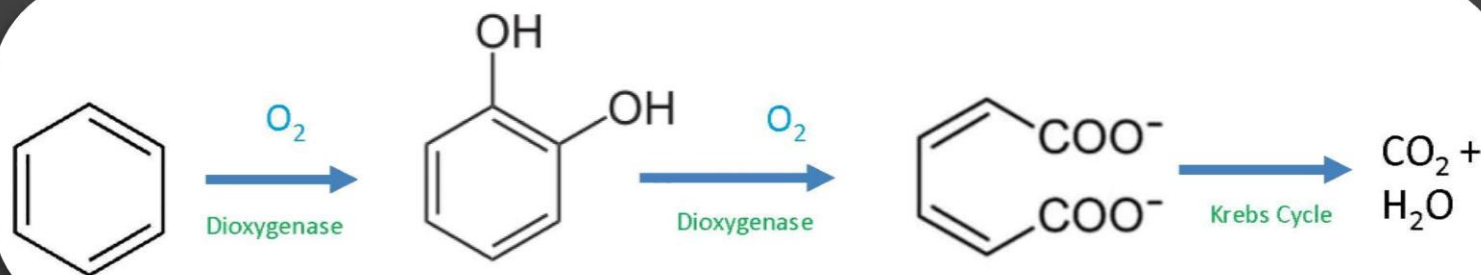


Enhanced In Situ Aerobic Biodegradation (Busting the Benzene Ring)

Lessons Learned from 5 Case Studies



Why Choose Enhanced In Situ Biodegradation?

When standard approaches don't work!

- ❑ Excavation not feasible
 - Overlying infrastructure
 - Source at depths >20 feet (standard excavator reach)
- ❑ AS/SVE not feasible or effective
 - Low permeability aquifer
 - Confined/semi-confined aquifer
 - Interbedded coarse and fine-grain units
- ❑ Heterogeneous, low-permeable sites – mature contamination strongly sorbed and less accessible, slowly back-diffuses over time. Reduces effectiveness of ISCO, etc.

Why Aerobic Degradation?

| Electron Acceptor | Type of Reaction | Mass of EA Needed to React Mass of Benzene | Redox Potential/ Reaction Preference |
|-------------------|------------------|---|---|
| Oxygen | Aerobic | 3.1 | +820 Most Preferred |
| Nitrate | Anaerobic | 4.8 | +740 |
| Ferric Iron | Anaerobic | 21.5 | -50 |
| Sulfate | Anaerobic | 4.6 | -220 |
| Carbon Dioxide | Anaerobic | 2.1 | -240 Least Preferred |

Which Oxygen Source?

Commercially Available Slow Release Oxygen Compounds

- Safe to handle
- Injected through direct-push borings
- Lasts up to 12 months
- Multiple injections required
- \$50-60/pound oxygen

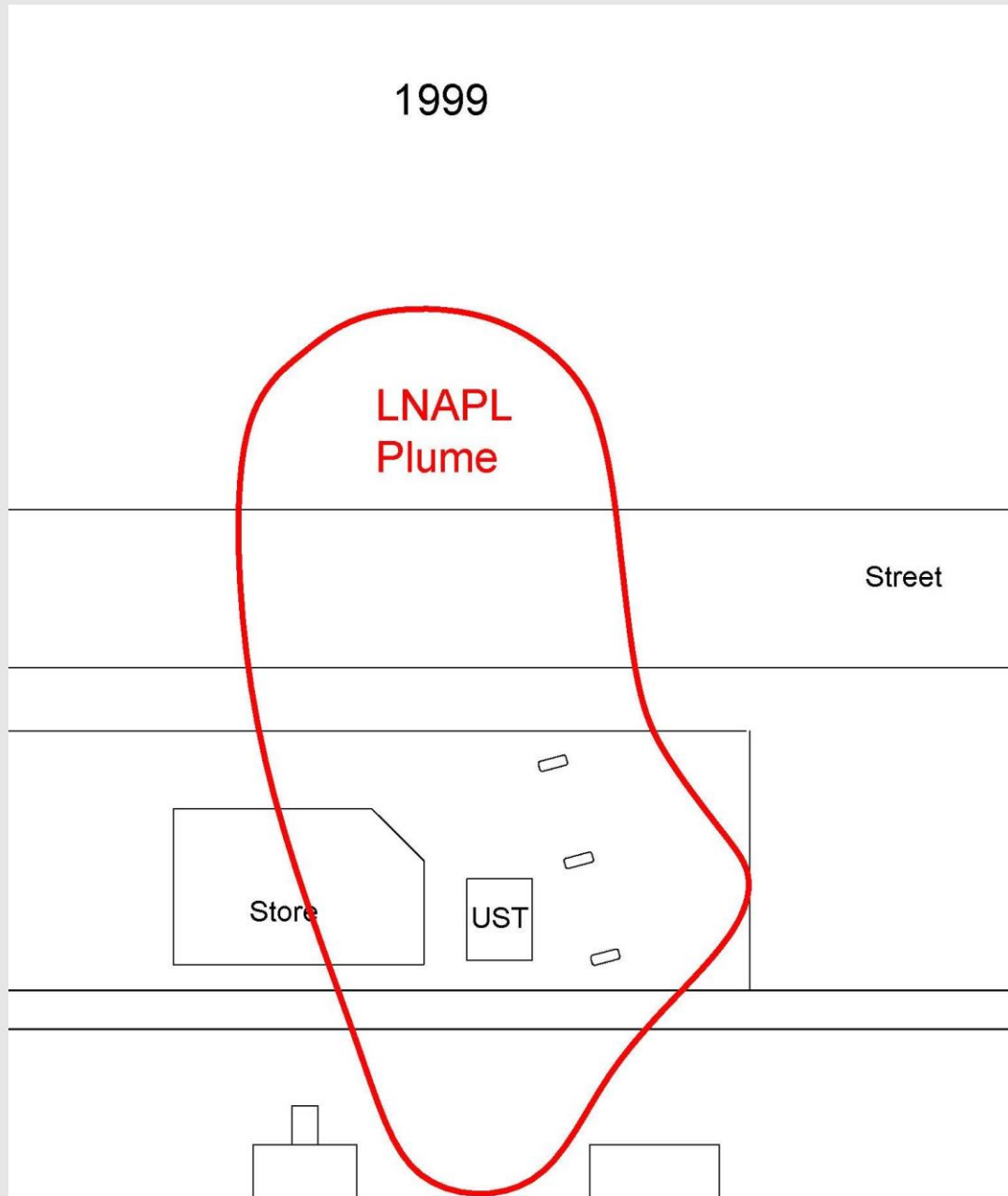
Hydrogen Peroxide

- Strong oxidizer at high concentrations
 - Compatible w/ SS, Al, PVC, polycarbonate, Teflon
- Continuous injection into vertical or horizontal wells
- \$4/pound oxygen



Requires 3 pounds of oxygen to degrade 1 pound of benzene

Case 1



- ❑ 11,000 gallons of diesel released from UST between October 1998 and February 1999
- ❑ Aquifer
 - Fractured shale bedrock
 - DTW is 20-30 feet bgs
 - Groundwater flow to N to NNW
- ❑ LNAPL plume with apparent thickness up to 6 feet in several wells. LNAPL was diesel, no gasoline.
- ❑ Recovered ~7,000 gallons of LNAPL from March 1999 to August 2003, after which little LNAPL was observed.

