

# Systematic Approach to Optimization of a Permanganate In Situ Chemical Oxidation System

Operable Unit 4, Naval Training Center Orlando

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# Project Team



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# Overview



- ❑ Operable Unit 4, Former Naval Training Center Orlando**
- ❑ In situ chemical oxidation (ISCO) design**
- ❑ ISCO performance data**
- ❑ Optimization efforts**
  - Supporting laboratory work**
  - Source zone delineation**
- ❑ Optimization alternatives**
- ❑ Conclusions/lessons learned**

# NTC Orlando, Operable Unit 4 (OU 4)



# Operable Unit 4, NTC Orlando



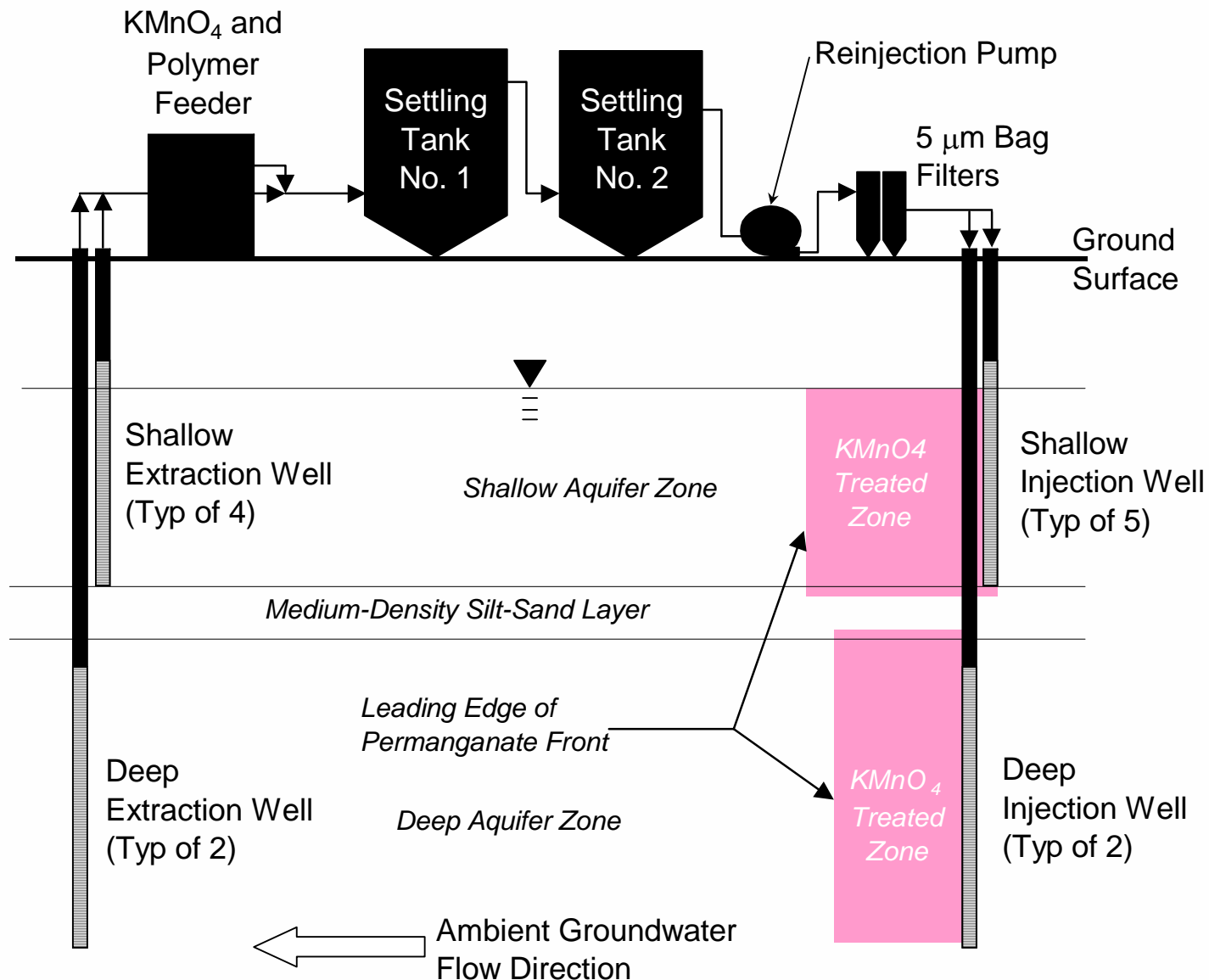
- ❑ Building 1100 was industrial dry cleaning facility**
- ❑ PCE detected in groundwater as high as 23 mg/L**
- ❑ PCE detected in soil as high as 2,940 mg/kg**
- ❑ TCE and cis-1,2-DCE detected as high as 13.2 mg/L and 4.6 mg/L, respectively**
- ❑ 70-foot saturated thickness of very fine to fine-grained silty sand**
- ❑ Hydraulic conductivity = 10 to 100 ft/day**
- ❑ Depth to water = 5 to 6 ft bgs**
- ❑ Total organic carbon (TOC) ranges from 200 to 8200 mg/kg**

# ISCO Design



- Pilot test conducted in 2000
- 5 Shallow injection wells
  - Total shallow injection rate = 10 GPM
- 2 Deep injection wells
  - Total deep injection rate = 5 GPM
- Design  $\text{MnO}_4^-$  concentration = 1,000 mg/L
- Aboveground re-circulation system designed to remove manganese dioxide solids and re-inject permanganate into aquifer
- Theoretical permanganate “front” to treat organic compounds (natural and contaminants) in situ
- Operational difficulties prohibited use of polymer feed system for enhanced manganese dioxide particle flocculation

