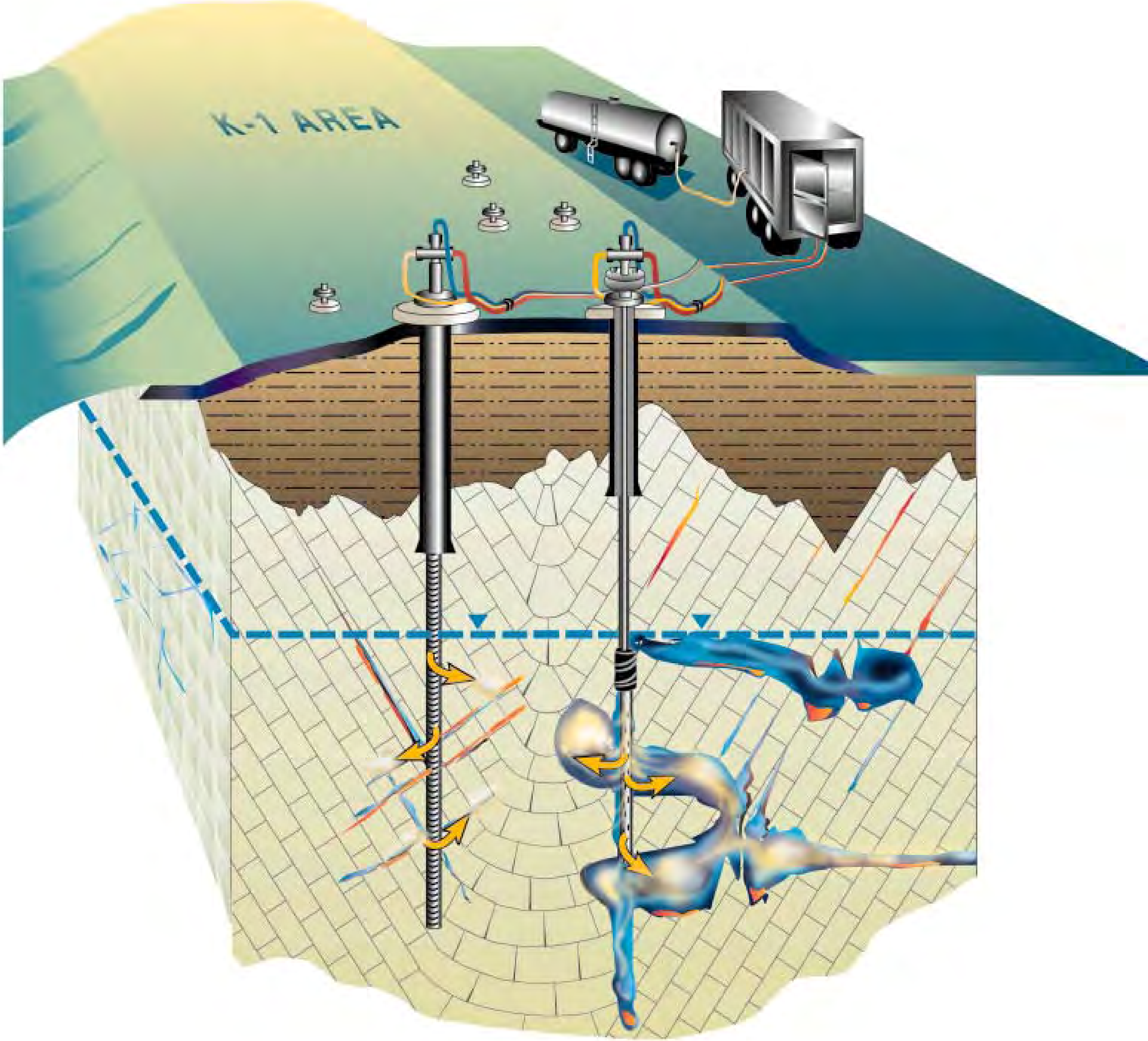

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K-1 Area - Pilot Study Objectives

- Determine effectiveness in Karst setting
  - Reactivity of injection fluids with limestone
  - Success in high flow conditions
  - Ability to achieve proper pH
- Determine if reductions can be maintained
- Determine if organic and inorganic COCs mobilized

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Injection Approach

- Inject from upgradient edge and along bedrock strike
- Use both fixed injectors and movable packer sealed injectors
- Monitor multiple water-producing zones individually during injection
- Collect pre- and post-injection groundwater samples

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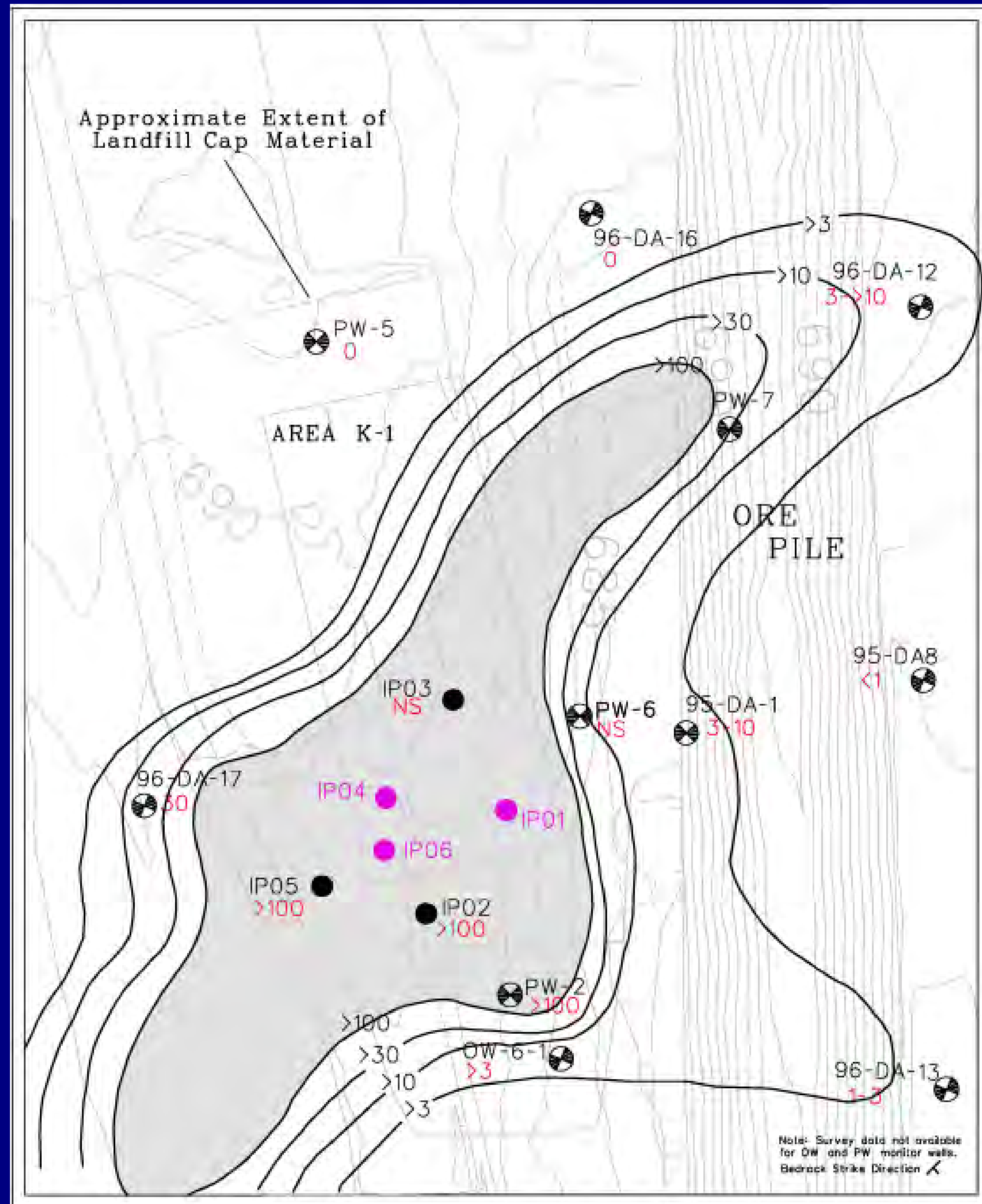
H_2O_2 Distribution Round 7 (03:40-09:50)



Legend

- Roads
- Injection/Monitor Well
- 95-DA-1 Monitor Well
- Injection Point

N

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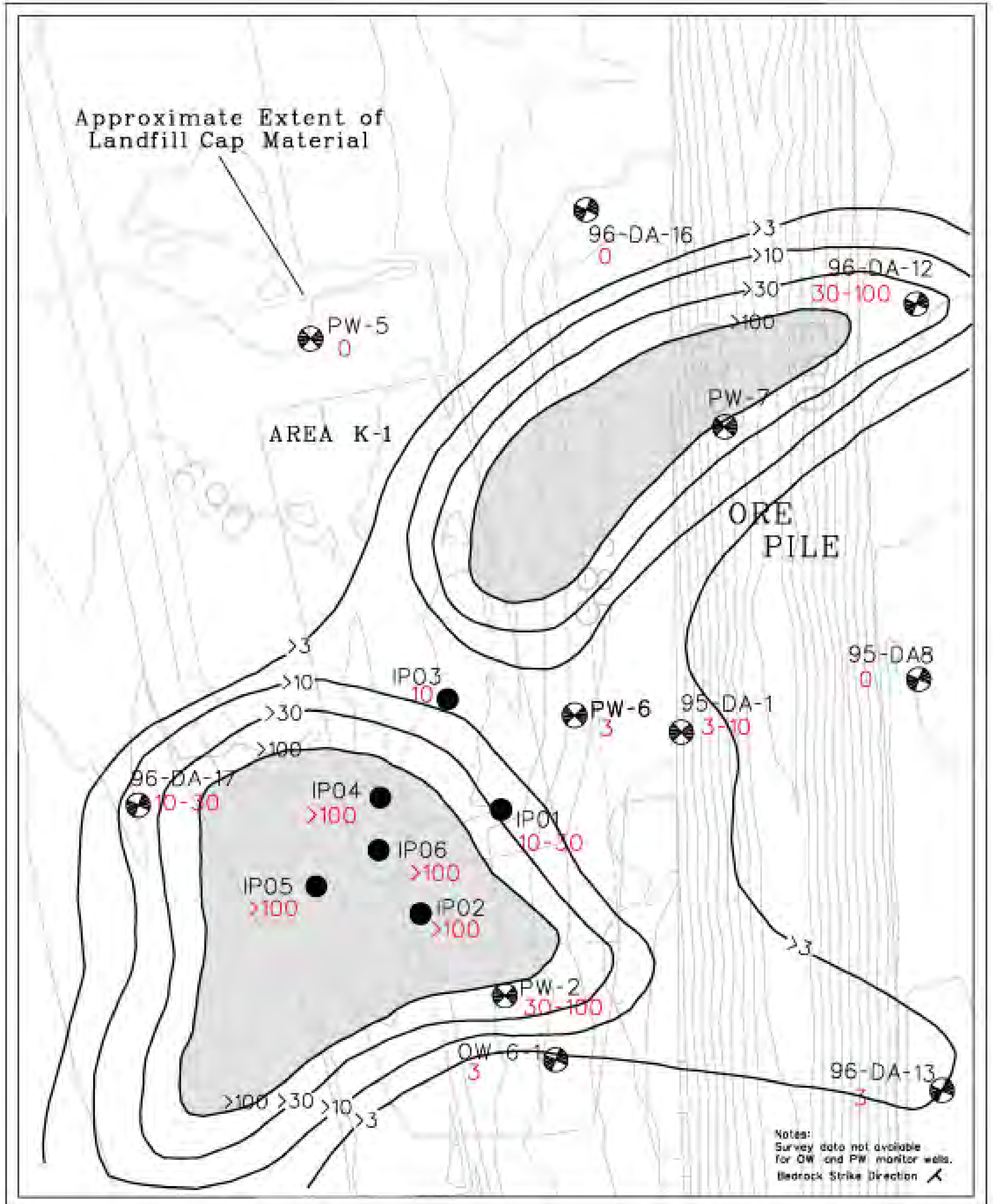
H_2O_2 Distribution Round 9 (24 Hours Following Shutdown)