2003

5

400

800

1200

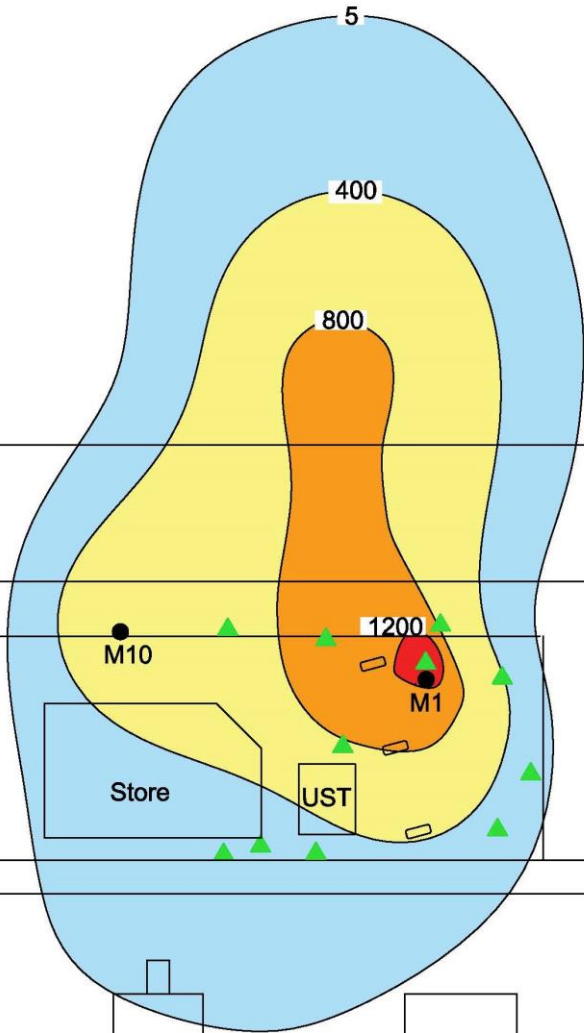
Street

Store

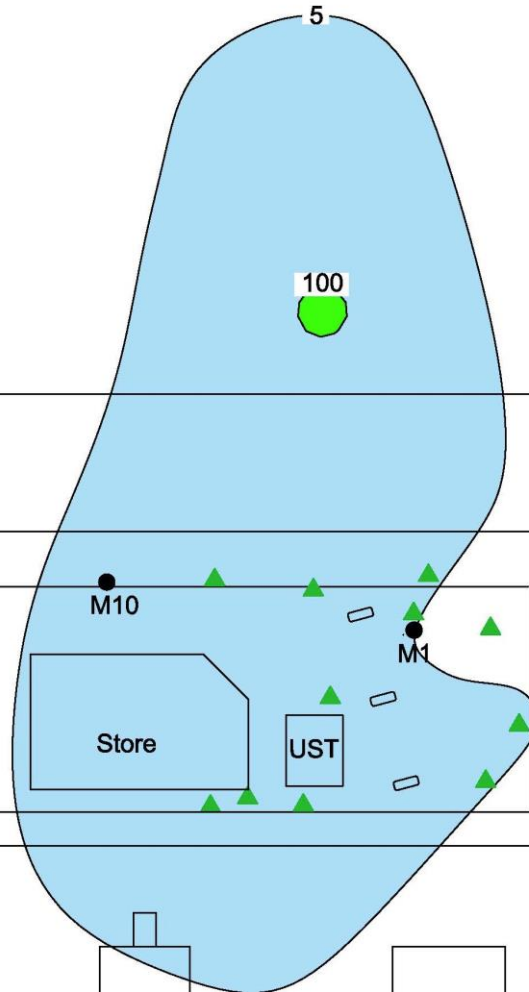
UST

- ❑ During NAPL recovery, historical gasoline release discovered. Flat-line dissolved phase BTEX plume covering an area of ~85,000 SF, with benzene concentrations as high as 1,500 $\mu\text{g/L}$
- ❑ Estimated total petroleum hydrocarbon mass of 15,000 pounds, of which ~20% was BTEX
- ❑ Aquifer
 - Strongly anaerobic
 - Seepage velocity calculated at 20 feet/year, observed to be ~300 feet/year
- ❑ Obstacles to standard approaches
 - Overlying infrastructure, street & UST system
 - Source >20 feet bgs
 - Low-perm bedrock aquifer
 - Mature, sorbed contaminants