# ISCO Re-circulation System



# ISCO Equipment



**Aboveground Settling Tanks**



**KMnO<sub>4</sub> Drum Feeders**



# ISCO Equipment



↑  
**Extraction Manifold**



↑  
**Injection Manifold**

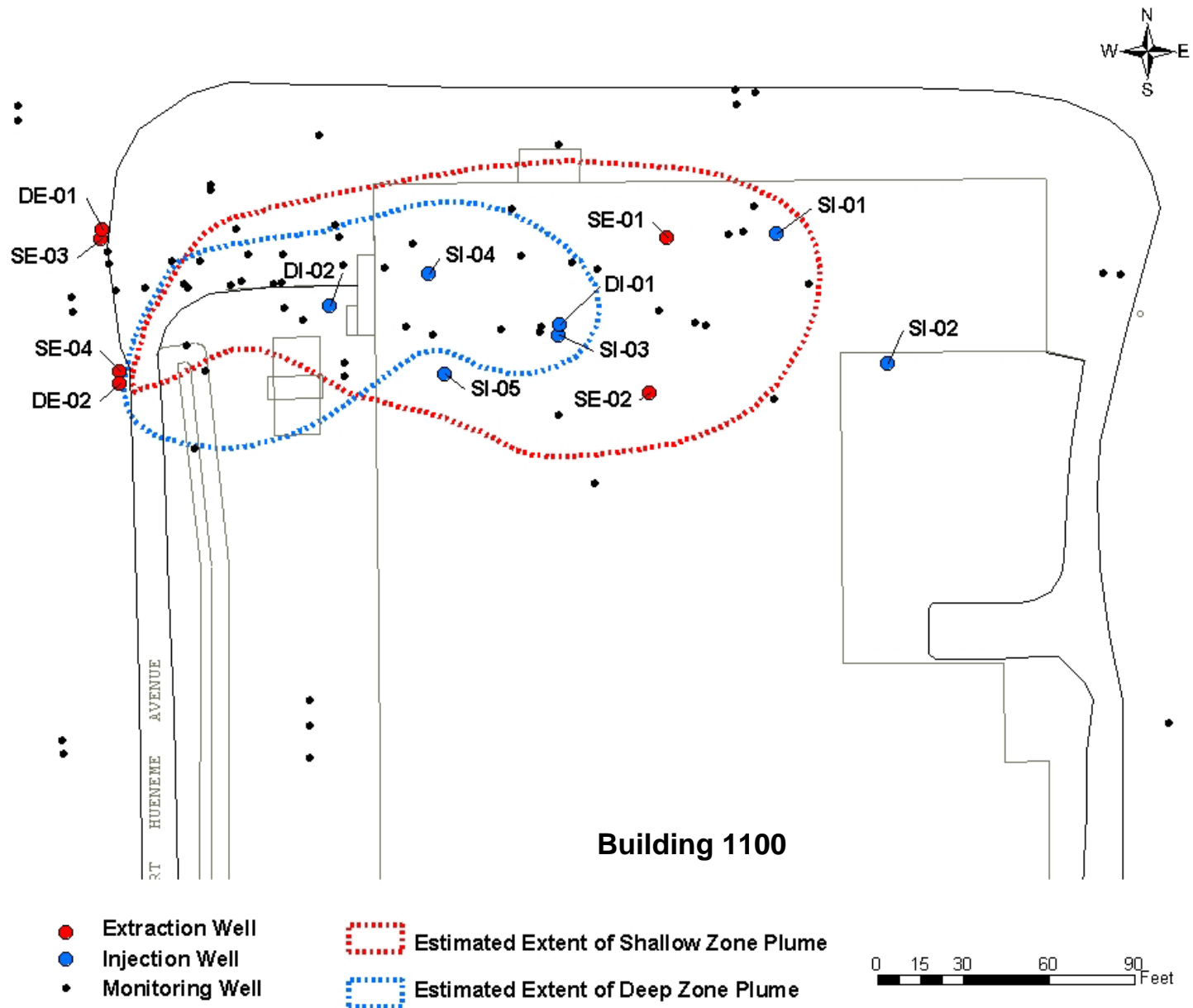


**Bag Filter System** →

# Target Treatment Zone



# ISCO Well Field

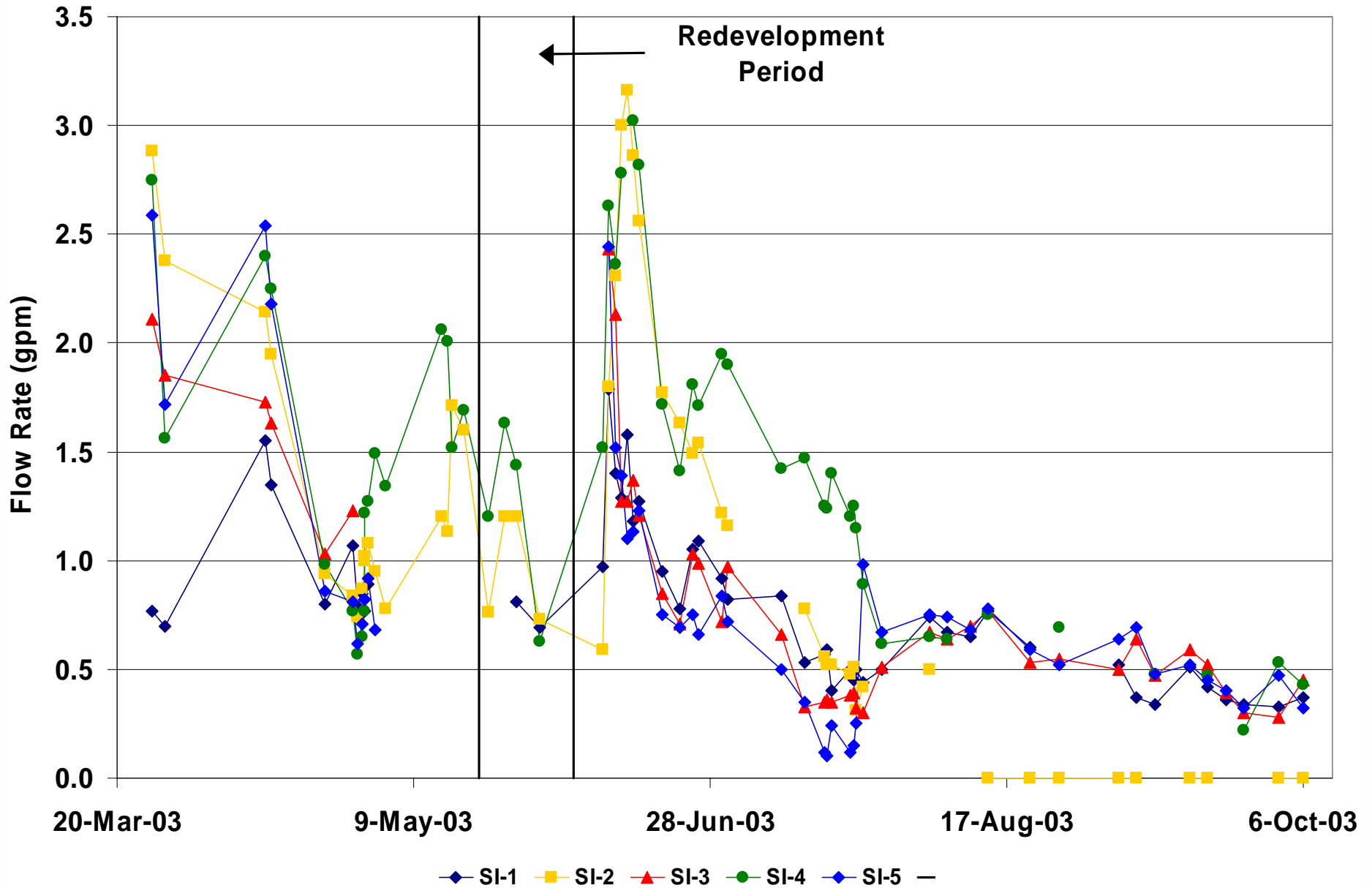


# ISCO Performance



- Low sustainable injection rates (< 0.5 gpm per well)**
- Water levels increased in injection wells**
- Low  $\text{MnO}_4^-$  loading to the aquifer**
- Erratic subsurface distribution of  $\text{MnO}_4^-$**
- Injection well fouling/formation plugging caused by accumulation of manganese dioxide ( $\text{MnO}_2$ ) particles**
- Excessive downtime caused by O&M activities (e.g. power failure, well redevelopment, feeder operation)**