Legend

Roads

Injection/Monitor Well

95-DA-1 Monitor Well

N

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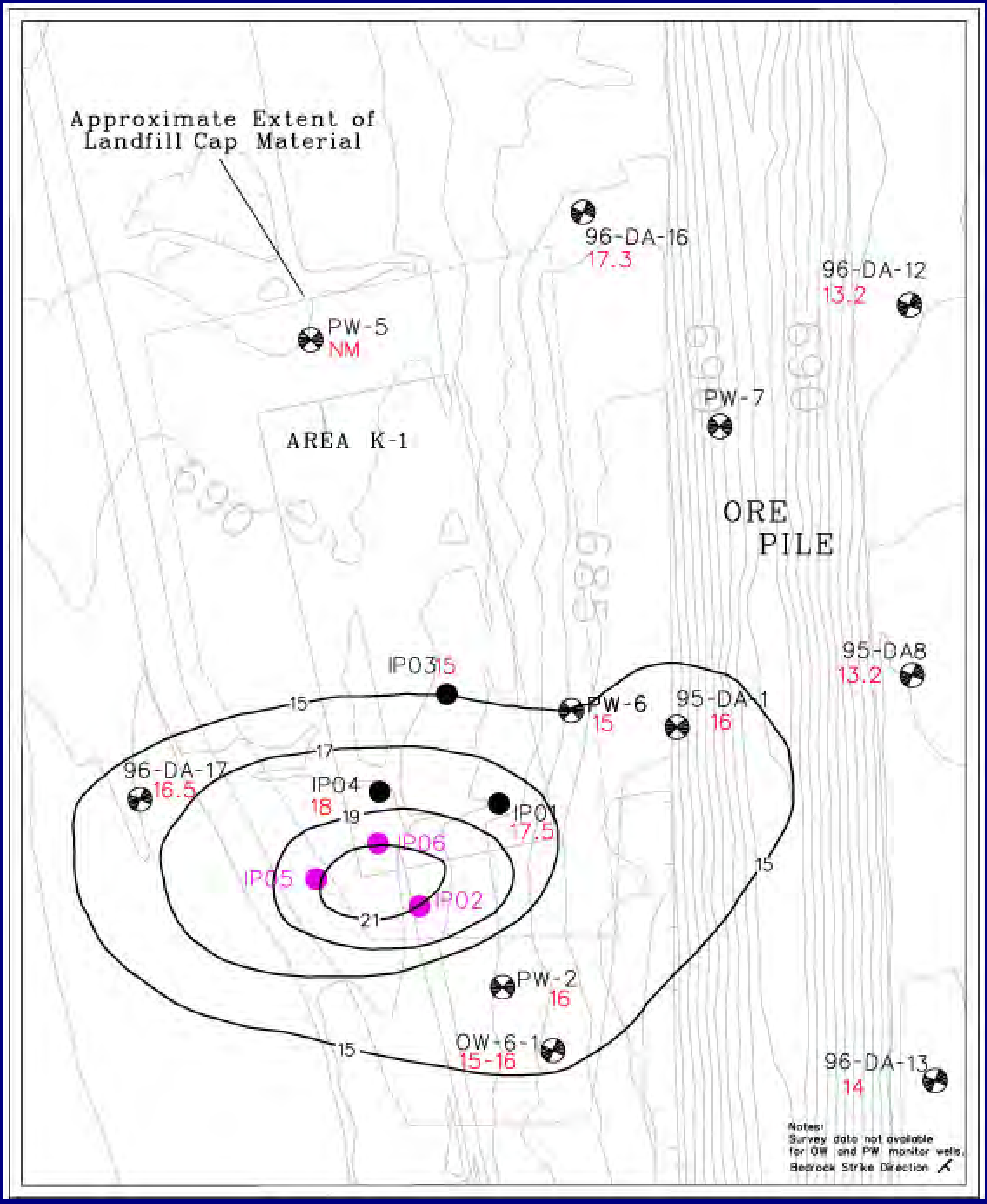
Temperature (°C) Baseline

Legend

- Roads
- Injection/Monitor Well
- 95-DA-1 Monitor Well
- Injection Point

N



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Temperature (°C) Round 8 (4 Hours Following Shutdown)

Legend

- Roads
- Injection/Monitor Well
- 95-DA-1 Monitor Well
- Injection Point

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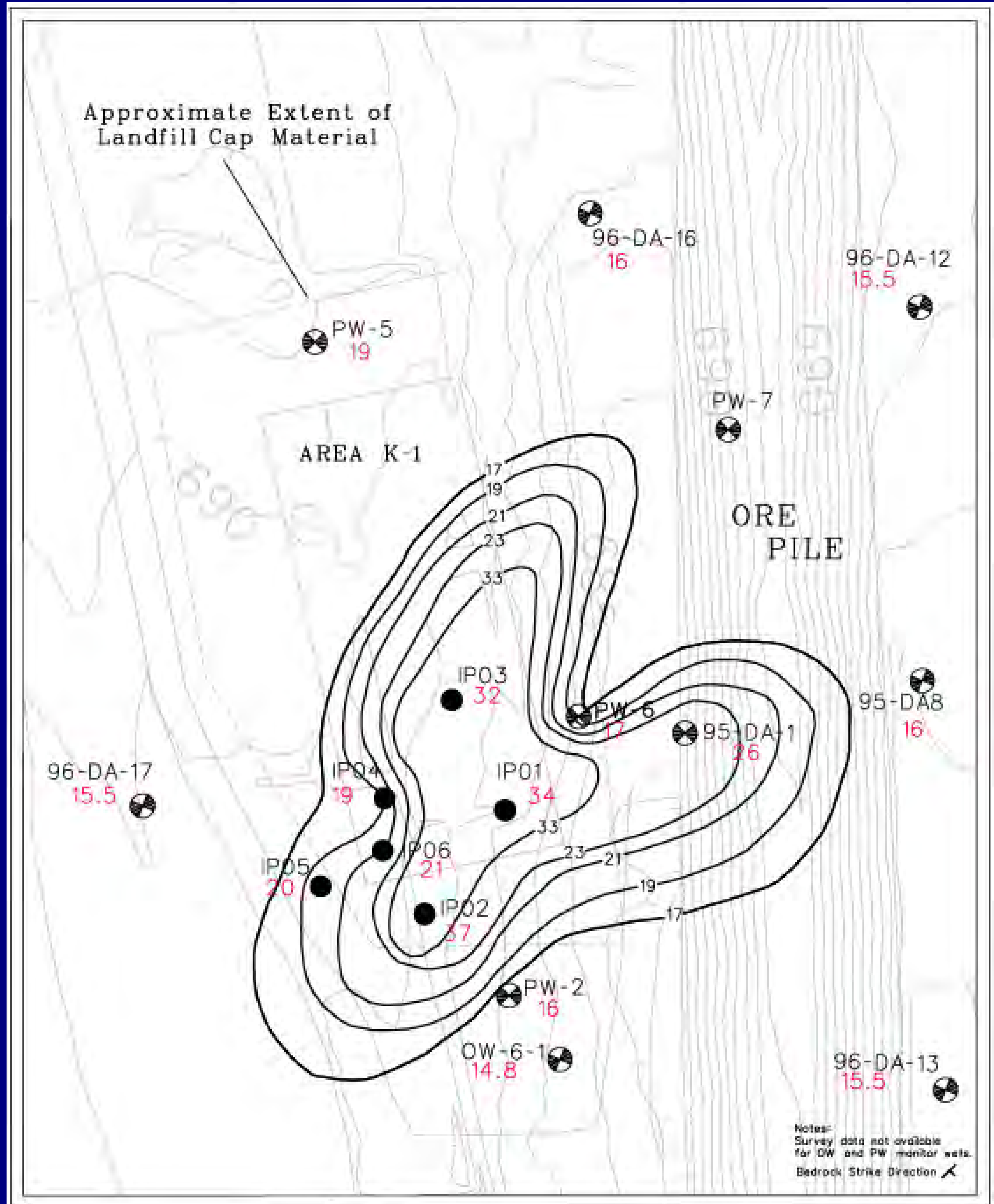

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Pilot Study Operation Summary

- Operated 24 hrs/day for 3.5 days
- Injected 12,700 gallons H_2O_2 (50%)
- Injected 36,000 gallons catalysts
- Collected 7 field monitoring rounds

