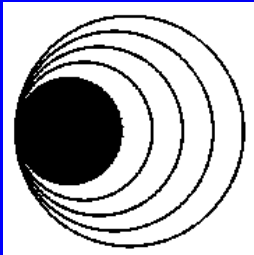


# CHEMOX-ENHANCED REDUCTIVE DECHLORINATION

BY

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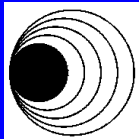
George Hoag, Pradeep Chheda

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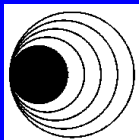
# Presentation Outline

- Technology Overview
- Pilot Study Overview
- Post-Injection Monitoring Results
  - Concentration Contours
  - Chloride Mass Balance Results
  - Additional Investigation Results
- Conclusion



# Technology Overview

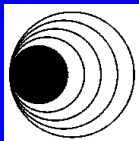
- Sequential/simultaneous injection of persulfate (reduce SOD) and permanganate (destroy VOCs)
- Commonly  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{KMnO}_4$
- Advantages:
  - Reduced clogging potential for high SOD application
  - Reduced cost over permanganate alone (SOD)
  - Destruction of chlorinated & petroleum hydrocarbons feasible
  - Potential enhanced biodegradation via persulfate injection



# $\text{Na}_2\text{S}_2\text{O}_8$ - Enhanced Biodegradation

$\text{Na}_2\text{S}_2\text{O}_8$  injection may enhance biodegradation by one or more of the following:

- Making the CVOCs more bioavailable by reducing sorption sites
- Providing simple organic carbon (a food source) for bacteria by degrading naturally occurring complex organic carbon
- Enhancing sulfate-reducing bacteria growth

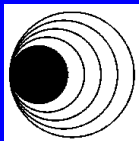


# Test Site

- Manufacturing facility – historically used TCE
- Hydrogeology:
  - Water bearing strata: gravely-sand, semi-confined, 8-10 ft thick, 5 ft/day velocity
  - Residual DNAPL in silt lenses and at the aquitard interface
  - Main contaminants: TCE, cis-DCE, VC
  - Generally reducing groundwater conditions (ORP: 0 to –150 mV)

# Oxidant Injection Pilot Test

- Laboratory treatability studies
- Source area characterization: 3-D, high resolution
- Pilot test design:
  - Two treatment zones ~160 ft x 175 ft x 10 ft each
  - Two rows of injection wells (total of 12 locations and 16 wells)
  - Eight rows of nested monitoring points (total of 36 locations and 80 points)
  - Chemox delivery system



# LEGEND

- SINGLE LEVEL INJECTION WELLS (IW) FOR CHEMICAL OXIDANTS
- DUAL LEVEL INJECTION WELLS (IW) FOR CHEMICAL OXIDANTS
- △ THREE NESTED GROUNDWATER MONITORING POINTS
- ▲ TWO NESTED GROUNDWATER MONITORING POINTS
- ▲ SINGLE GROUNDWATER MONITORING POINTS
- ⊙ GROUNDWATER MONITORING WELLS
- BUILDING FOOTPRINT
- ← DIRECTION OF AQUIFER FLOW SHOWING DATES OF SEASONAL VARIATION.