# Shallow Injection Well Performance



# MnO<sub>2</sub> Particle Generation

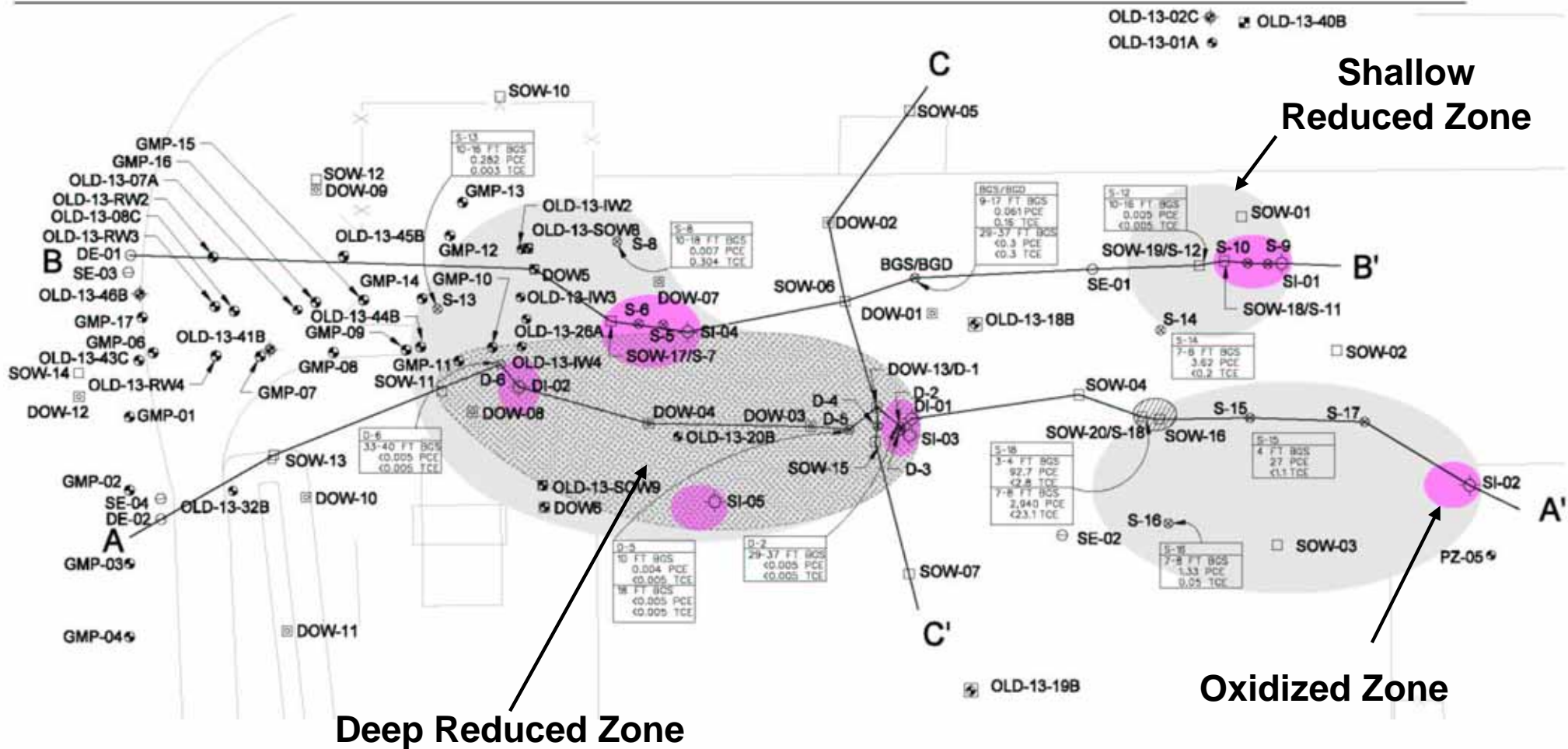


**New Filter**

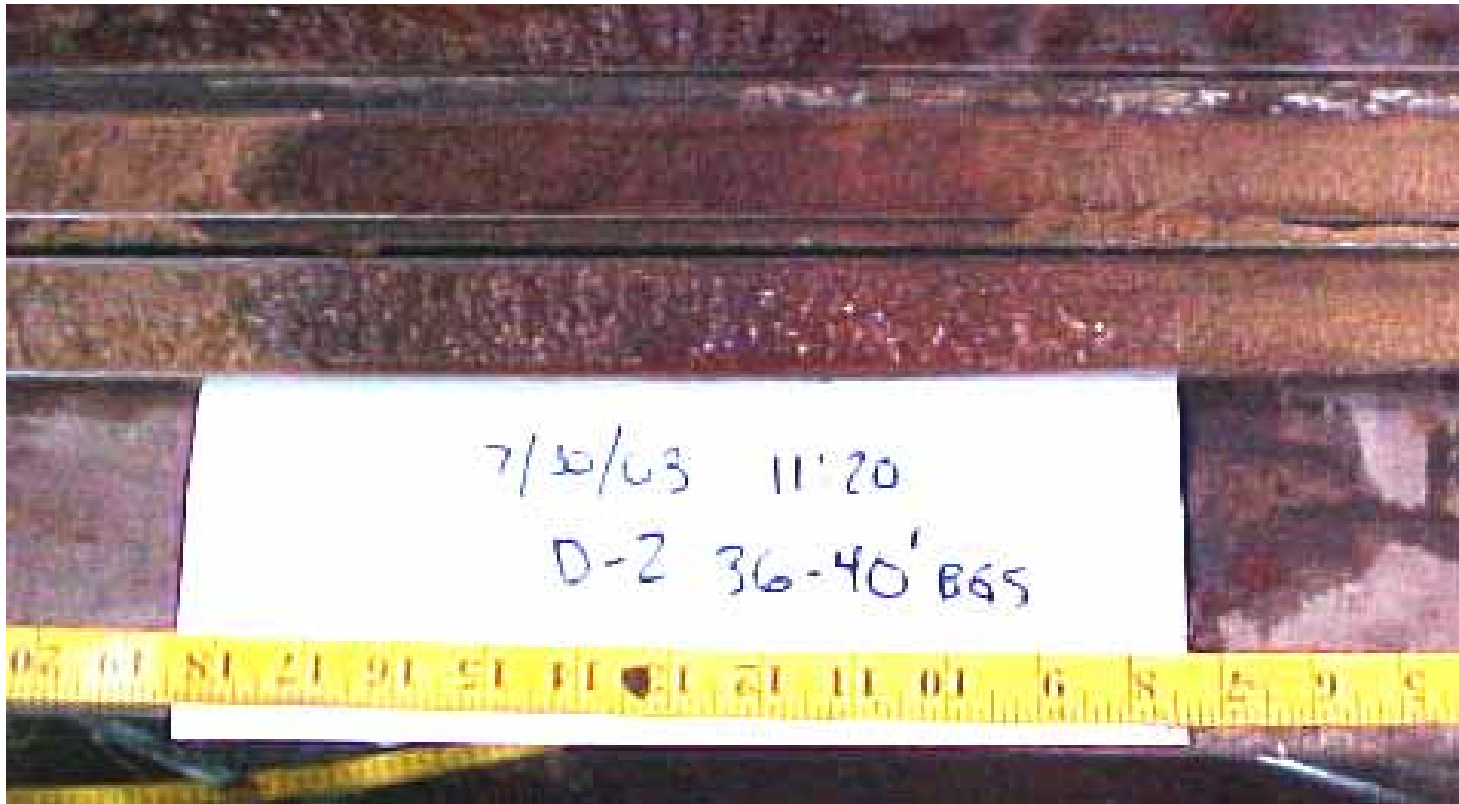


**Spent Filter**

# Subsurface Distribution of $MnO_4^-$



# Soil Coring – Oxidized Zones



**Permanganate Staining**



# Soil Oxidant Demand (SOD)



- ❑ Original SOD estimate was based on 30-minute batch test by permanganate vendor
- ❑ Field and laboratory batch tests confirmed SOD ranges from 1 – 10 g/kg for 1,000 mg/L  $\text{MnO}_4^-$
- ❑ Lab flow-through column tests yielded SOD estimate of 0.3 to 0.4 g/kg for 1,000 mg/L  $\text{MnO}_4^-$
- ❑ Two methods to minimize natural oxidant demand:
  - Lower permanganate concentration
  - Faster flow rate (less oxidant contact time with porous media)
- ❑ Lab column tests with  $\text{MnO}_4^-$  concentration of 250 – 500 mg/L experienced no plugging, pressure increase, or flow reduction