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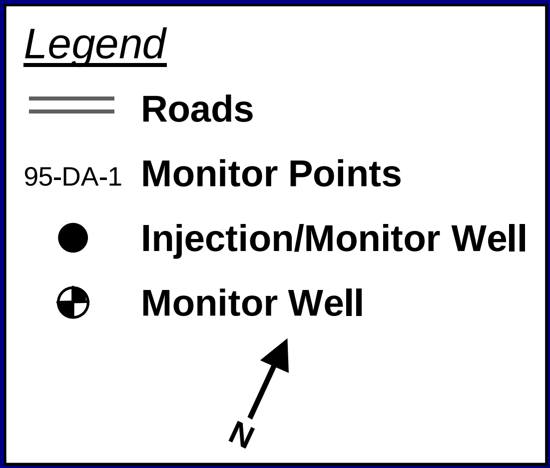
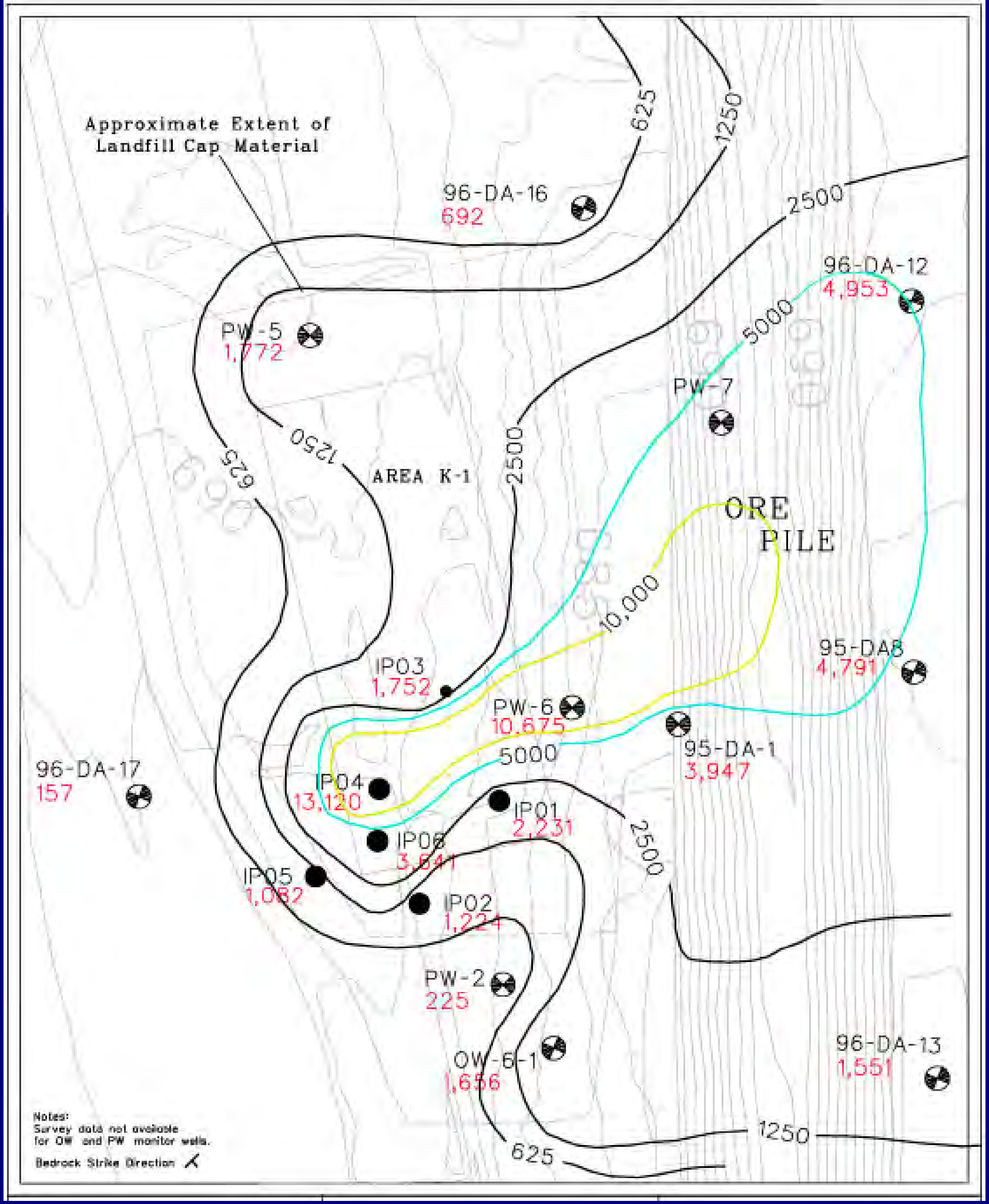
Chlorinated VOCs (µg/L) Baseline Sampling Round





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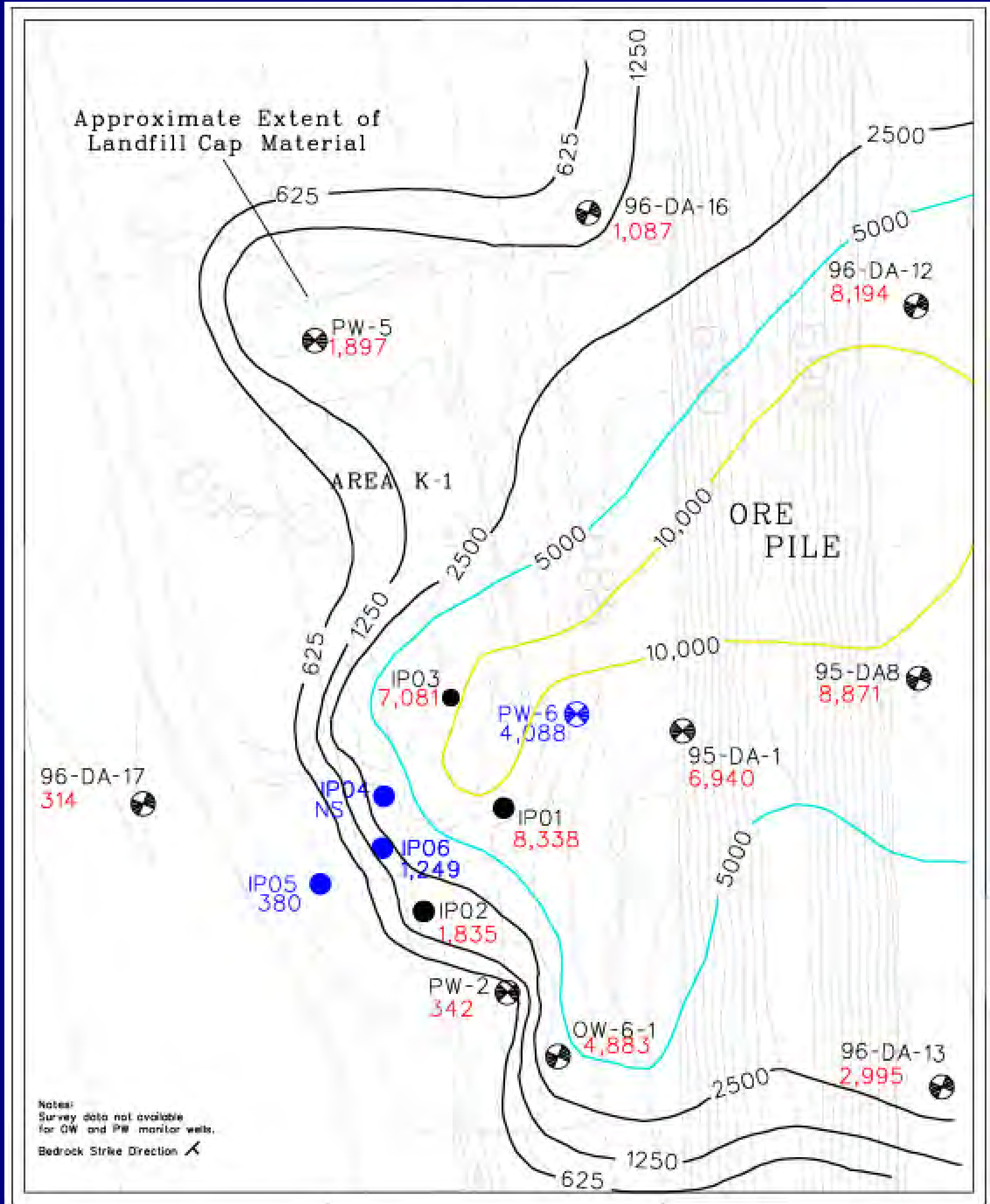
Chlorinated VOCs (µg/L) Post 1 Sampling Round

Legend

- Roads
- 95-DA-1 **Monitor Points**
- ● **Injection/Monitor Well**
- **Monitor Well**
- **VOC Levels Reduced From Baseline**

N



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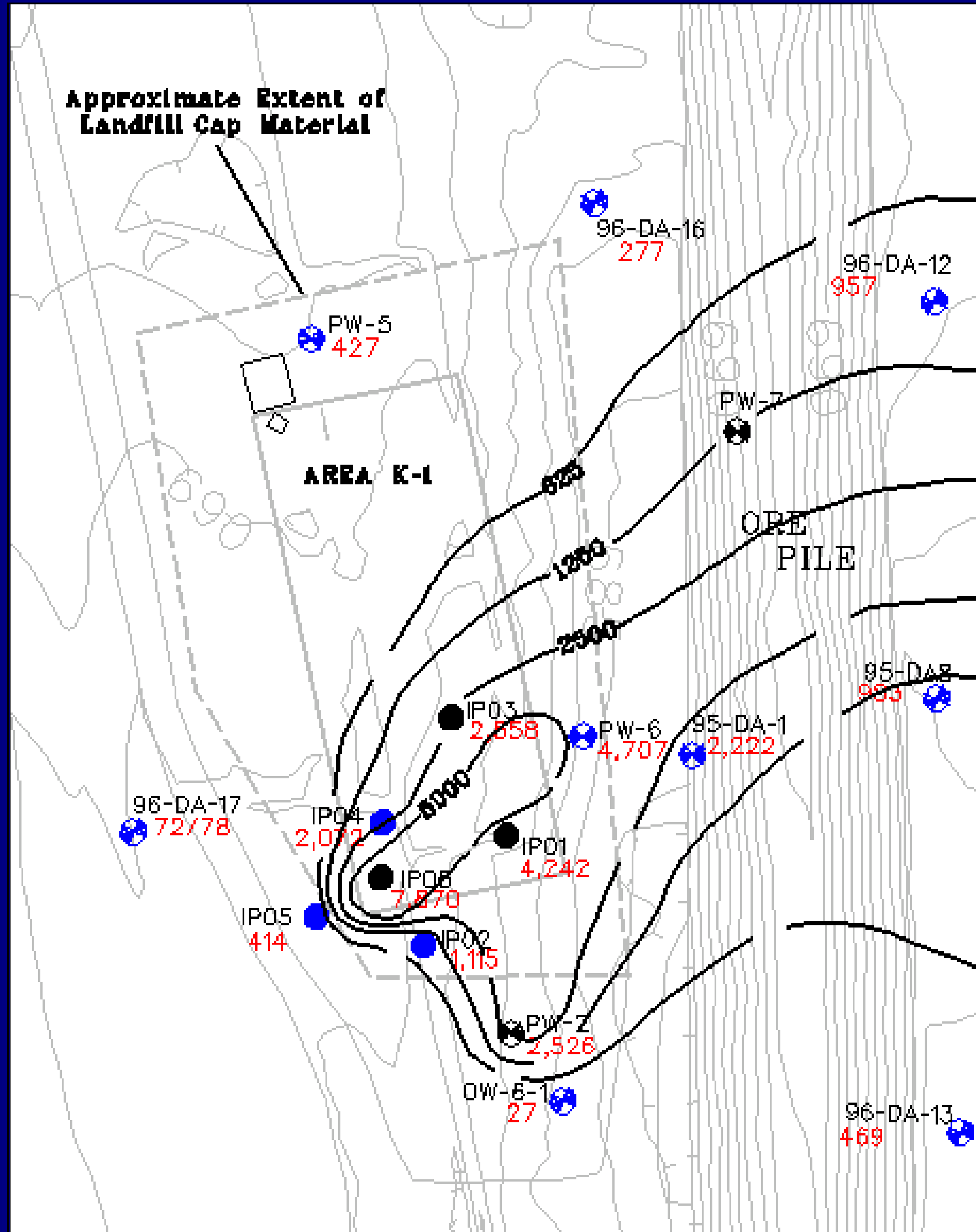
Chlorinated VOCs (ug/L) Post 4 Sampling Round (9 Months)