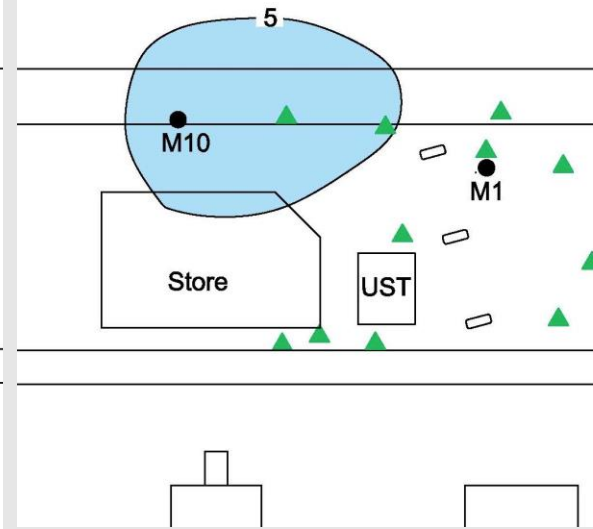
2003



2007



2019



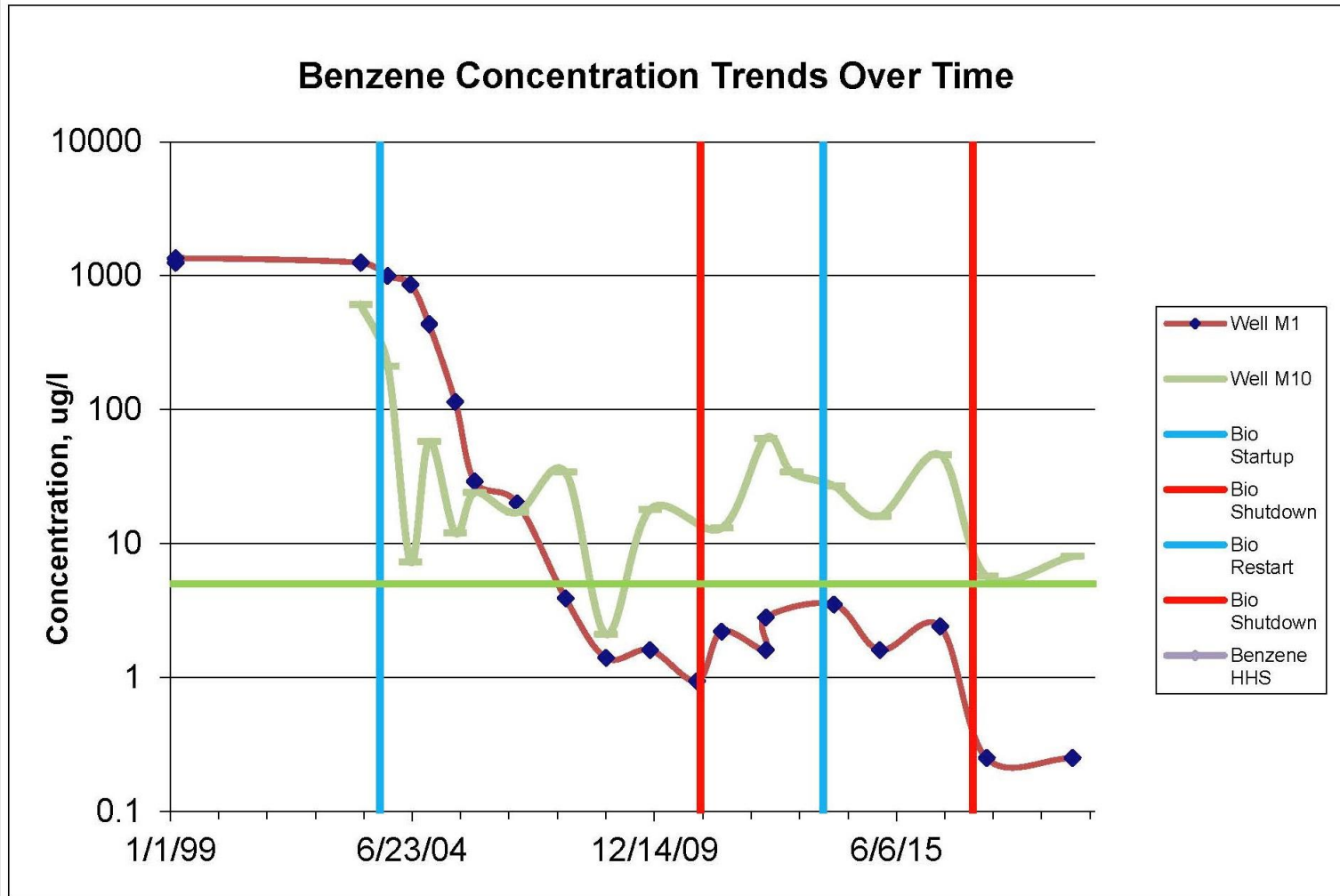
Injection started
in 2003,

Shut down in
2011

Restarted in
2013

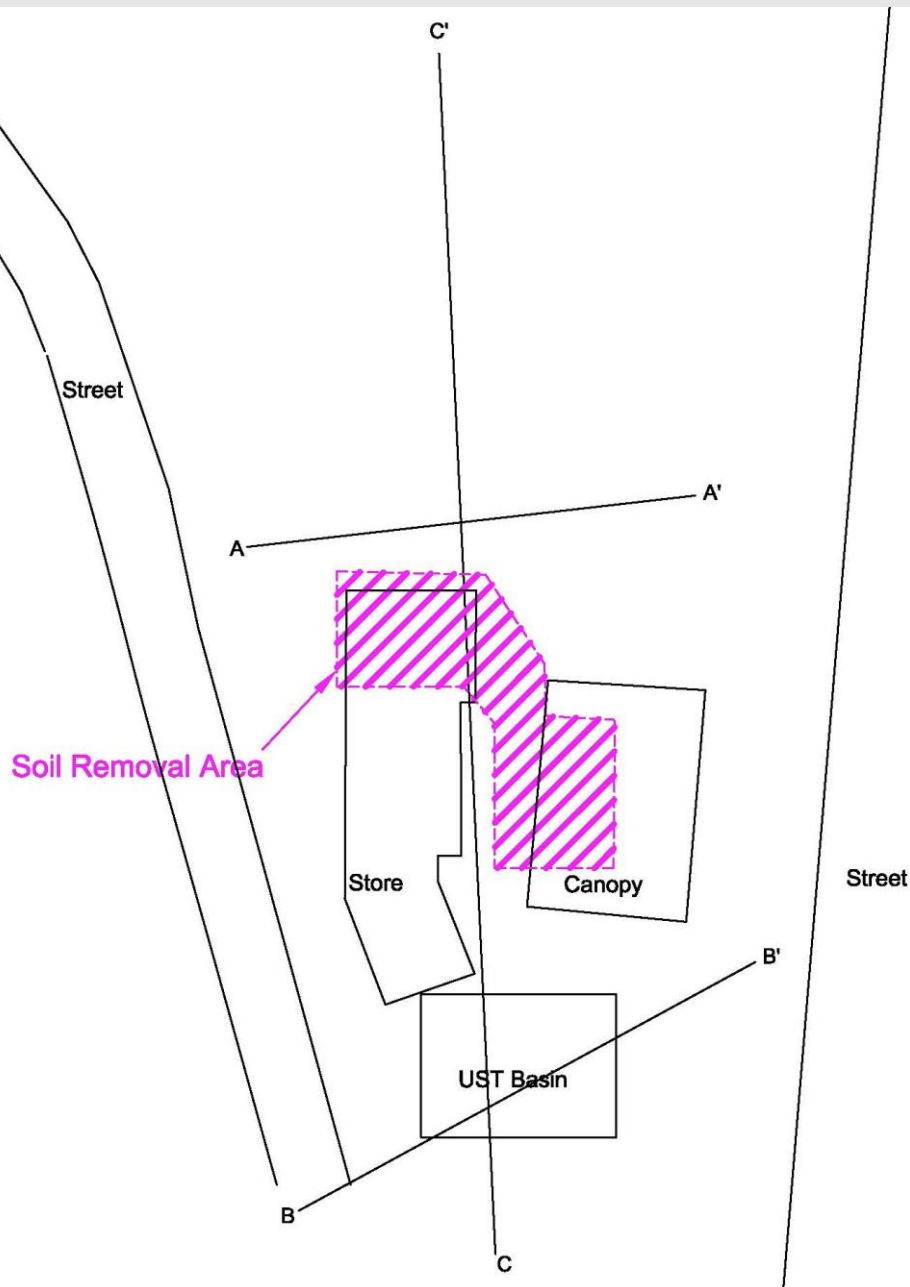
Shut down for
good in 2017

Case 1 - Lessons Learned



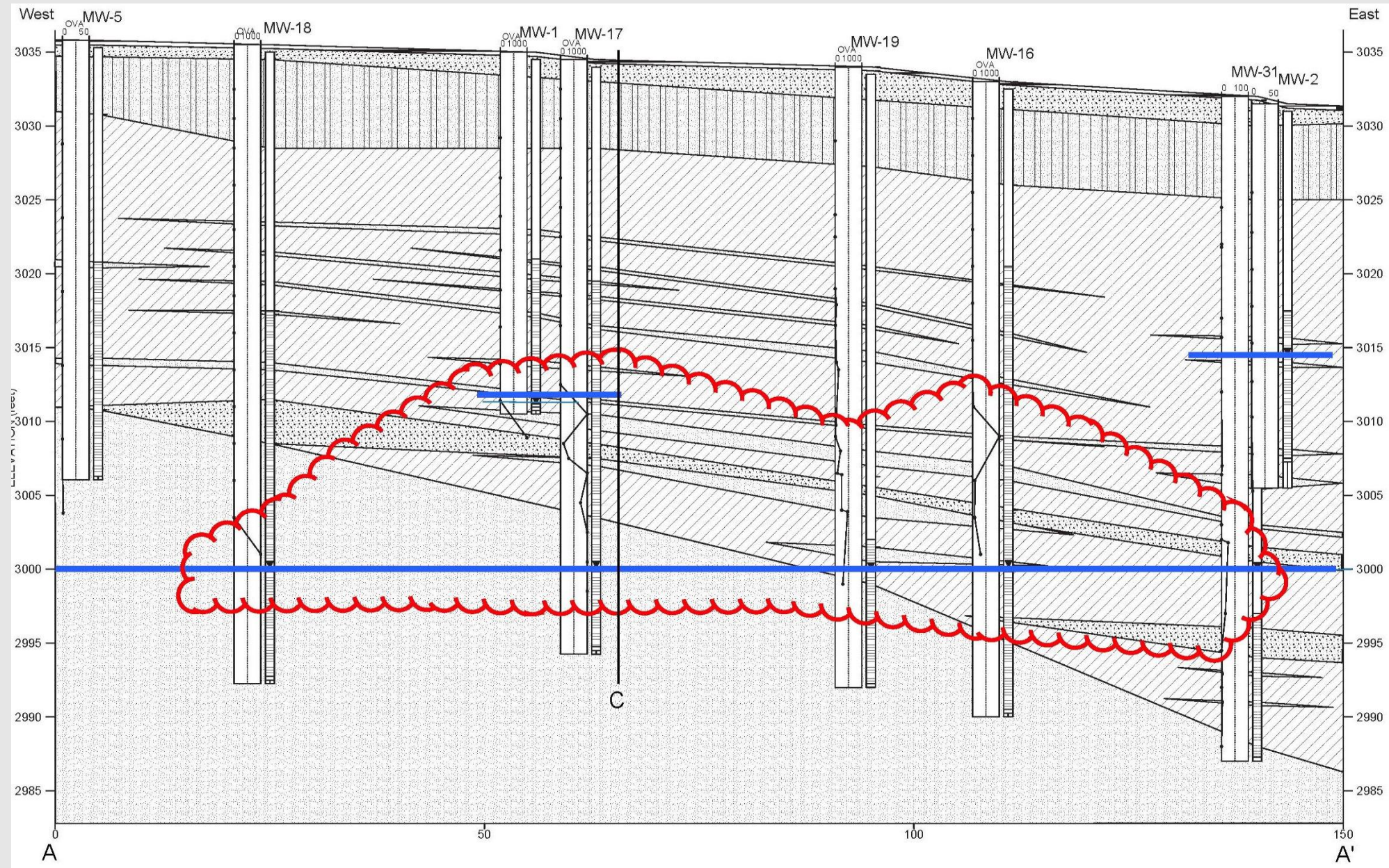
- ❑ M10 - Poorest performing location
 - Fringe of targeted injection area
- ❑ M1 – One of the better performing locations
 - Targeted injection area
- ❑ Demonstrated effectiveness
 - 99% benzene reduction across the site by end of operation
 - Little to no rebound
 - Performance limited solely by how quickly oxygen could be delivered