# Soil Oxidant Demand Testing



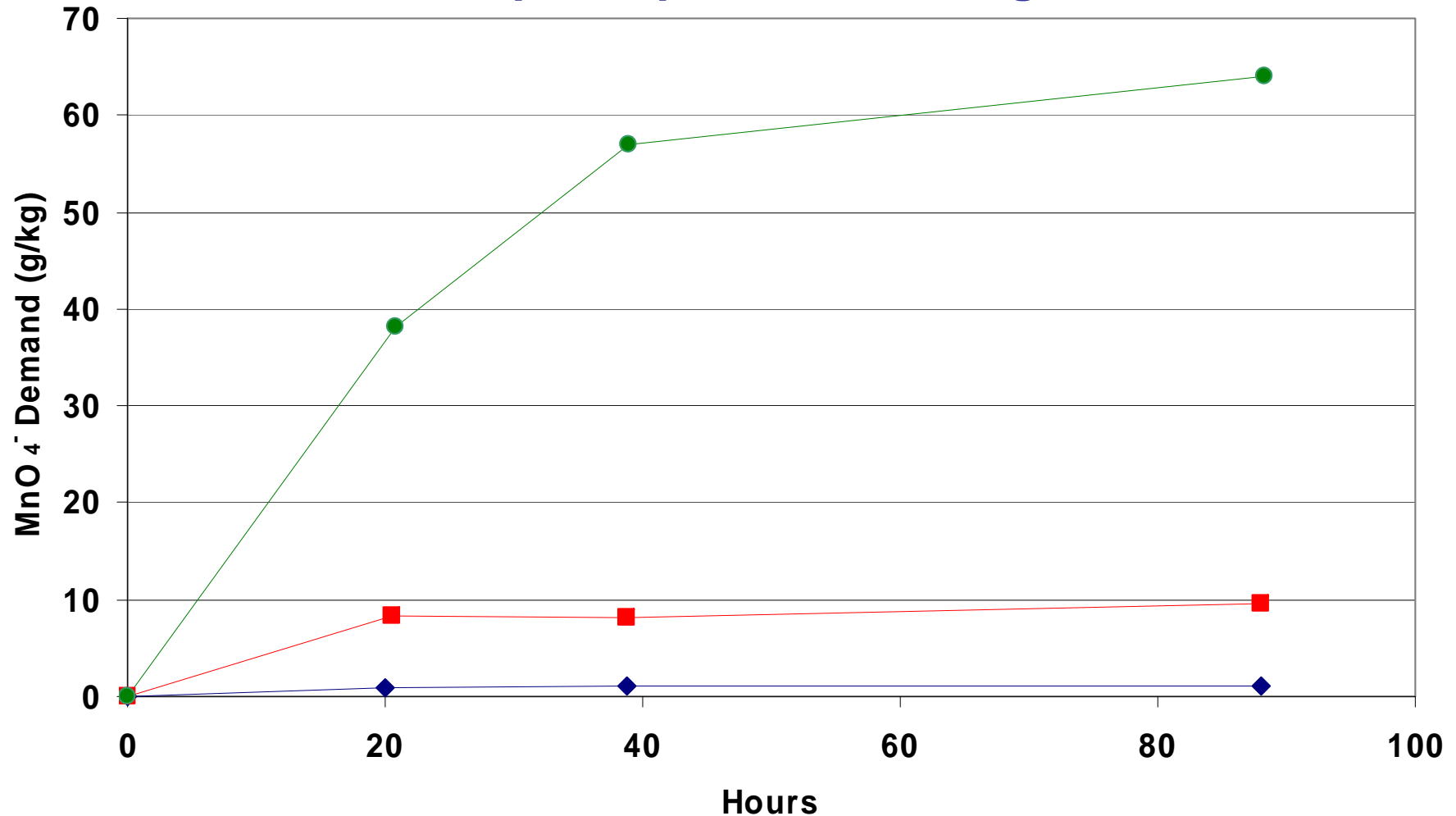
## Field Laboratory Setup



# Soil Oxidant Demand Testing



Sample Depth: 10 – 18 ft bgs



\* Field Test

◆ S1A - 100 mg/L    ■ S1A - 1,000 mg/L    ● S1A - 10,000 mg/L

Settling tank

Manometer board

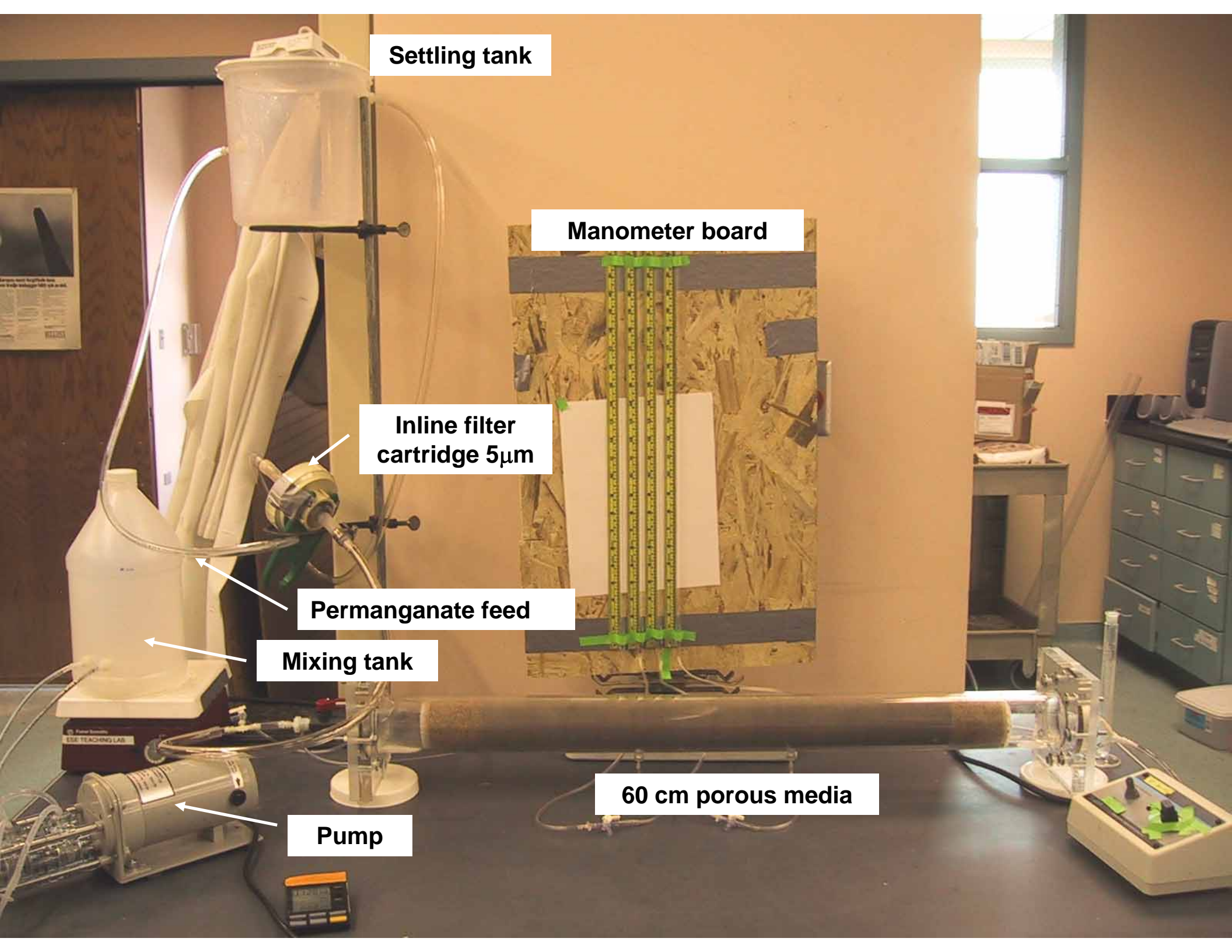
Inline filter cartridge 5 $\mu$ m

Permanganate feed

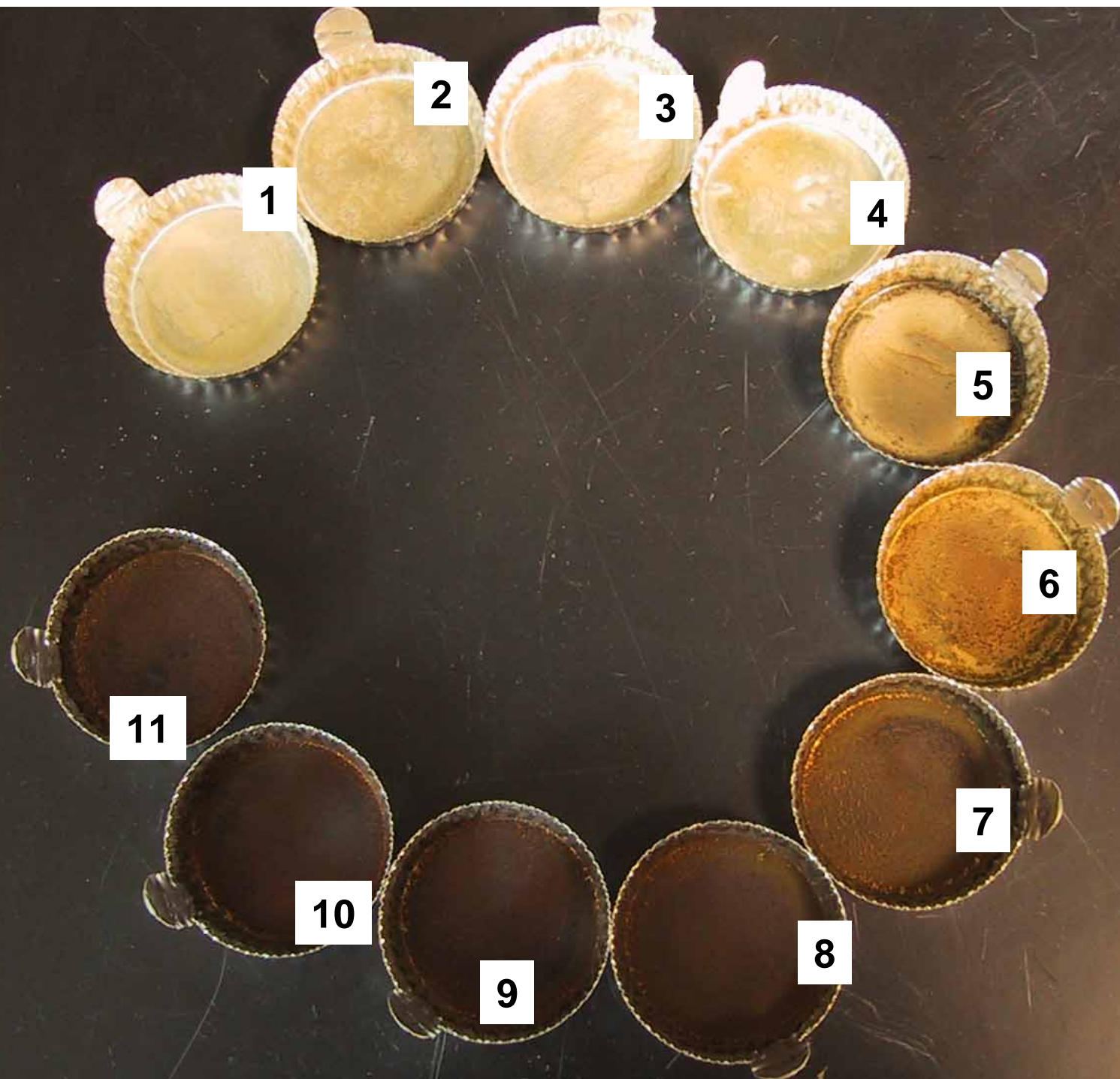
Mixing tank

60 cm porous media

Pump



# Total solids in column effluent for each Pore Volume of throughput



Note: MnO<sub>4</sub><sup>-</sup> Breakthrough at 4 PV

# Soil Oxidant Demand Testing



**Soil Prior to  
Treatment**