Legend

- Roads
- 95-DA-1 Monitor Points
- Injection/Monitor Well
- Monitor Well
- VOC Levels Reduced From Baseline

N



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Summary of Key Findings

- Both injector designs are effective
- Chemical oxidants effectively delivered
- Destruction ratio of 7:1 predicted during initial stages (12,519 lbs H_2O_2 to 1,942 lbs VOCs destroyed)
- Reduction maintained along upgradient edge
- Organics were mobilized
- Limestone bedrock not measureably degraded

In Situ Chemical Oxidation Pilot Test in a Karst Aquifer Southeast Operable Unit 11 IWTP Lagoons

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Performed by:
Science Applications International Corporation (SAIC)

SAIC
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Site Map

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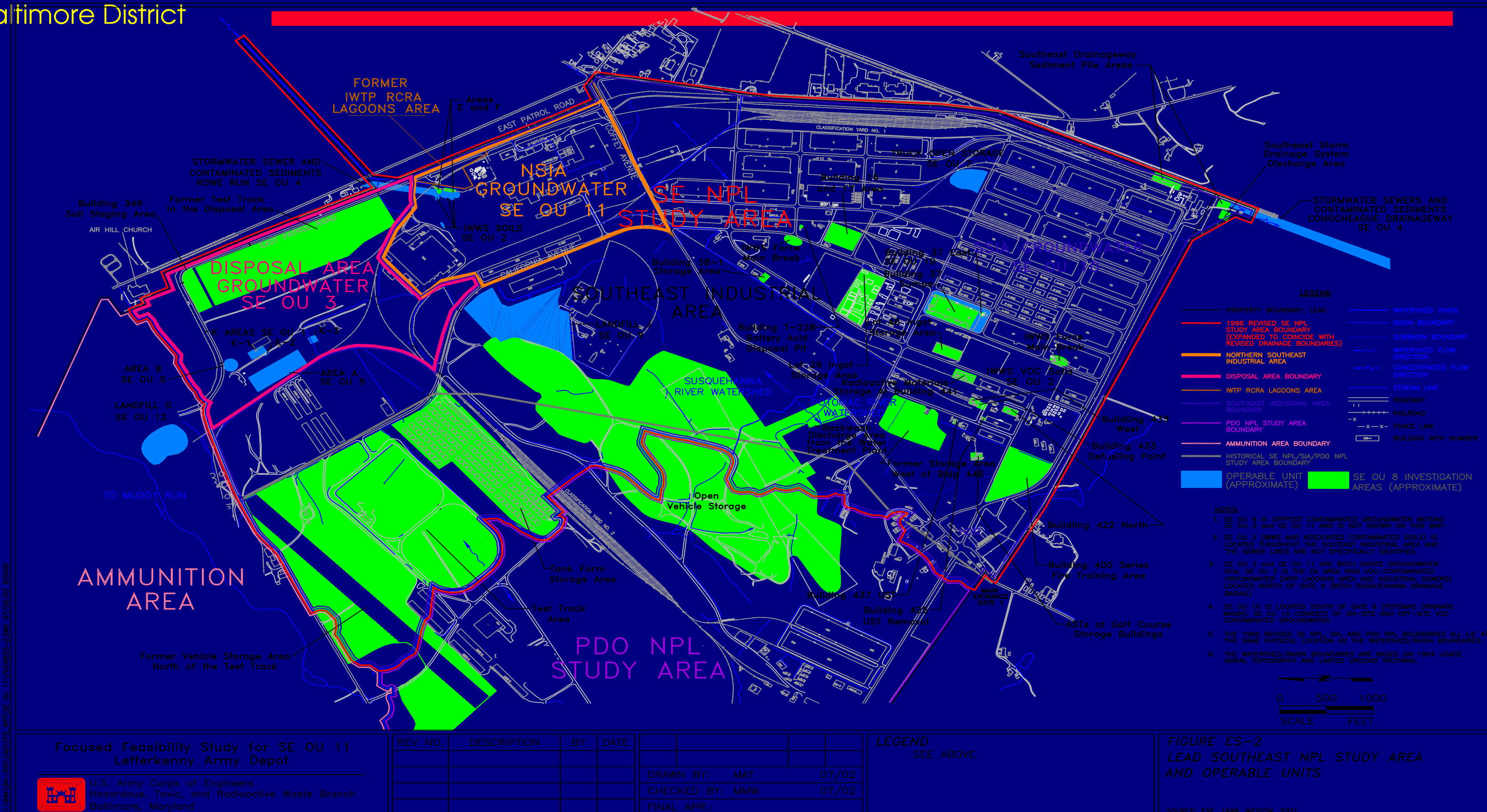

Site History

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- Industrial Wastewater Treatment Lagoons (IWTP)
  - Lagoon constructed in 1954 and operated until 1967, when sinkhole opened under lagoon. Two new reinforced concrete lagoons constructed and operated until 1988.
- Groundwater contamination is the result of uncontrolled release of wastewater containing solvents and other industrial residuals.
- 200 gpm Pump and treat no effect
- Soils removal no effect

1967 Air Photo

Excavation of Lagoons

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Environmental Setting

Hydrogeology

- Water table averages 30 ft. bgs, with storm event and seasonal fluctuations
- Regional groundwater gradient to the east
- Groundwater crosses NE boundary, discharging at springs 2 miles offpost
- Epikarst zone – Top 75 feet of aquifer .
- Below 100 feet, decreasing fractures and voids

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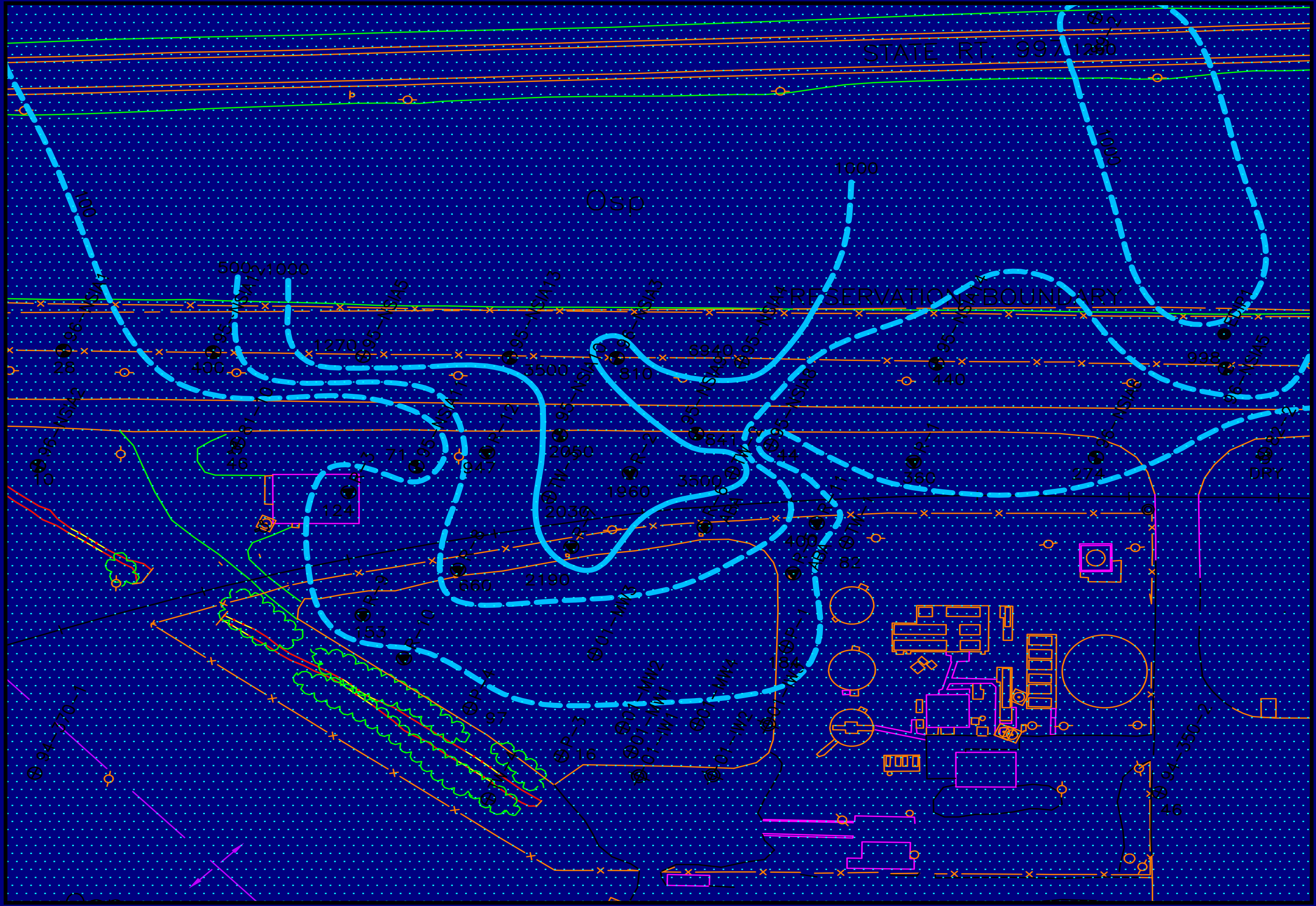
Total VOCs – Iso-concentration Map



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Conceptual Site Model – OU 11

- Epikarst - Highly karstified (top 100’), with sediment-filled & open voids in fractured limestone bedrock.
- Fractured Bedrock - Preferential flow along bedding planes.
- Release of DNAPL from lagoon through sink hole
- Contaminant source (DNAPL) resides in fractures, mud-filled seams, and is smeared on rock surface.
- DNAPL dissolves in groundwater, migrates with groundwater, offsite, rapidly discharging to off post springs. Frequent flushing by precipitation events.