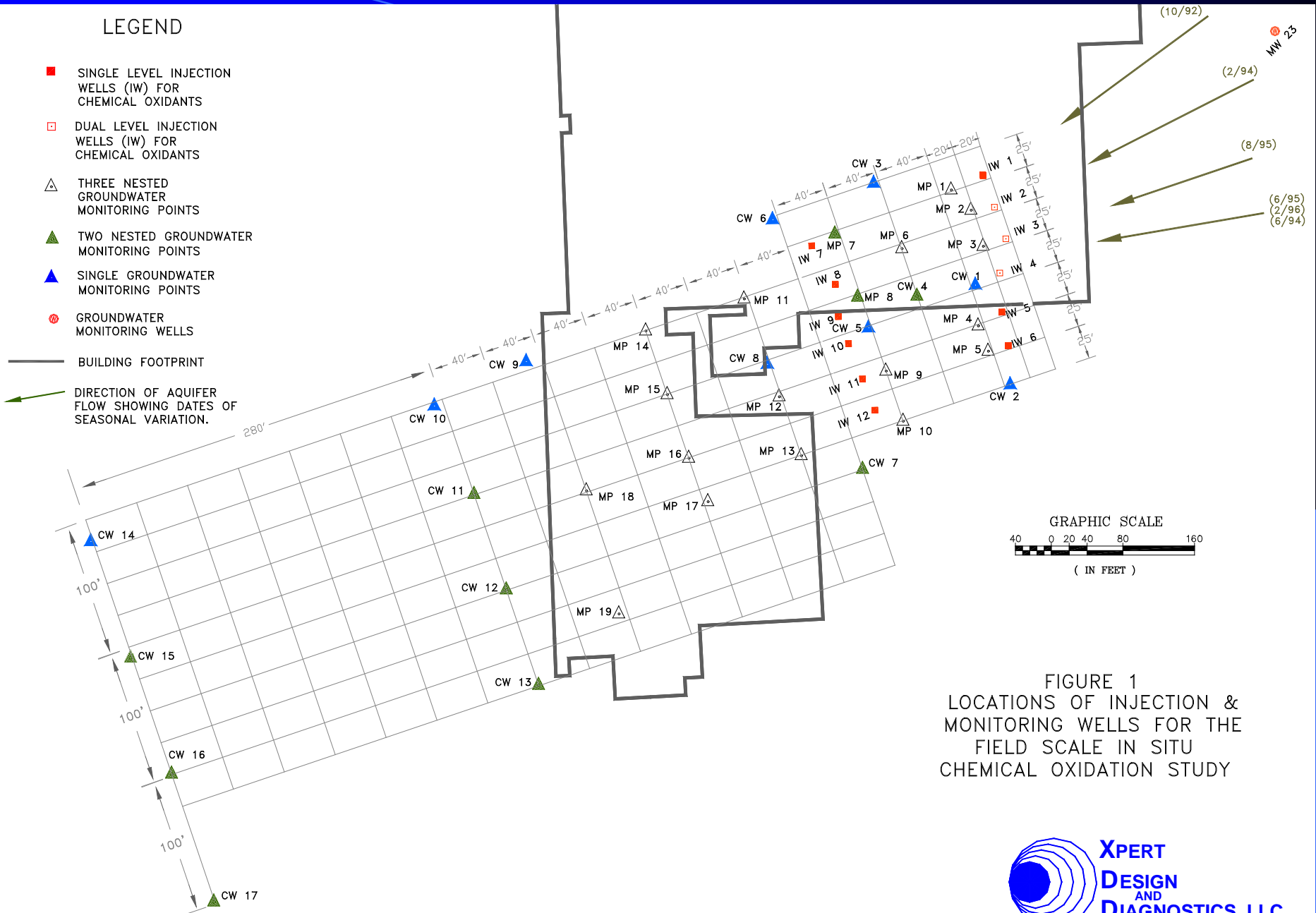
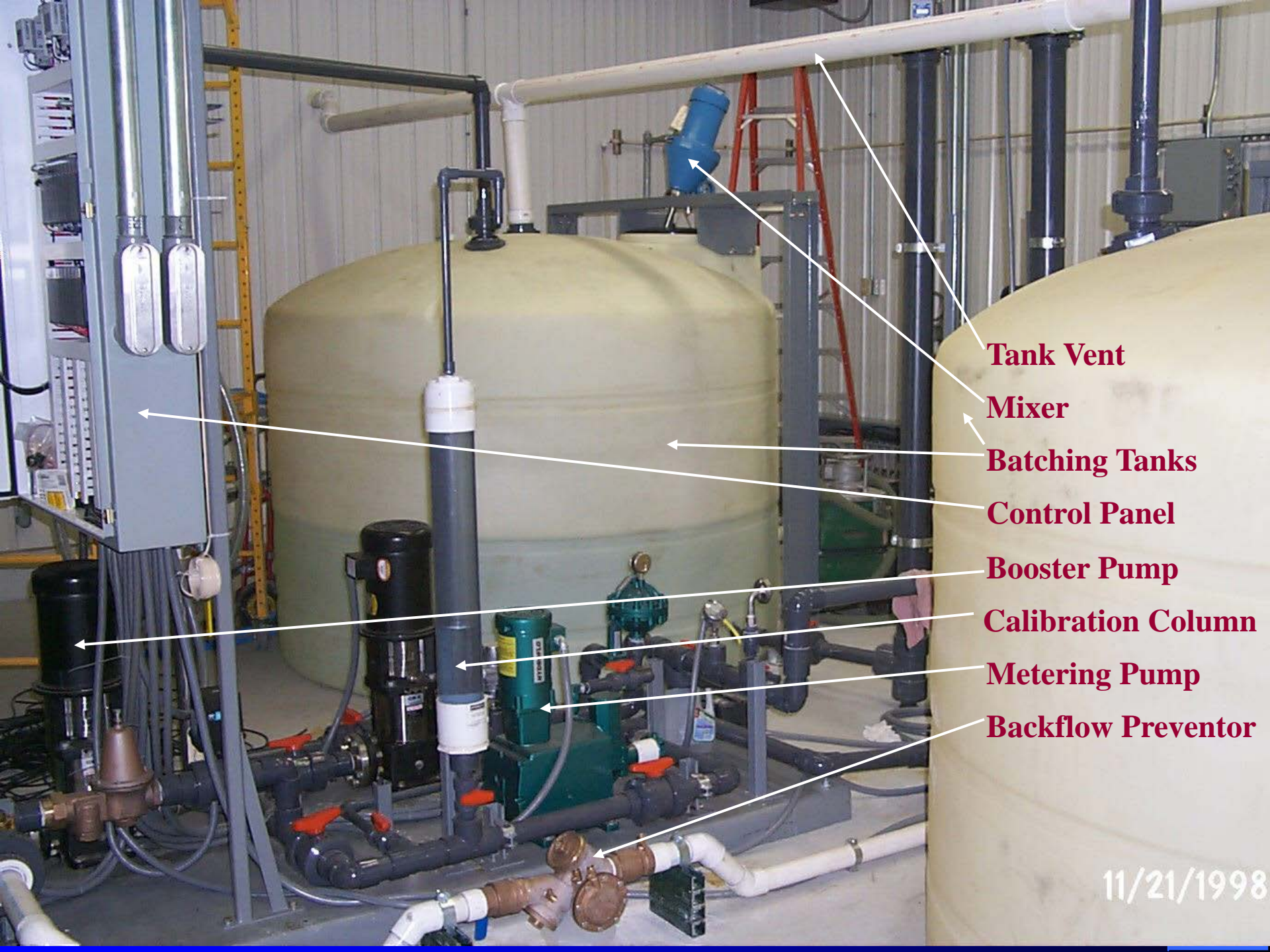