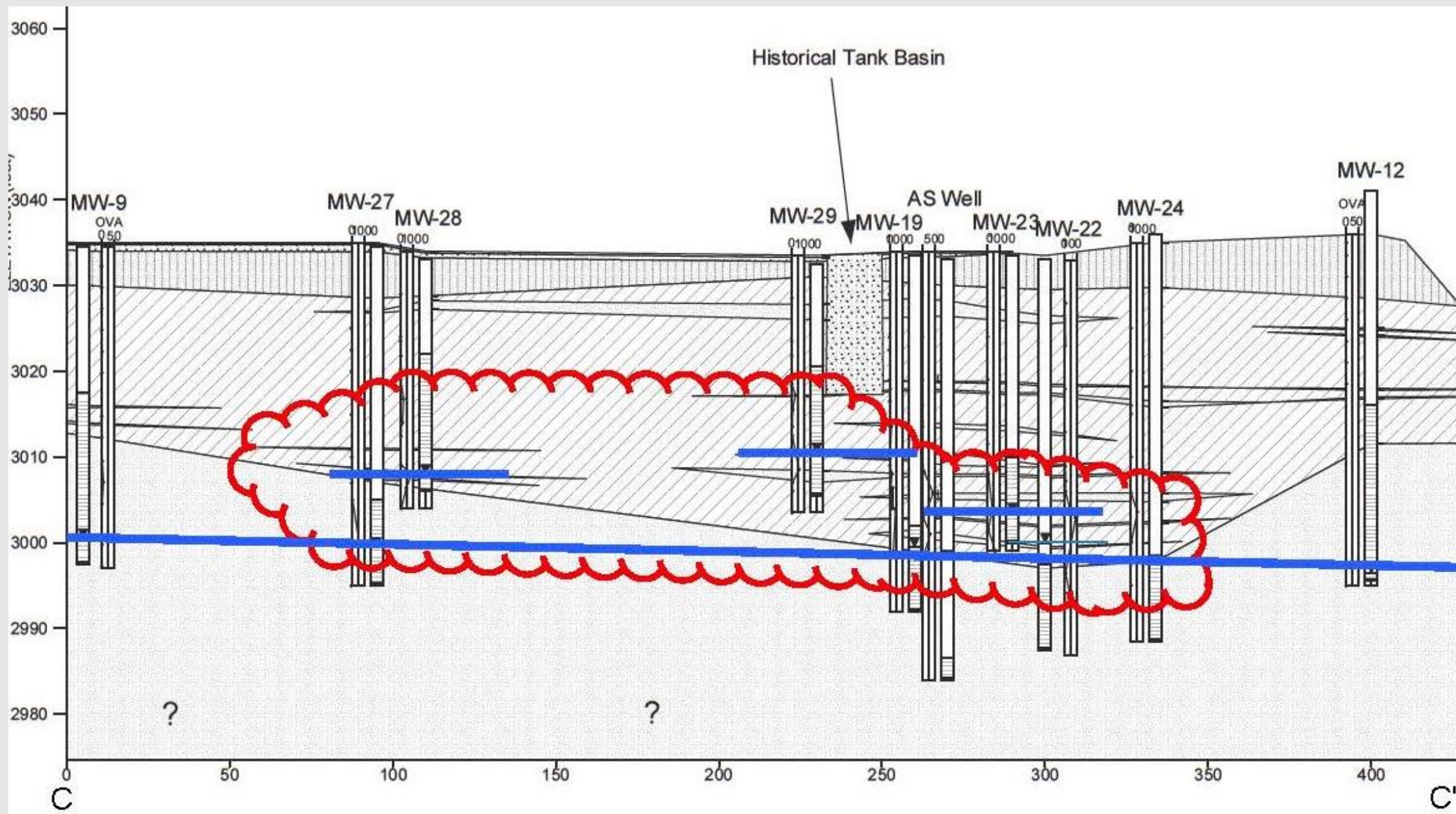
Case 2



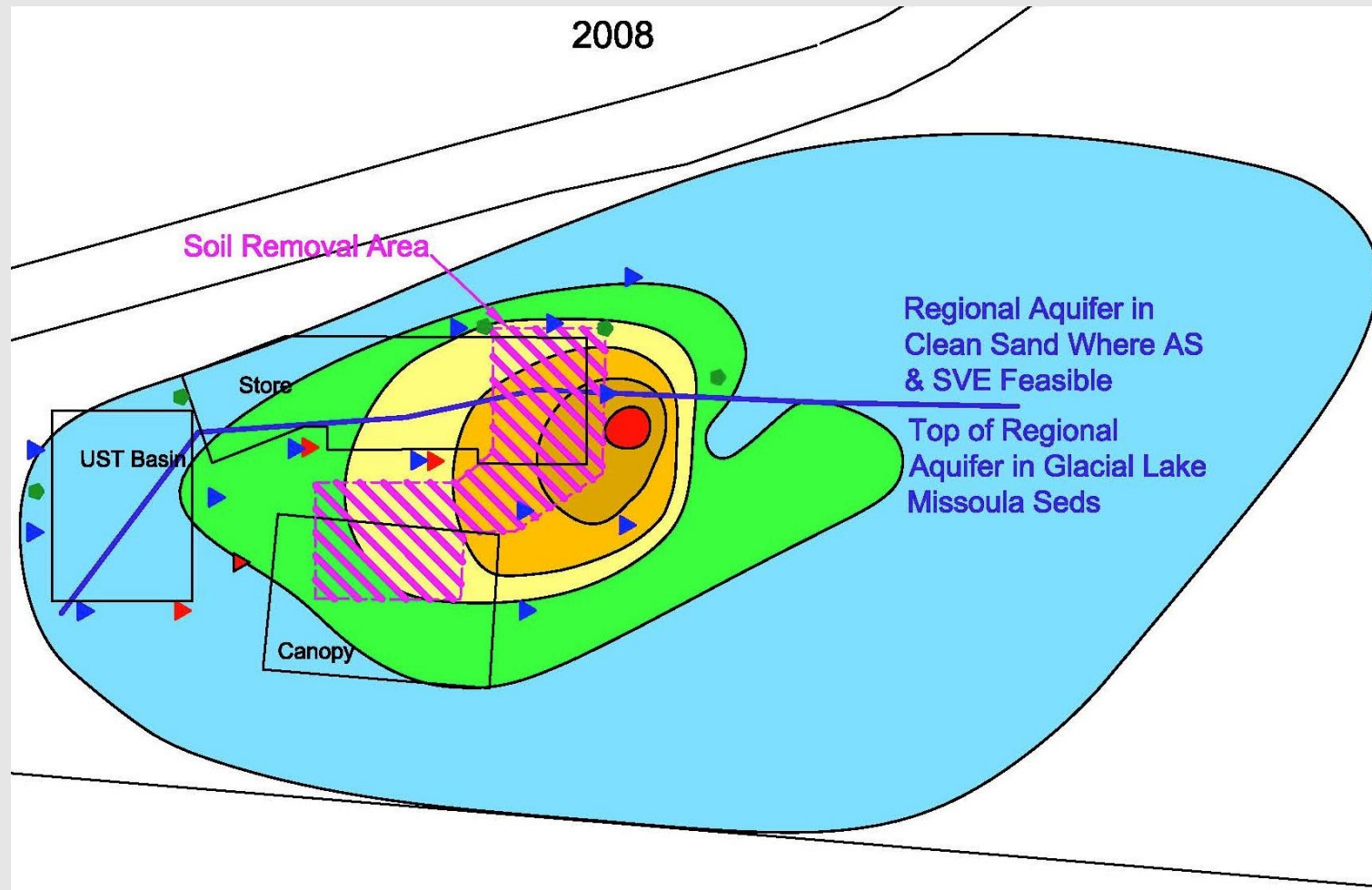
- ❑ Site was redeveloped in 1989
 - ~2,500 cy of gasoline impacted soil was removed to depths of 15 to 22 feet bgs
 - Store was expanded over the northwestern portion of excavation (historical UST basin)
 - The release was closed, and a new release reported in 2003