Peroxone Oxidant

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- $H_2O_2 + 2O_3 \rightarrow 2 \cdot OH + 3O_2$
- Off-post flushing little concern
- New ozone generation technology
- Super-saturated solution increases O_3 concentration
- Pilot applicable to other oxidants

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Pilot Test Goals

- Determine ability to displace aquifer water with oxidant solution
- Determine ability to deliver/sustain oxidant in the target zone
- Test the generator and delivery system
- Collect design information for construction of full-scale system.

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Pilot Test Steps

- Design of injection, delivery and monitoring systems
- Install injection/monitoring wells
- Determine background chemical constituent concentrations
- Perform dye injection
- Conduct Peroxone injection

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Design of Injection, Delivery and Monitoring System

- Estimate from available data:
  - Porosity/pore volume
  - Injected solution flow direction
  - Area of influence (target zone)
  - Reasonable injection rate

- Available information

– Well drilling logs	Geophysical logs
– Pumping, slug tests	Dye studies
– Pumping records	Geologic Mapping
– Aerial photo analysis	Previous pilot tests

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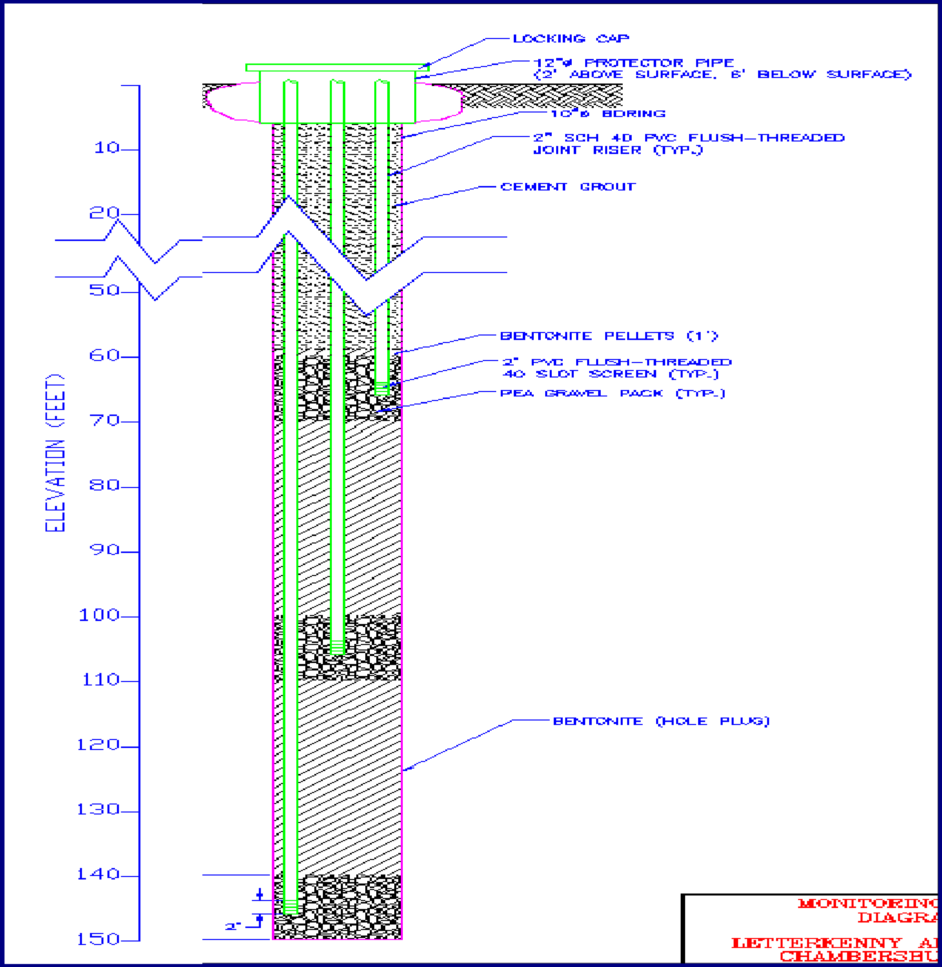
Design of injection, delivery and monitoring system

- **Three 3-level injection wells, oriented to test preferential flow directions in epikarst and fractured bedrock**

- **Four 3-level monitoring wells spaced 20, 40 and 100 feet along suspected flow pathways**



Design of injection, delivery and monitoring system

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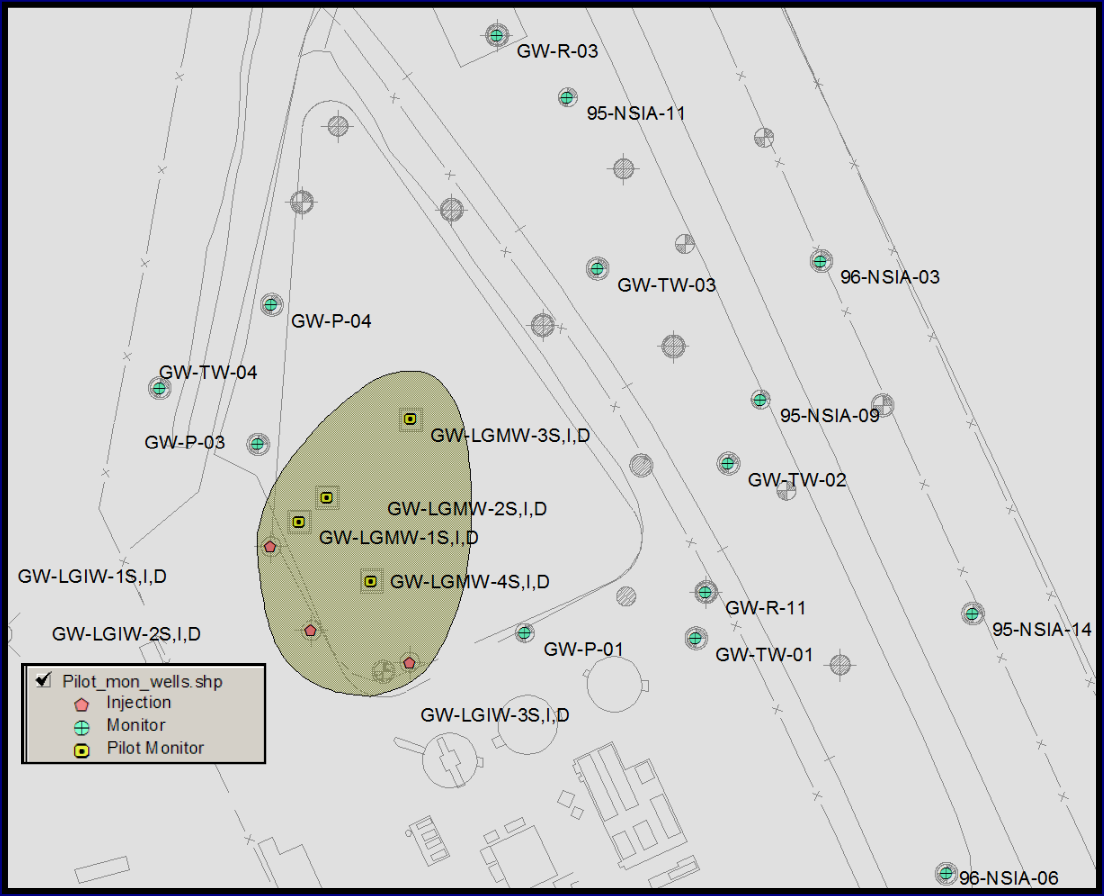
- Injected quantity of fluid to occupy 1 aquifer pore volume (15 gpm for 5 days).
- Injection rate chosen to minimize contaminant mobilization.
- Injected fluid immediately up-gradient of contaminant source.



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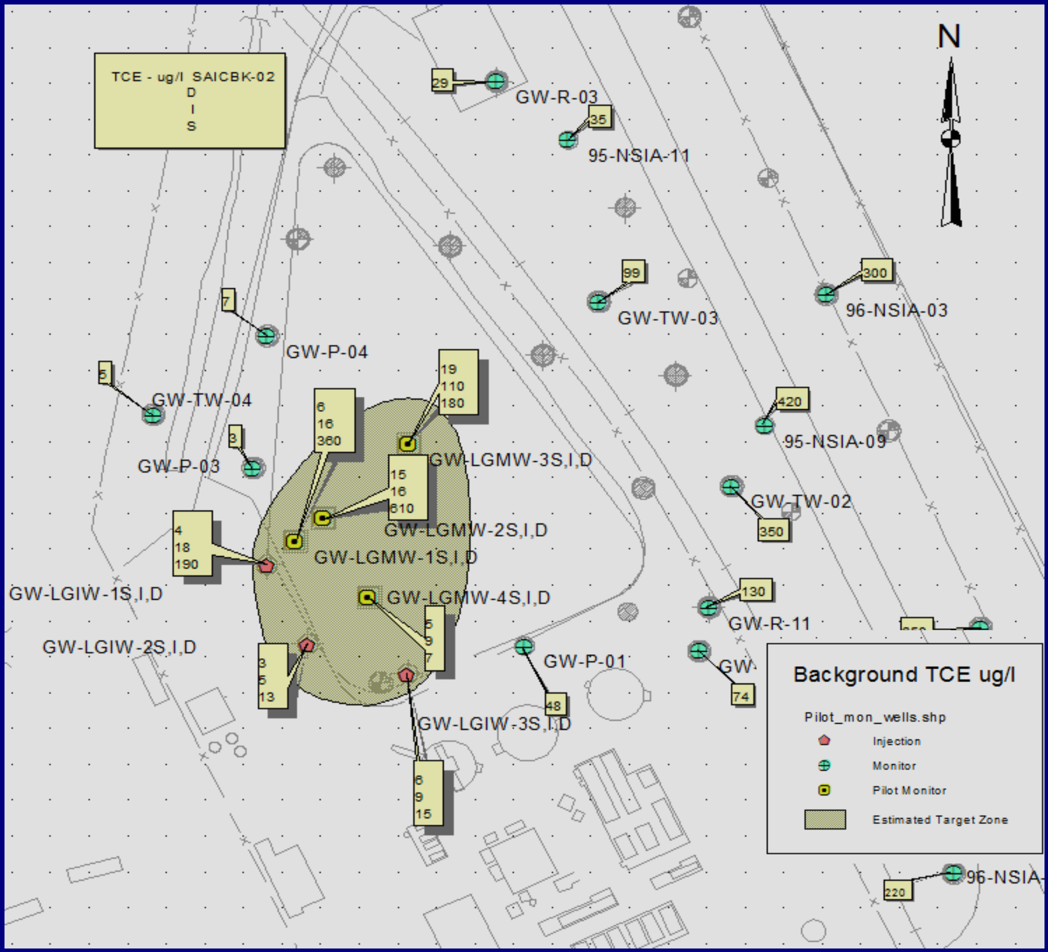
TCE – Baseline Concentrations