FIGURE 1  
LOCATIONS OF INJECTION &  
MONITORING WELLS FOR THE  
FIELD SCALE IN SITU  
CHEMICAL OXIDATION STUDY



**Tank Vent**

**Mixer**

**Batching Tanks**

**Control Panel**

**Booster Pump**

**Calibration Column**

**Metering Pump**

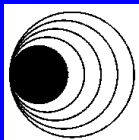
**Backflow Preventor**

11/21/1998



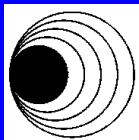
# Pilot Test Operational Overview

INJECTION	Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> Injection	KMnO <sub>4</sub> Injection
Injection Duration, days	64	172
Monitoring Duration, days	during injection+7 post-injection events	
Oxidant Quantity, Kg	8,200	45,000
Volume of Water, L	4,300,000	4,400,000
Injection Flow Rate/Location, Lpm	4.33	1.57, 1.89 and 3.78
Injection Concentration, g/L	2	5 and 10
Geochemistry Monitoring	pH, ORP, Conductivity and Temperature	
Chemical Parameter Monitoring	VOCs, Cl <sup>-</sup> , residual Na <sub>2</sub> S <sub>2</sub> O <sub>8</sub> , residual KMnO <sub>4</sub> , Na <sup>+</sup> , SO <sub>4</sub> <sup>2-</sup> , K <sup>+</sup> and Mn (dissolved and total)	