**1,000 mg/L  
KMnO<sub>4</sub>**

**4,000 mg/L  
KMnO<sub>4</sub>**



# Building Demolition



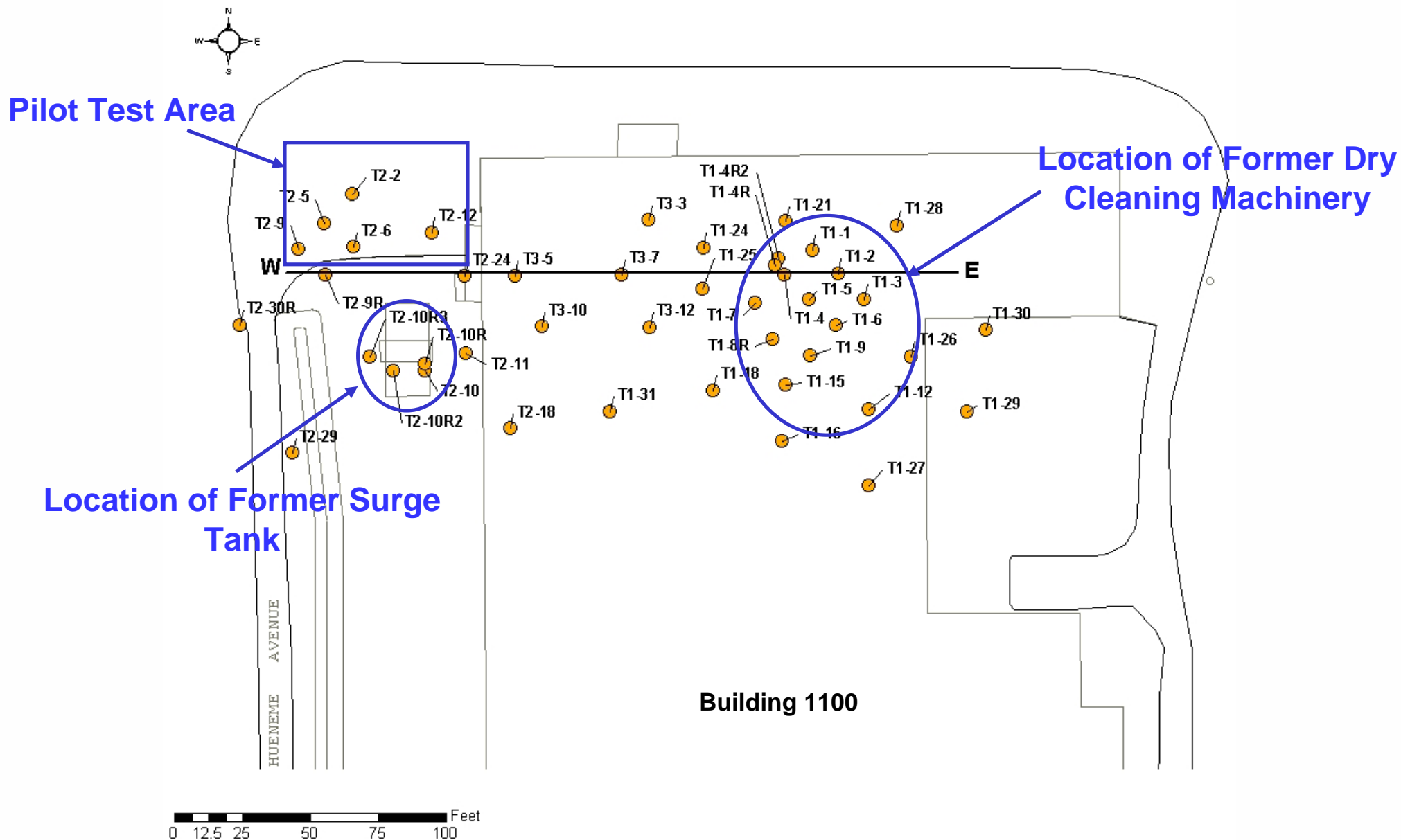
# MIP Investigation



- ❑ Building demolition allowed better access to site for detailed DNAPL source zone characterization**
- ❑ Goals of Membrane Interface Probe (MIP) investigation were to better define limits of ISCO treatment and evaluate site stratigraphy**
- ❑ 46 Points installed to an average depth of 70 ft bgs**
- ❑ MIP and soil conductivity measurements collected at 0.05 ft vertical interval**
- ❑ Soil and groundwater confirmation samples collected**