- Two rounds
  - 3 Injection wells
  - 4 Pilot monitoring wells
  - 14 existing monitoring wells
- 10-650 ppb TCE
- 10-1170 ppb TVOCs



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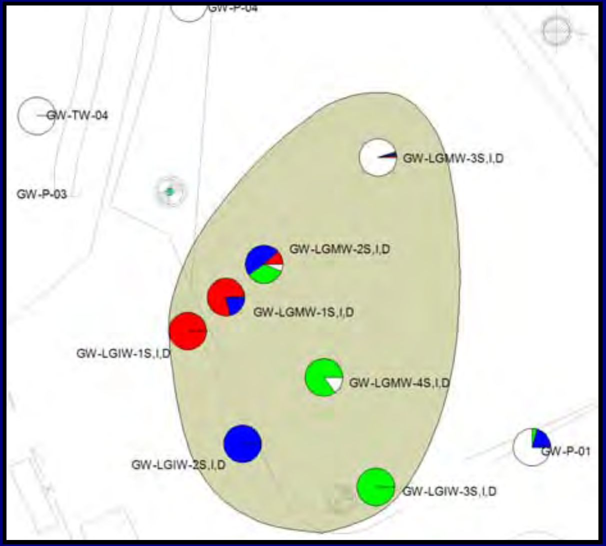
Dye Injection - Depth Differential

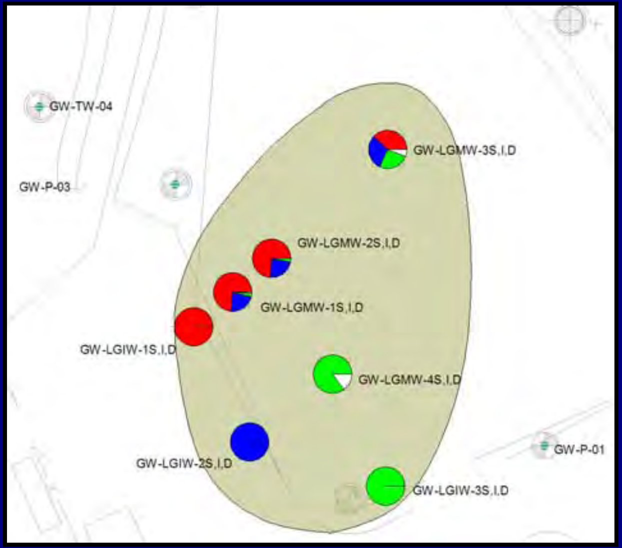
- Shallow injection to the northwest
- Deep injection to the northeast
- High level of displacement achieved

Pilot_mw_s.shp
- RWT%day5
- EO%daay5
- Flu%day5
- GW%day5

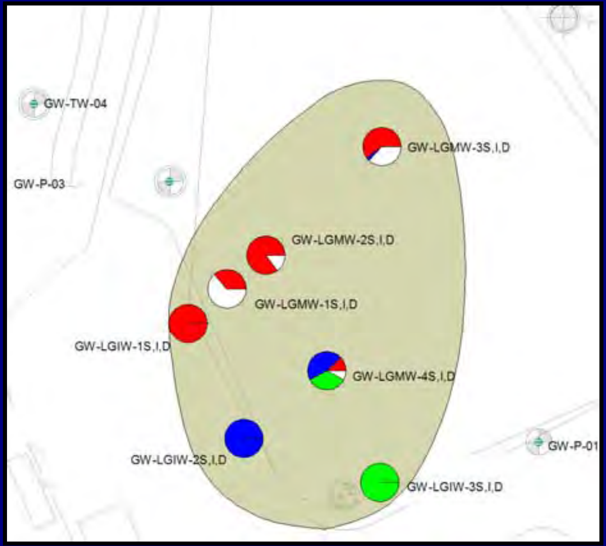
Shallow 50-70’



Intermediate 100-110’



Deep 140-150’



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Peroxone Injection

- Injected 5 gpm/well 15 gpm for total system
- Continuous injection for 13 days.

Peroxone Injection

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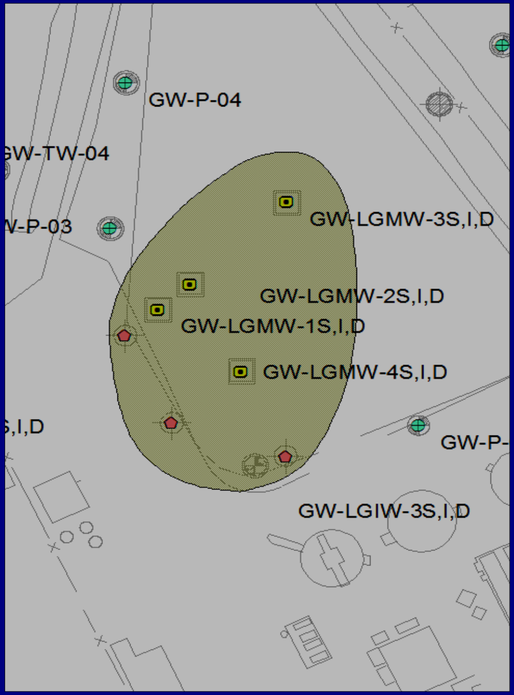
- **Monitored for:**
  - VOCs, anions, carbonate, chlorides
  - DO,ORP,pH,Temp,Sp.Cond ,H_2O_2,Fe,CO_2,O_3



Peroxone Injection

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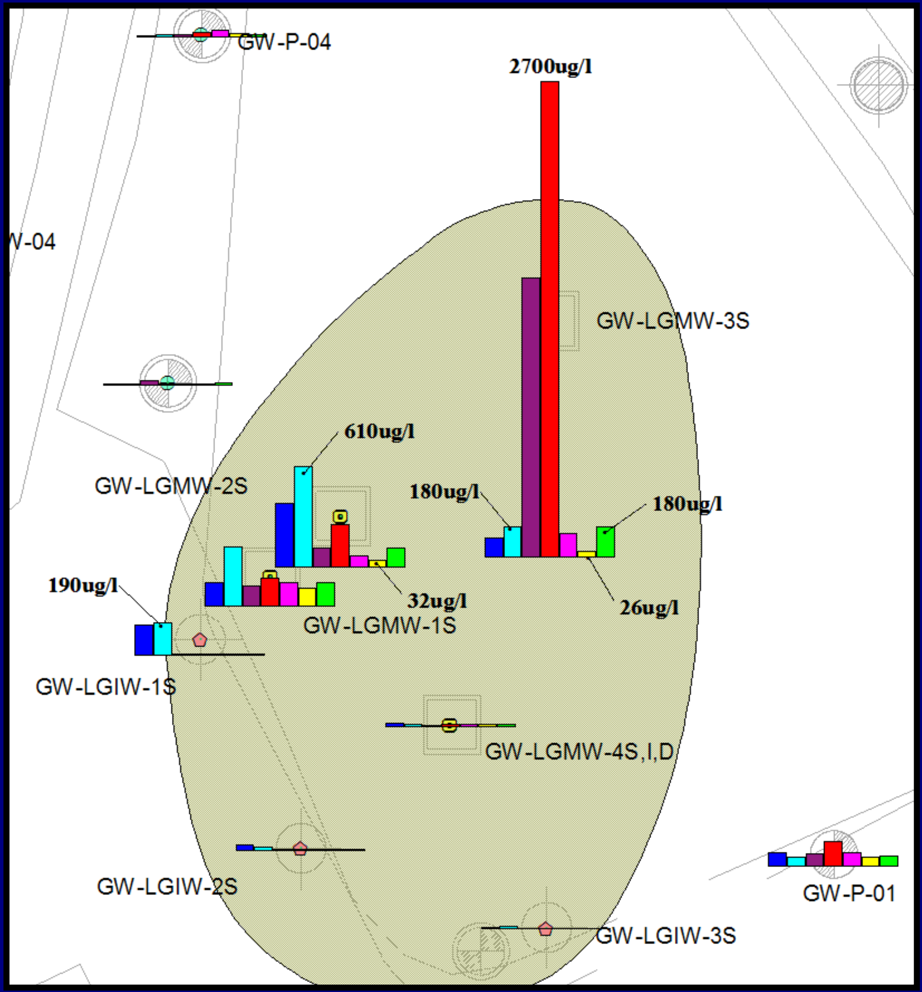
- TCE concentrations in target zone reduced significantly with injection of oxidant

Background 1
Background 2
End of Dye Injection
8 days after end of Dye Injection
Day 6 of Oxidant Injection
Day 13 of Oxidant Injection
14 days after end of Oxidant Injection



Peroxone Injection (Cont'd)