- ❑ Complex Aquifer
 - Perched aquifer in glacial lake Missoula sediments -DTW varies from 8 to 30 feet bgs
 - Regional aquifer in clean sand and glacial lake Missoula seds – DTW varies from 30 to 42 feet bgs
 - Groundwater flow to north

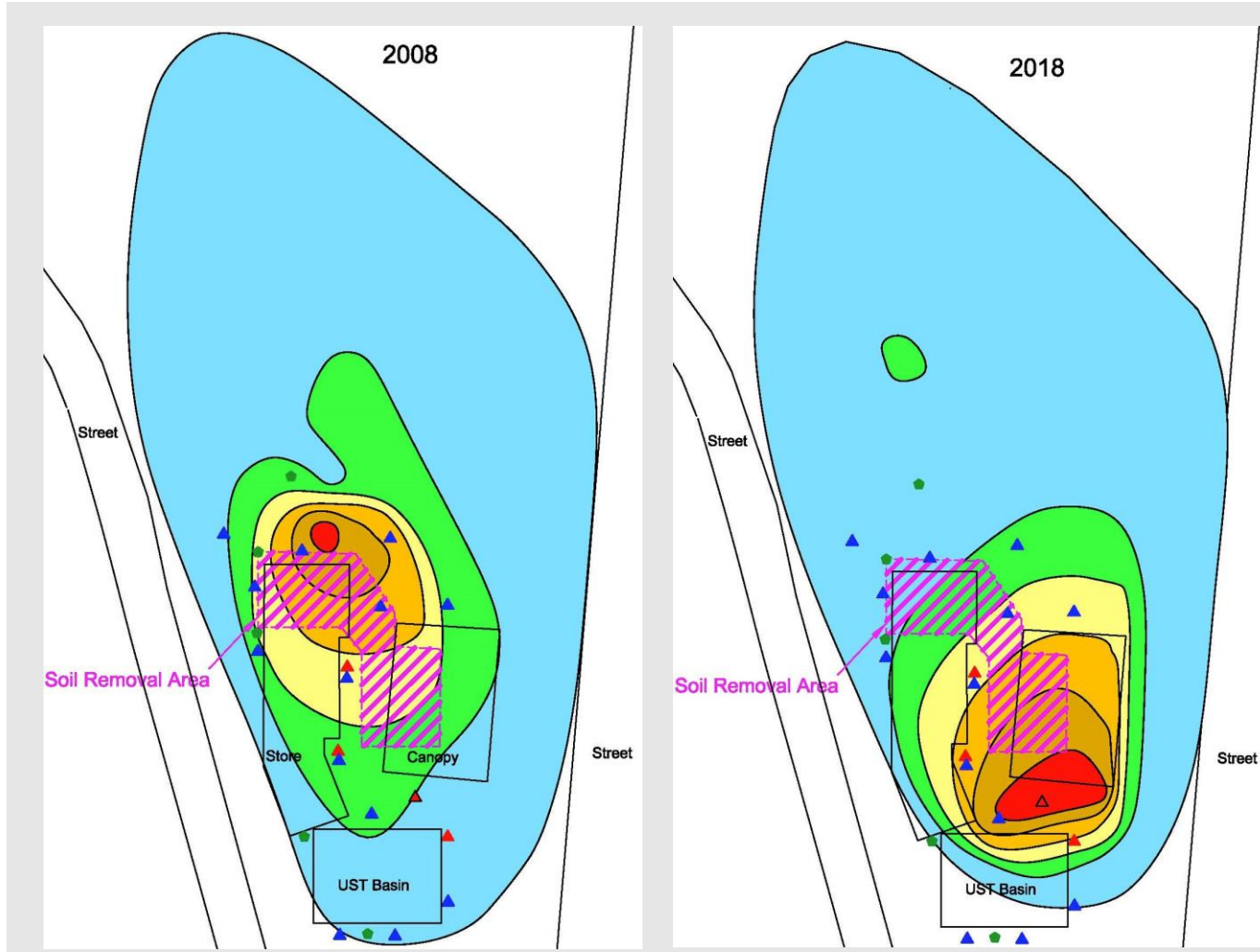




2008



- ❑ Benzene plume ~95,000 SF
- ❑ Max benzene concentration 5,830 µg/L, 1000 µg/L contours
- ❑ Mass of hydrocarbons estimated at 10,000 lbs, 10% of which was BTEX
- ❑ Why enhanced bio was selected
 - Impacts >20' bgs
 - Overlying obstacles
 - UST system
 - Store
 - AS/SVE not feasible in worst-case areas