# MIP Investigation Points



# MIP Equipment



**DPT Rig**

**MIP Equipment**

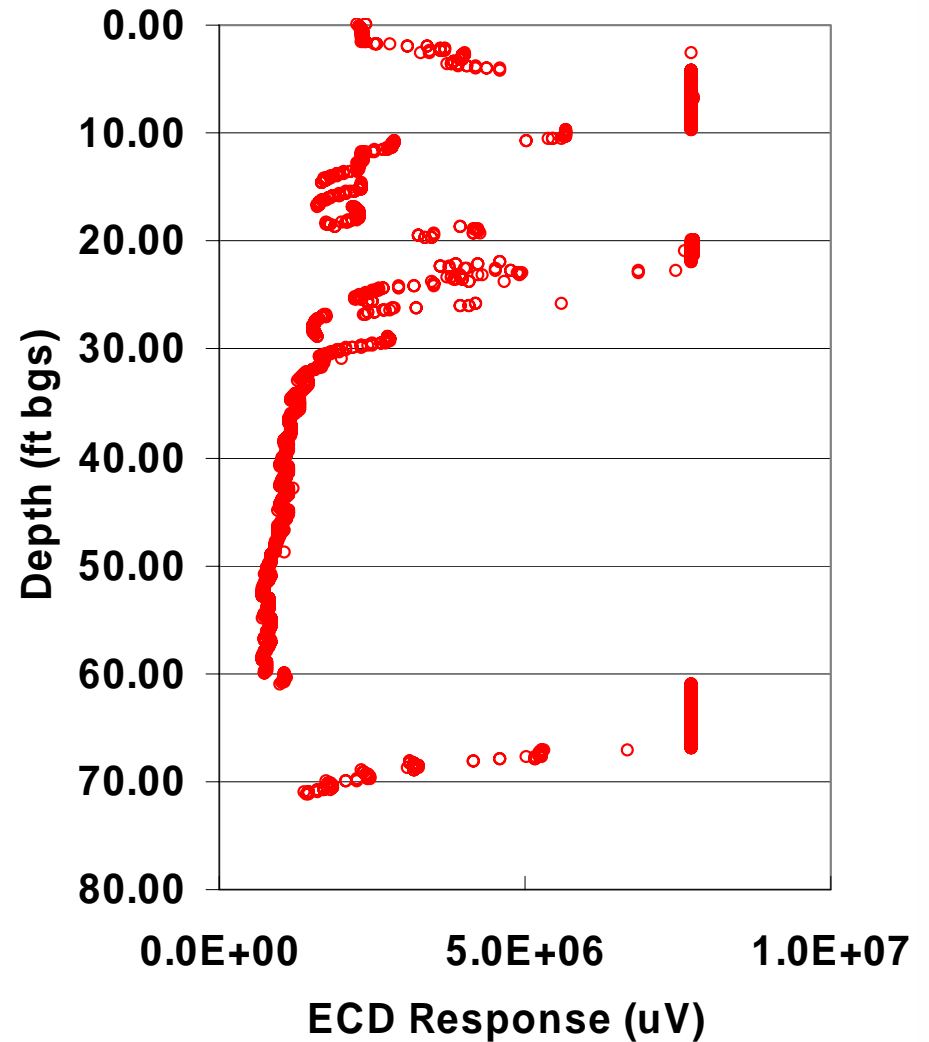
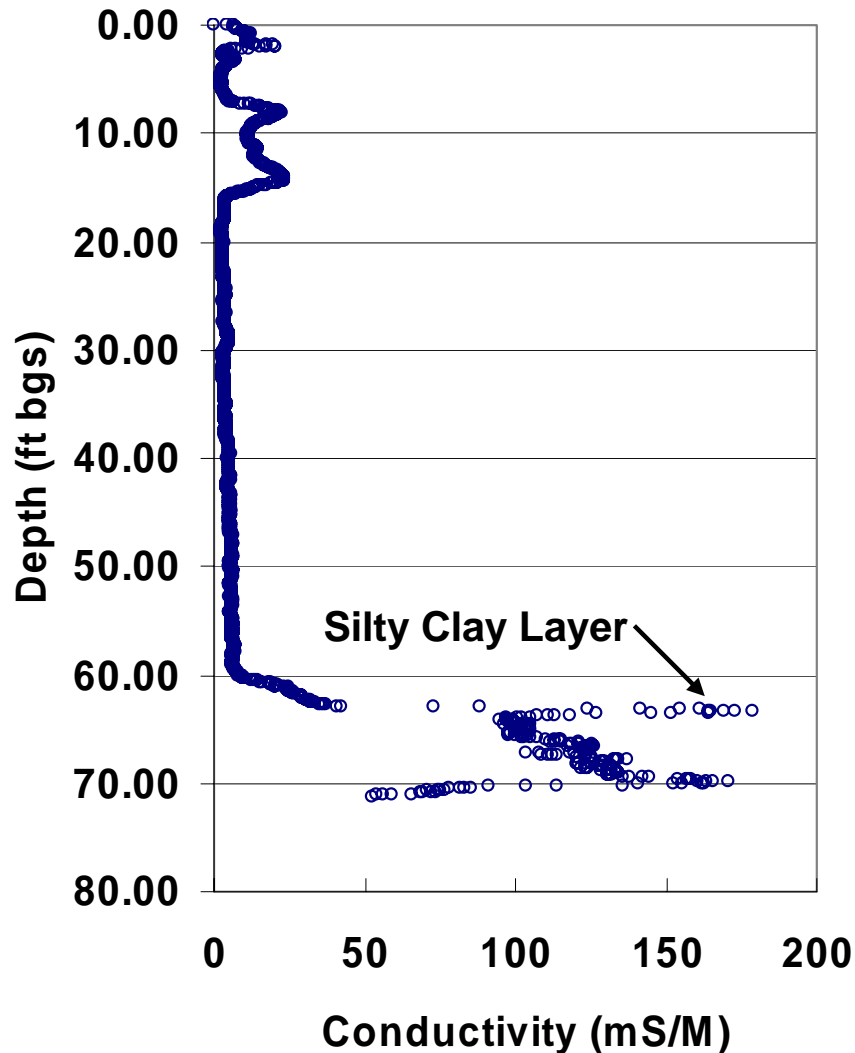
# MIP Investigation