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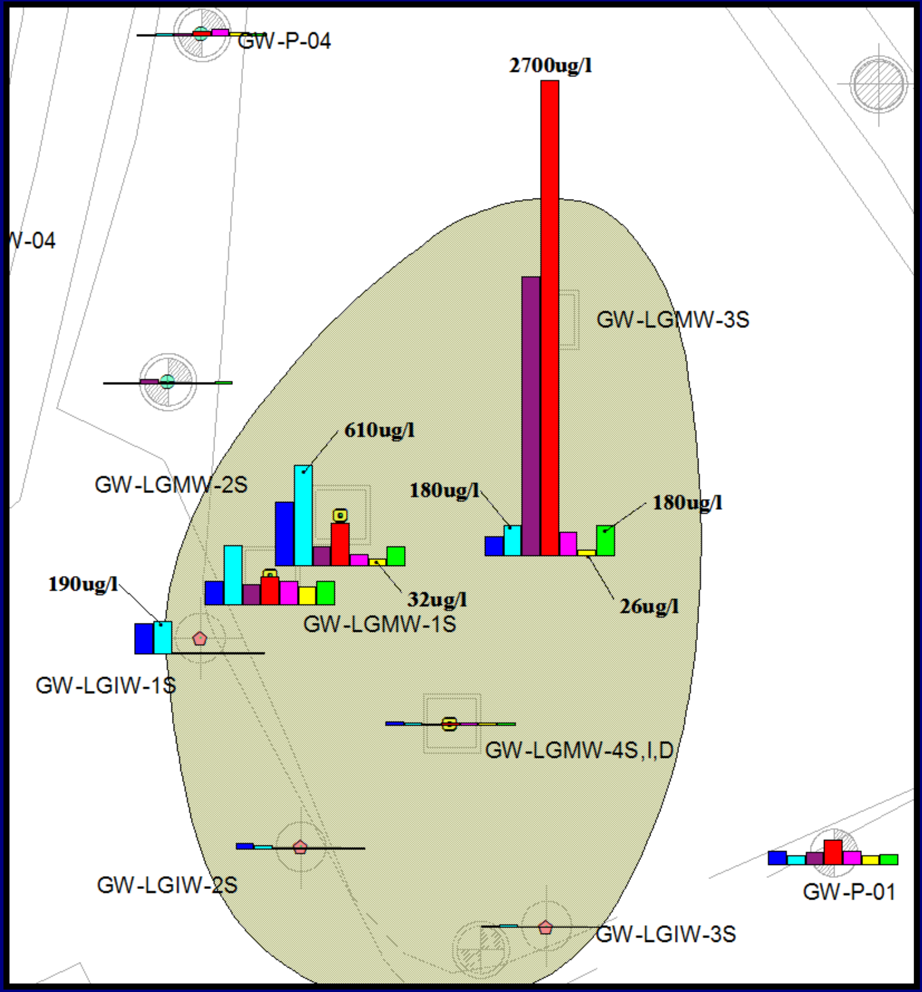
- Dye Injection raised concentration of COCs
- TCE concentrations in target zone reduced significantly with injection of oxidant
- Rebound to pretest levels indicates response time of system
- Did not expect to permanently reduce concentrations in pilot test time frame



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Conclusions

- Up front hydrogeologic characterization was sufficient to design injection system.
- Multi-level injection important to gain 3D distribution in target zone.
- Objective to displace aquifer water with injected solution was realized.
- Concentrations of TCE reduced by oxidant injection
- More testing required to evaluate ozone persistence and long term impacts.
- Microbial and cave shrimp populations rebounded

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Enhanced Bioremediation Of VOC-Contaminated Groundwater SE OU 10

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Chambersburg, PA

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Introduction/Site History

- Release of chlorinated solvents occurred from sewer lines around Building 37
- Release of petroleum products occurred from return line of UST system at the south end of Building 37
- Sewer system repaired and UST replaced
- FFS commenced to identify remedial action alternatives
- Enhanced bioremediation pilot study initiated

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Characterization Activities

- **Investigations Completed Before Field Biopilot Testing**
  - Geologic Mapping and Analysis
  - Surface Geophysical Surveys
  - Monitor Well Installation
  - Downhole Geophysical Logging
  - Aquifer Testing - Packer and Pumping Tests
  - Dye Studies
  - Groundwater Sampling for Contaminants & Natural Attenuation Parameters
  - Microcosm Studies

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Microcosm Study

Summary of Groundwater Analytical Results

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- VOCs in groundwater consisted mainly of TCE, 1,1,1-TCA, 1,2-DCE, 1,1-DCE, 1,1-DCA, Vinyl Chloride and Chloroethane.
- VOCs ranged from 7.4 ug/L to 574 ug/L.
- 4 wells within VOC plume contained BTEX (ranging from 7.3 ug/L to 916 ug/L.

Conclusions from Bench Top Studies

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- Microbial processes are destroying dissolved CAH contamination at Building 37.
- Microbial processes responsible for degradation are anaerobic (probably methanogenic). No evidence of aerobic degradation.
- Indigenous microbial communities are robust and can be stimulated to accelerate reductive dechlorination processes.
- Field biopilot study initiated to facilitate further development of anaerobic/methanogenic conditions by adding anaerobic substrate.

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Enhanced Biopilot Study Objective and Scope

- Evaluate the feasibility of in-situ enhanced bioremediation of dissolved CAHs
- Nutrient introduction
  - Continuously introduce sodium lactate solution at 3 locations for 44 days.
  - Inject 400 liters/day at 27,150 mg/L.
- Dye tracing
  - Add dye(s) to nutrient solution as a tracer.
- Six-Month monitoring period
  - Monitor geochemical parameters.
  - Monitor distribution of nutrients/tracer dye(s).
  - Monitor CAH concentrations, distribution, and presence/absence of degradation products.

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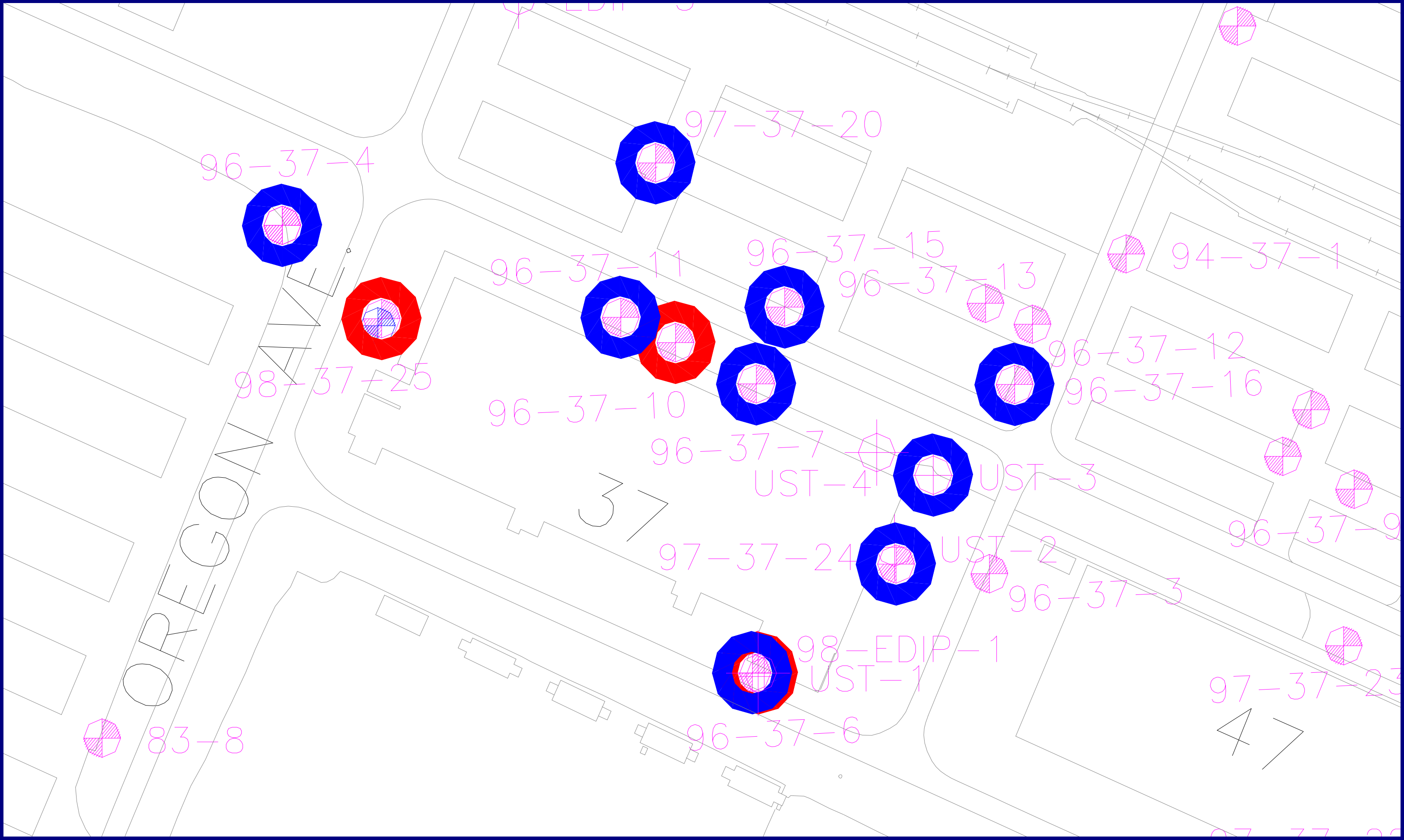
Nutrient Introduction and Monitoring Points for Field Biopilot Test