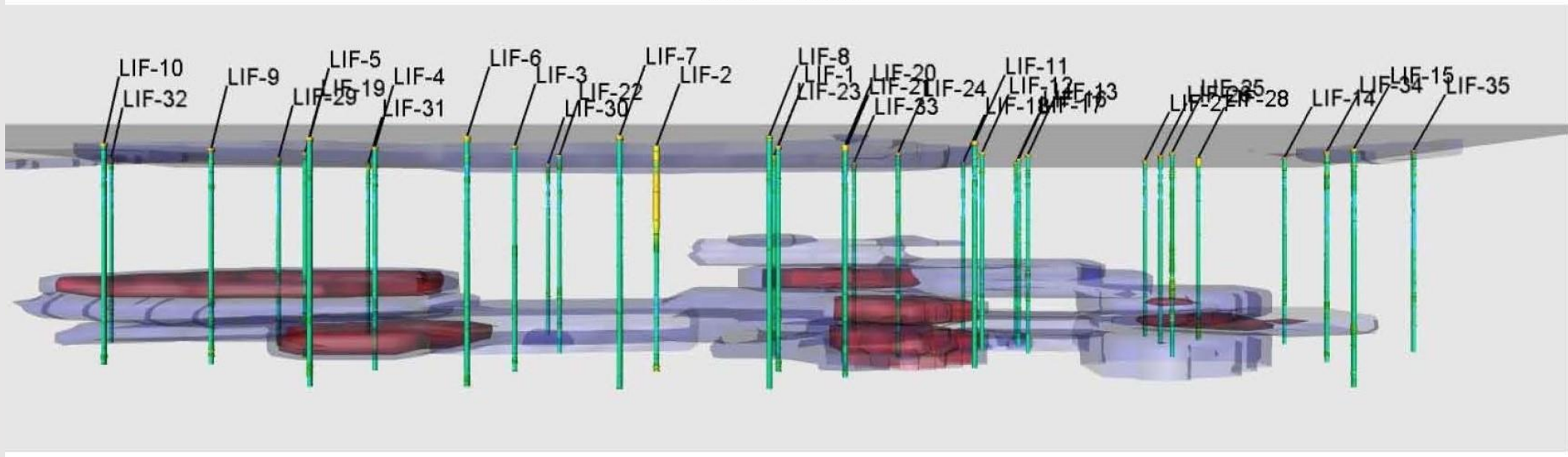


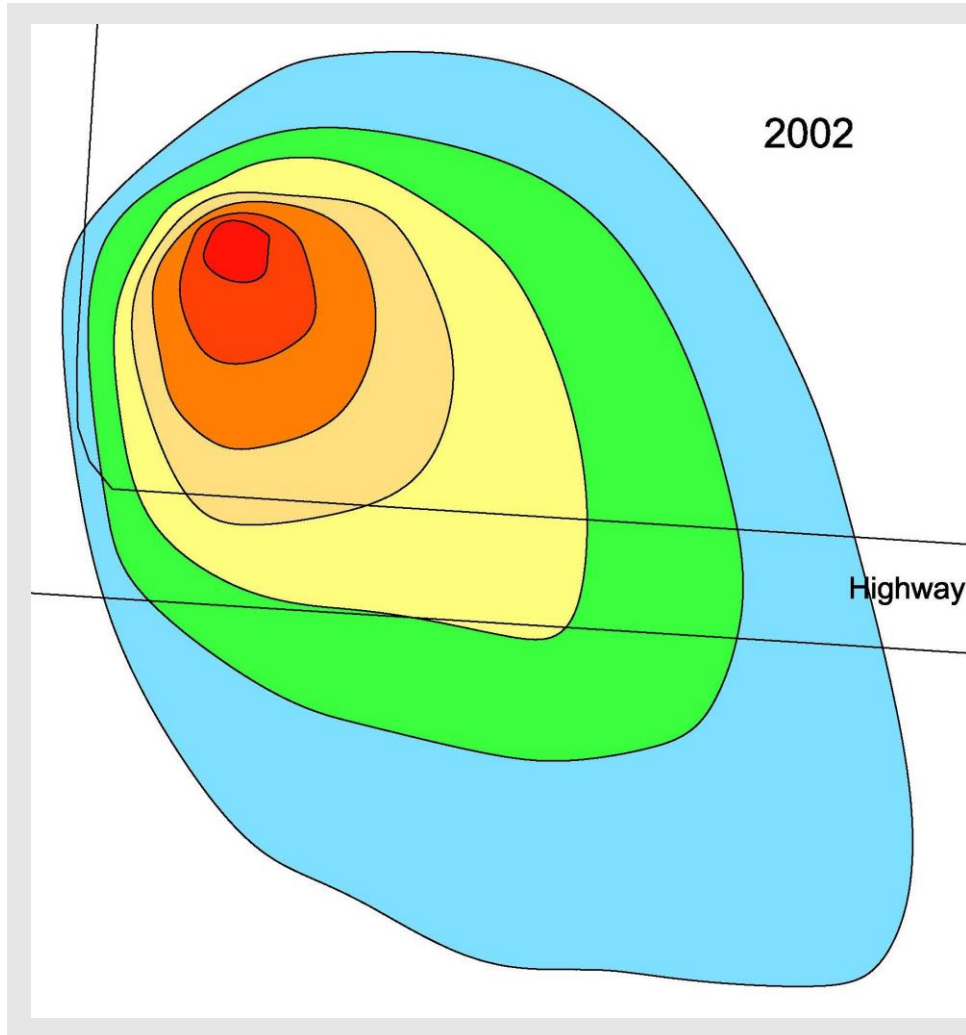
- ❑ Enhanced Bio Implemented 2011-2016
- ❑ Delivered 7,300 lbs O₂, ~50% more than Case 1 to treat an estimated 30% less mass
- ❑ Reduced benzene in former hot spot area, but new one appeared where NAPL had been discovered
- ❑ Led to a LIF investigation

Case 2 - Lessons Learned

- ❑ 3:1 ratio of O₂:Hydrocarbons – Knowing the mass is important
- ❑ Don't rely solely on laboratory data, particularly with thin sand stringers

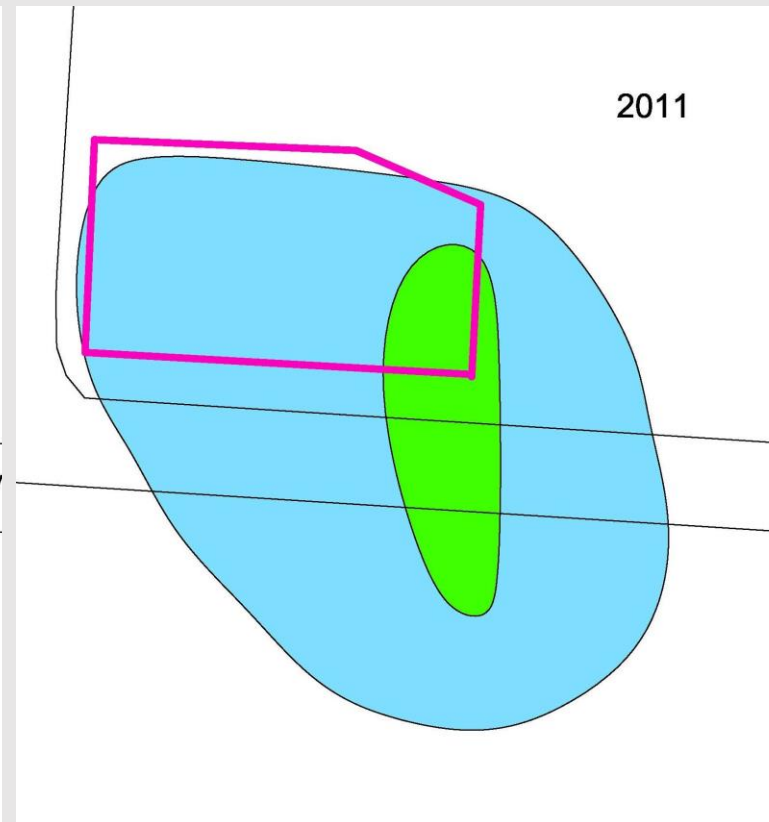
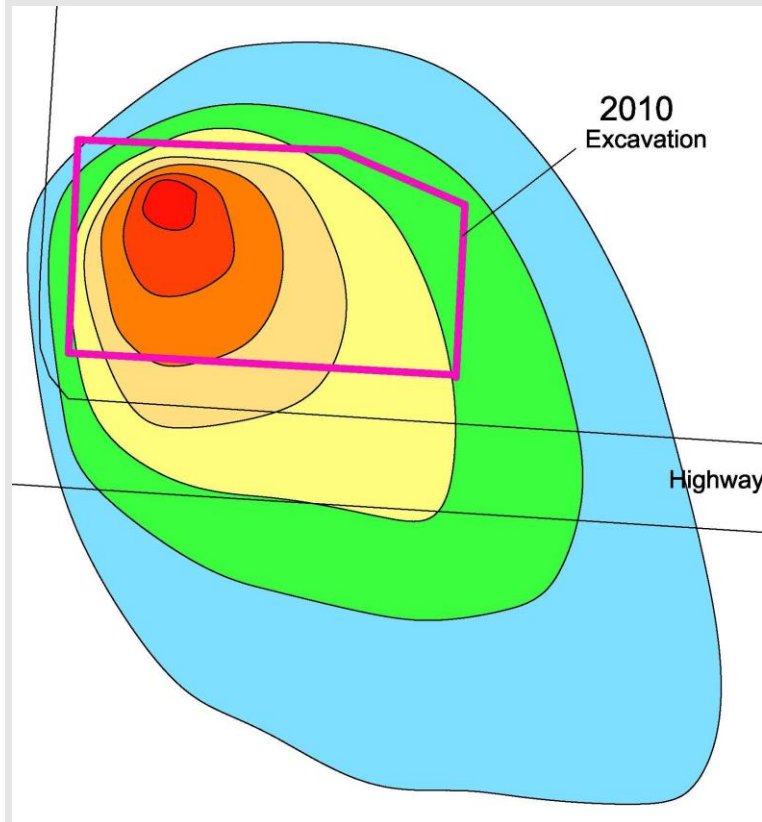
View to West