# Typical MIP Response



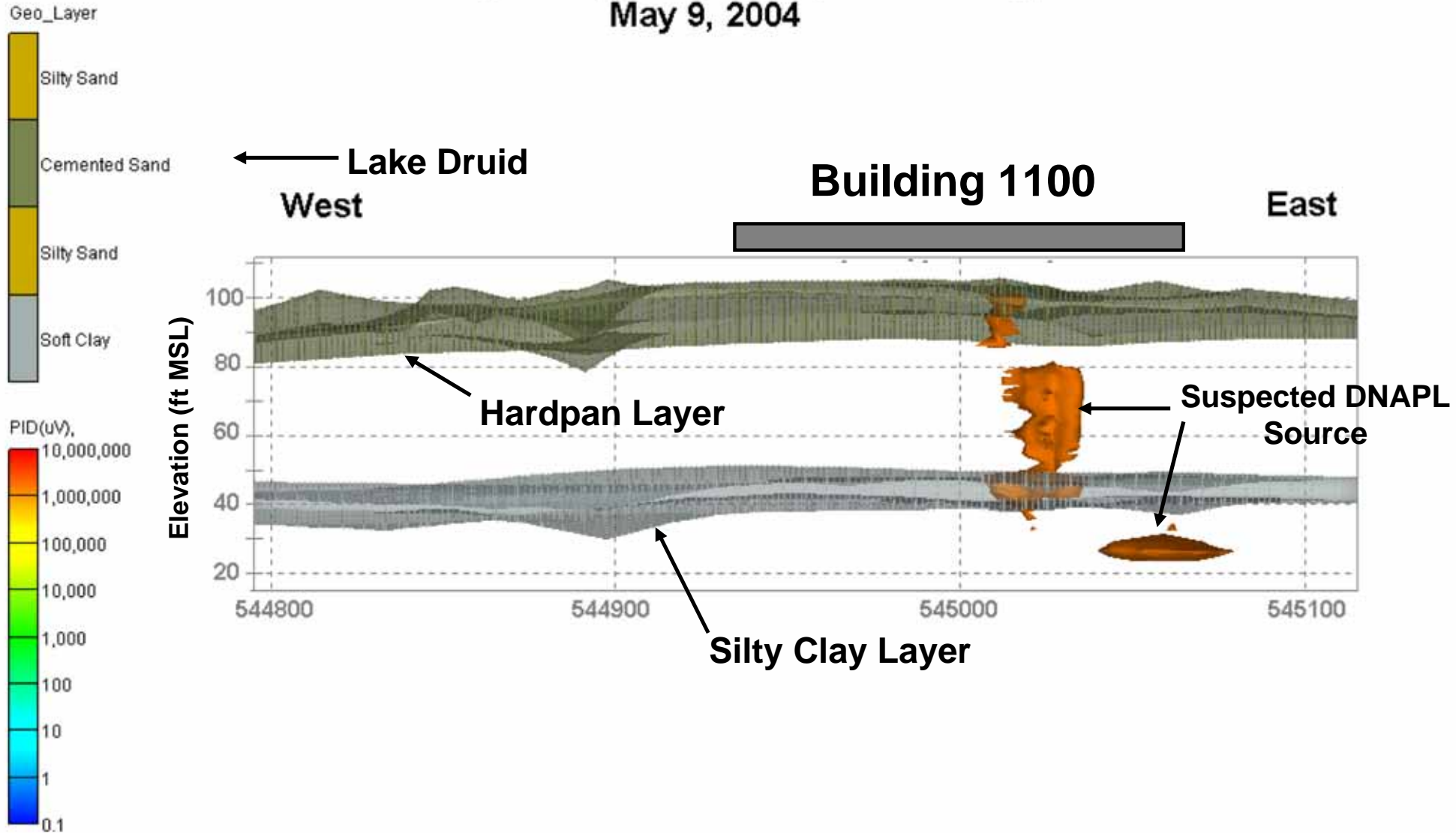
## T1-7 in DNAPL Source Area



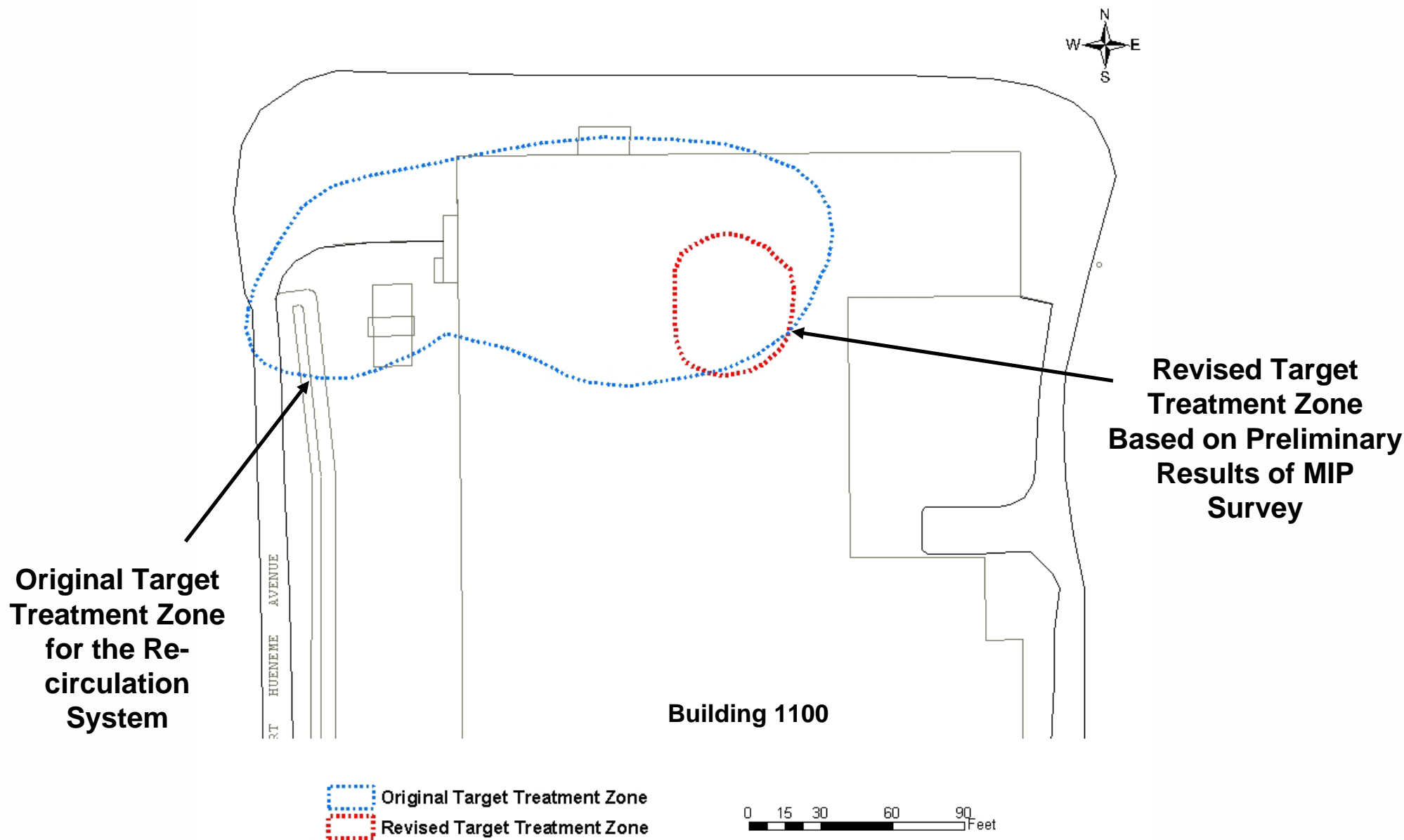
# MIP Results



PID Response (1,000,000 uV) and Geology  
May 9, 2004



# Reduction in Target Treatment Zone



# Optimization Alternatives



## **□ Option 1 – Optimize Re-circulation System**

➤ **Optimize existing re-circulation system by reducing the permanganate concentration. Injection well field would be designed based on design simulation using permanganate reaction kinetics.**

## **□ Option 2 – Permanganate Delivery Using DPT Injection**

➤ **Based on smaller target treatment zone, focus delivery of permanganate with use of DPT technology. Option would also include enhanced bioremediation as a polishing tool.**

# Summary



- ❑ Injection well fouling/formation plugging caused by buildup of manganese dioxide solids resulted in low oxidant loading
- ❑ Inaccurate estimation of natural oxidant demand of porous media
  - Oxidant consumed within short distance
  - Higher MnO<sub>2</sub> solids generated causing fouling
  - Reduce oxidant concentration to reduce MnO<sub>2</sub>
- ❑ Overestimation of oxidant transport in design model simulations
  - Design simulator did not take into account oxidant reaction kinetics



# Summary (Cont.)



- Improved DNAPL characterization will reduce target treatment zone; improve effectiveness and cost efficiency**
- Alternate delivery method using DPT technology may be more cost effective**

# Lessons Learned



## ❑ Critical design factors:

### ➤ Accurate estimate of SOD

- Depends on SOD test method (batch vs. flow through)

### ➤ Accurate source zone characterization

### ➤ Selection of appropriate reagent delivery method

### ➤ Account for aquifer geochemistry (e.g high SOD, anaerobic conditions)

### ➤ Design simulators need to include permanganate reaction kinetics

## ❑ Perform optimization reviews at all phases

### ➤ Particularly at FS, RD when optimization can be built in

### ➤ Involve specialized technical expertise as appropriate

# Questions?

Accelerating Site Closeout – Improving Performance – & Reducing Costs Through  
**OPTIMIZATION** June 15 – 17, 2004  
Dallas, Texas