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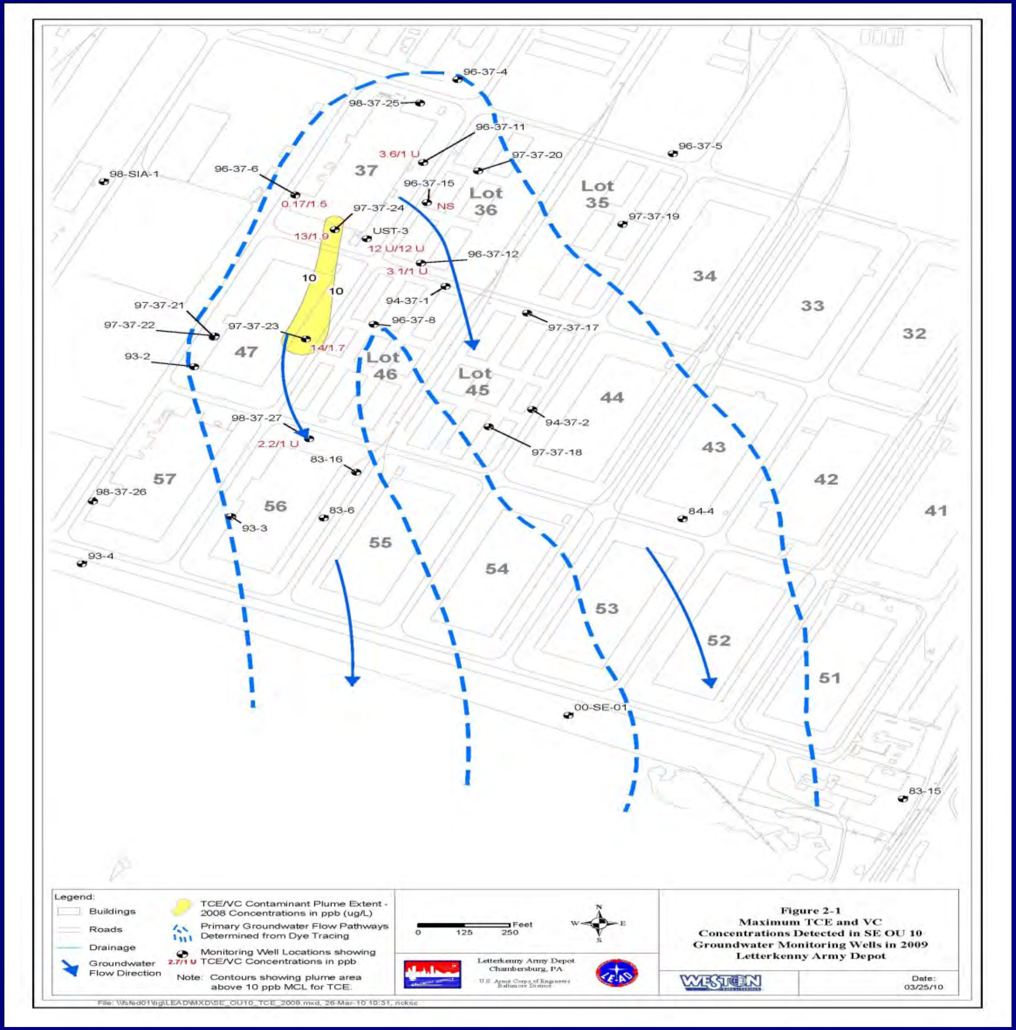
TCE and VC 2009



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Solvent Variation with Time
Well 96-37-11

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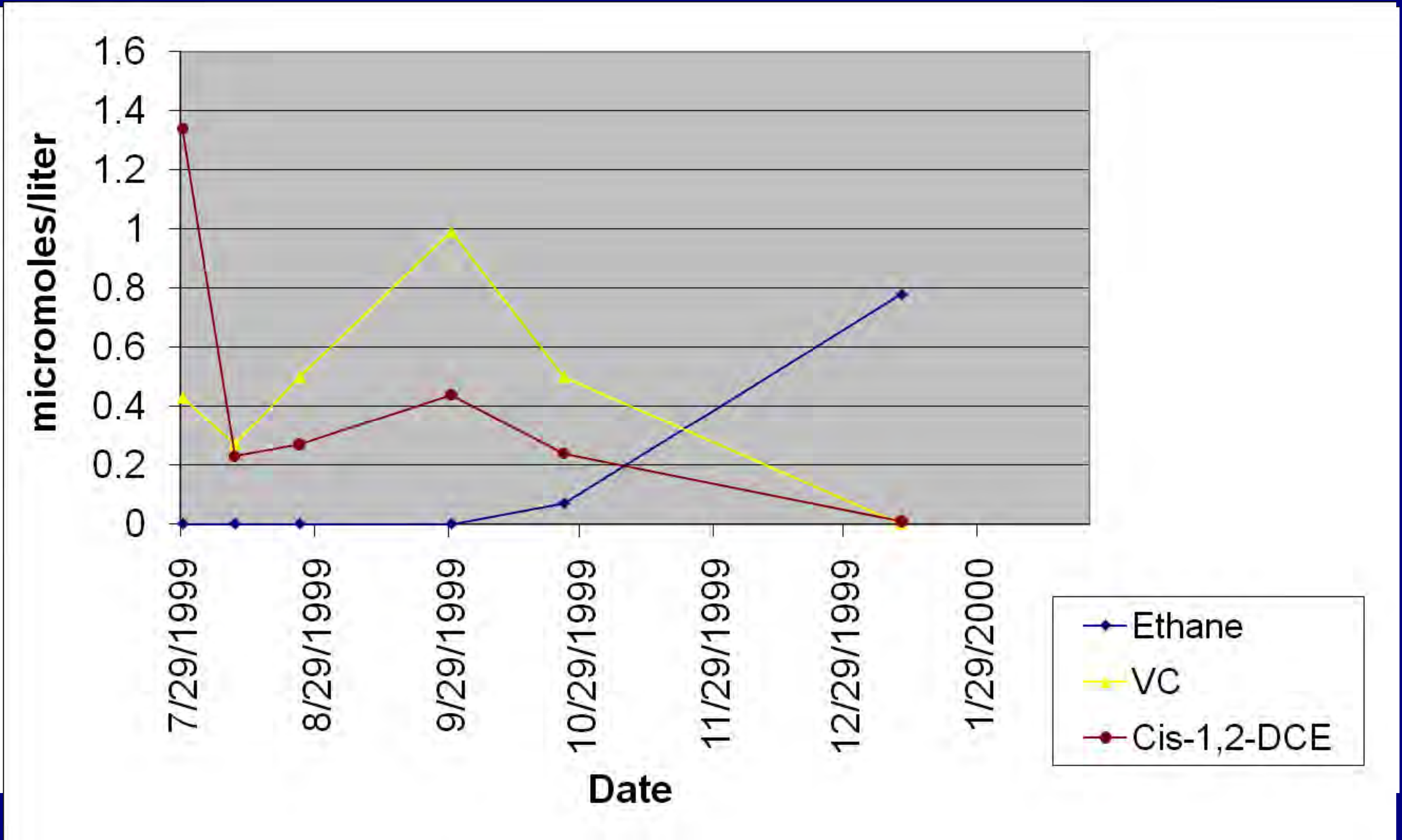

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Solvent Variation with Time
Hawbaker Spring

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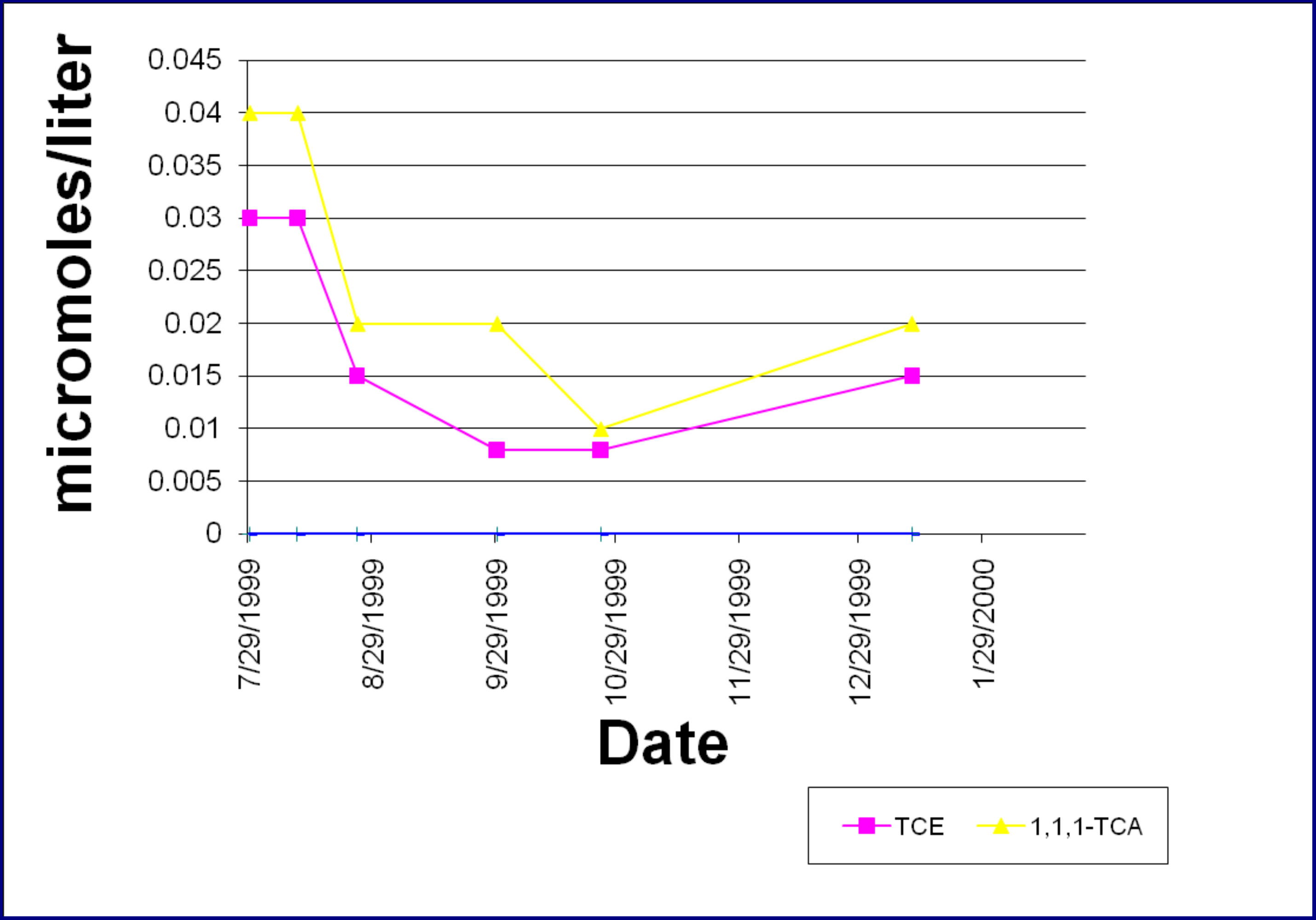

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Hawbaker Spring

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Summary

- Complete reductive dechlorination of VOCs demonstrated through production of end-point daughters
- Multiple degradation pathways have been observed in the natural environment
- Retention periods of up to 6 months have been observed for dye and nutrients.
- Total mass of chlorinated solvents in site groundwater has been reduced over study period
- Discharges to off-post springs have been reduced/eliminated

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Conclusions

- Extensive site characterization required before attempting to pilot a technology in karst
- Determining migration pathways crucial
- Law of diminishing returns for ISCO
- TI may be required (and information to support it)
- Natural Attenuation usually part of the remedy
- Monitoring costs may be substantial
- Verifying no migration of oxidants important
- RA issues and karst

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Cost of Pilot Studies

- **SE OU 3 – ~ 400K (DA In-Situ Chemical Remediation Oxidation Pilot Study; H2O2)**
- **SE OU 10 – ~ 260K (In-Situ Enhanced Biodegradation-Pilot)**
- **SE OU 11 – ~ 450K (In-Situ – Ozone Pilot Study (Lagoon Area)**