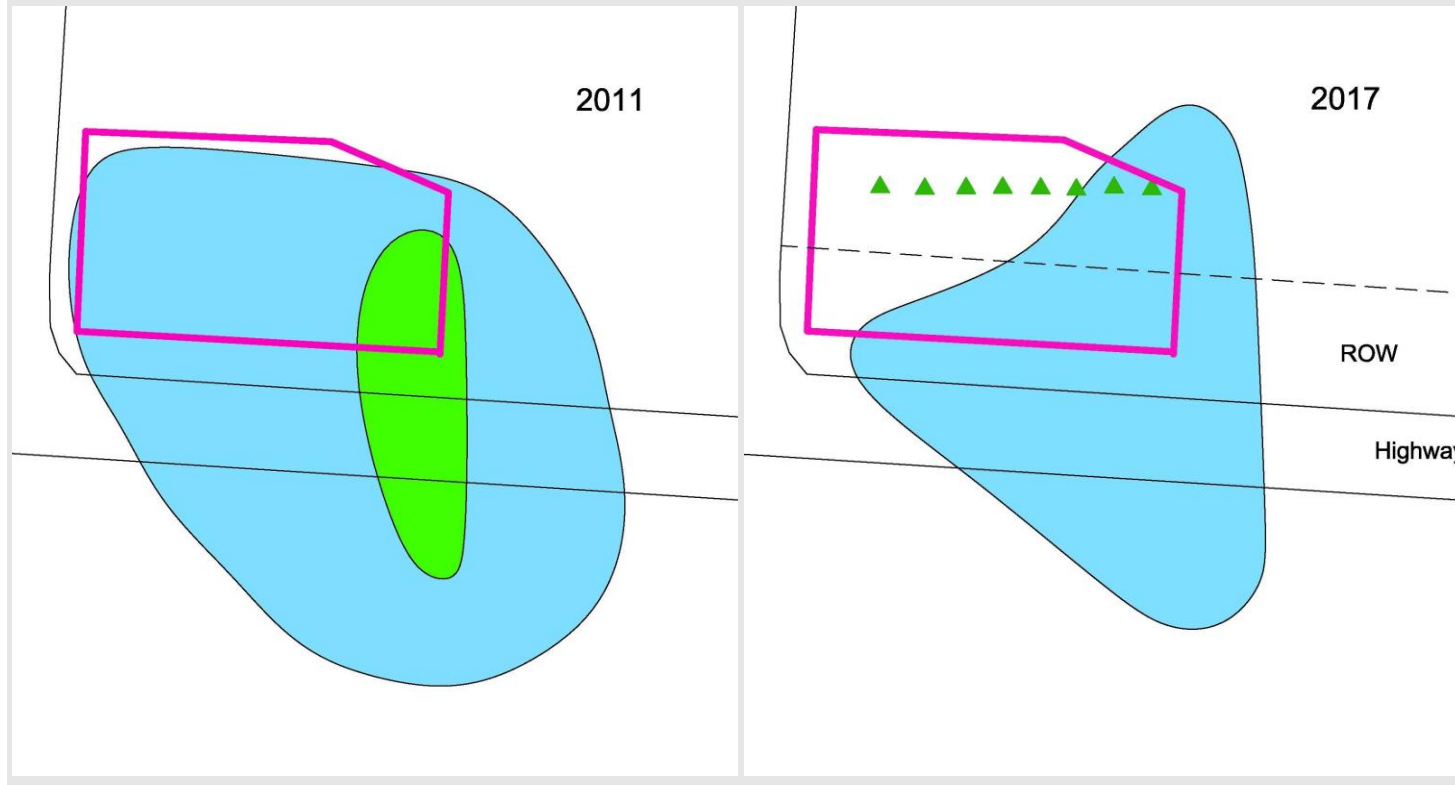
Case 3

- ❑ Silty to sandy clay with thinly interbedded sand lens extends to depths of 17-19 feet bgs underlain by gravel with sand and clay.
- ❑ Unconfined aquifer, SWL varies seasonally, 10 to 20 feet bgs. Flow to the south.
- ❑ Fueling occurred from 1930's to 1993.
- ❑ Stagnant, dissolved-phase plume with benzene concentrations as high as 8,720 $\mu\text{g/L}$.



- ❑ Excavated 3,200 CY impacted soil in April 2010
- ❑ South sidewall contained elevated hydrocarbons in fine grained sed with interbedded sand lenses.
- ❑ Dissolved phase plume persist with benzene $>1,000 \mu\text{g/L}$

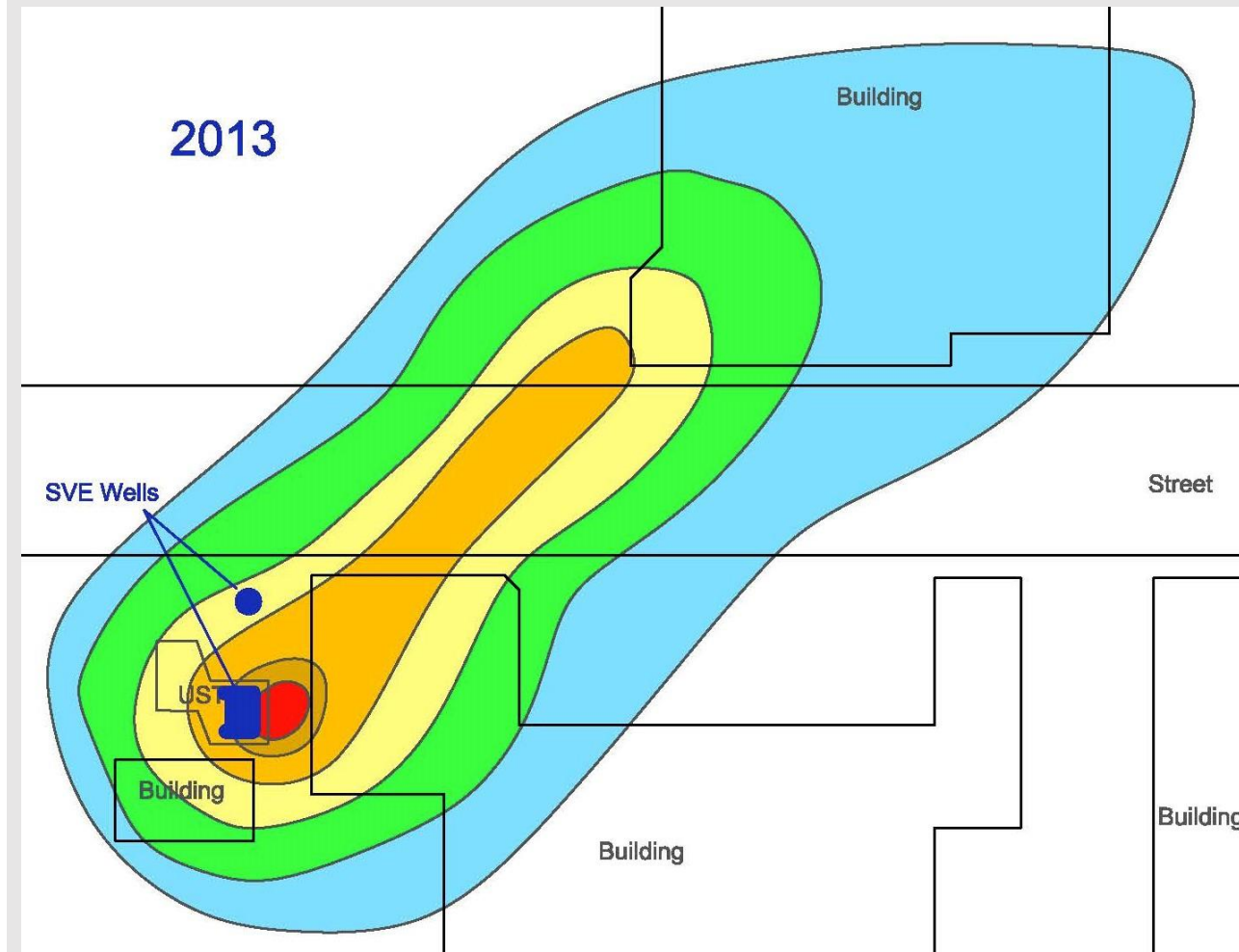
- ❑ 3,000 lbs O₂ delivered from 2014-2017
- ❑ Max benzene <10 µg/L north of highway but still as high as 742 µg/L south of highway



Case 3: Lessons Learned

- ❑ Preferential pathway indicated by widely varying concentrations in adjacent wells
- ❑ Injection hampered by fine grained sediment- Horizontal wells?
- ❑ Not an immediate fix, requires time to deliver the O₂

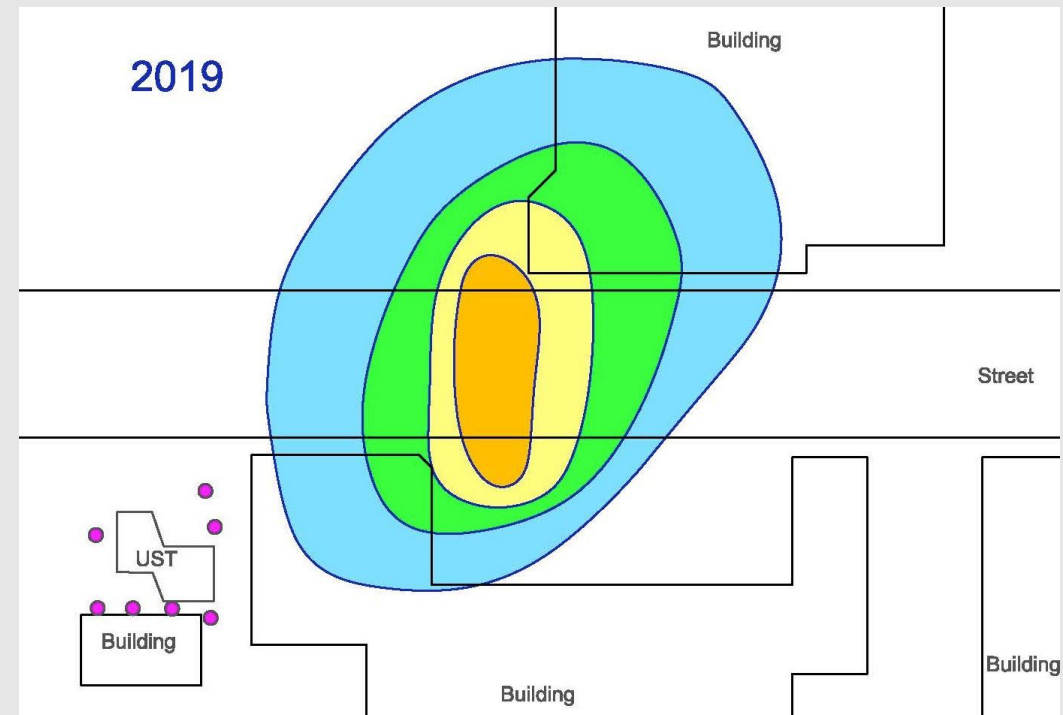
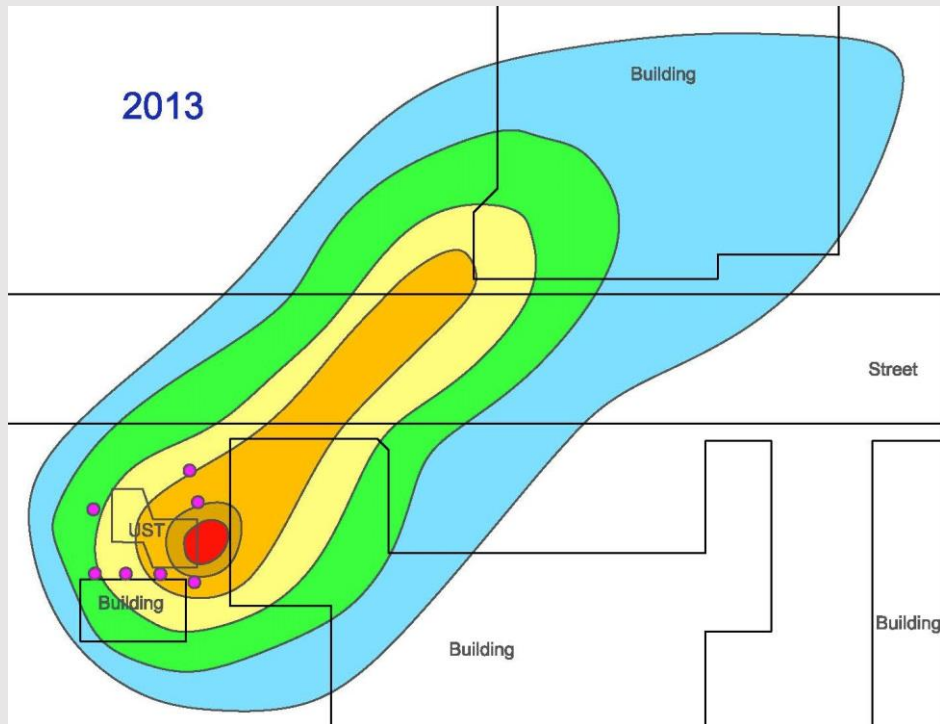
Case 4



- 450 CY impacted soil removed from UST basin in 1993
- Aquifer – sand and gravel with clay. DTW 10-16 feet bgs.
- SVE recovered 9,350 pounds of hydrocarbons between 1994-2015, No measurable vapors after 2010.
- 123 gallons of NAPL recovered
- Max benzene concentration in 2013: 5,830 µg/L - Stable
- Why enhanced bio was selected
 - Overlying obstacles
 - AS/SVE not feasible

Case 4 -
Lessons
Learned

- ❑ System startup in 2015 and by 2018 BTEX <RBSLs on site, injection ongoing for down-gradient treatment
- ❑ Good delivery resulted in rapid reduction in petroleum hydrocarbons



Lessons Learned

Enhanced Aerobic Biodegradation Can Be Effective

- ❑ Mass Matters
 - Most effective after source removal is completed
 - NAPL is not always readily obvious but has a large affect on the amount of O₂ needed
- ❑ Delivery
 - Geologic conditions can hamper delivery
 - Design with over-delivery in mind
 - Be adaptable, assess and modify as necessary
- ❑ Be Patient
 - Typically used at mature, heterogeneous sites where hydrocarbons have diffused deep into pore spaces. It will also take time for the O₂ to access those hydrocarbons.