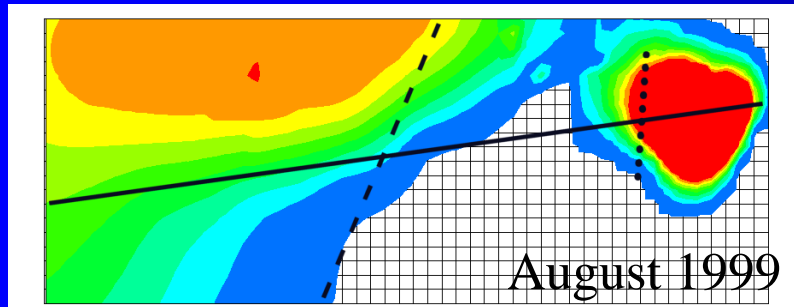


# Post Injection Monitoring

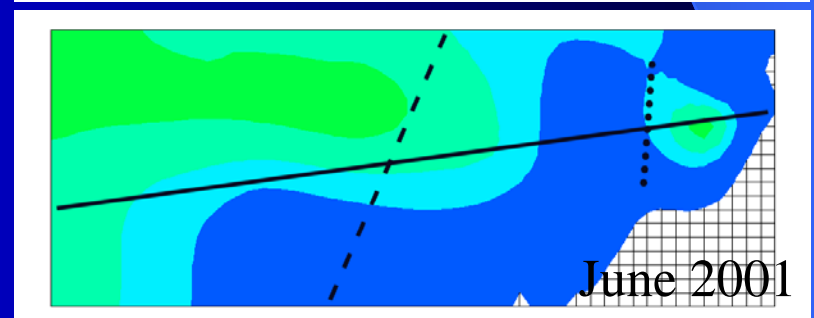
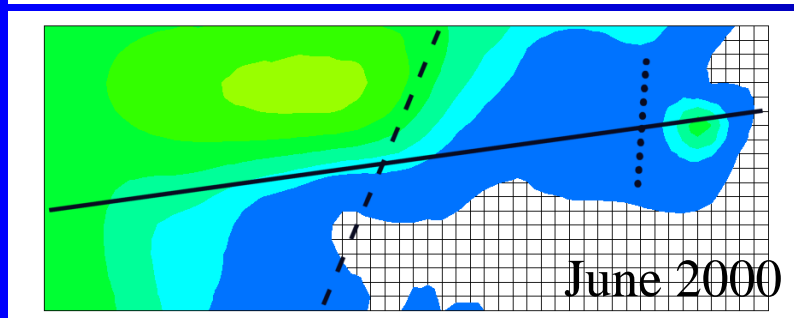
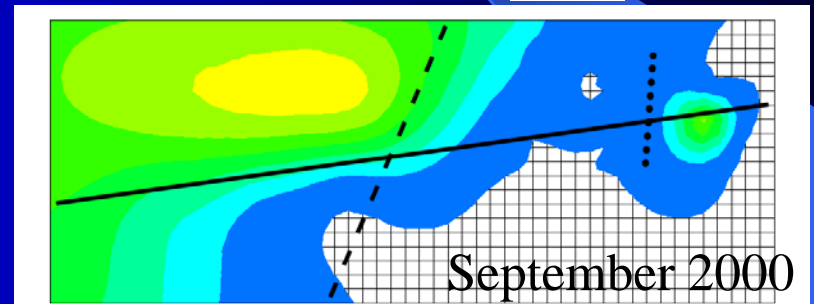
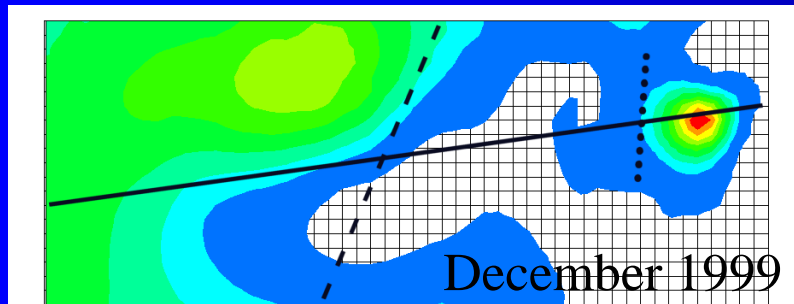
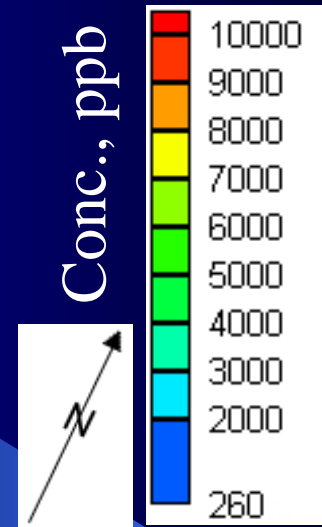
- 7 post-injection monitoring events: quarterly August 1999 - December 2000 + June 2001
- Significant increase in daughter product concentration.
- Increased daughter product:parent compound ratios: cis-DCE:TCE, VC:cis-DCE
- Reductive Dechlorination Evaluation:
  - 3-D interpolation using GMS® developed for TCE, cis-DCE, VC, Cl<sup>-</sup> and ORP
  - Molar ratio of cis-DCE:TCE, VC:cis-DCE
  - Chloride mass balance
  - Additional investigation sampling



# TCE Contours



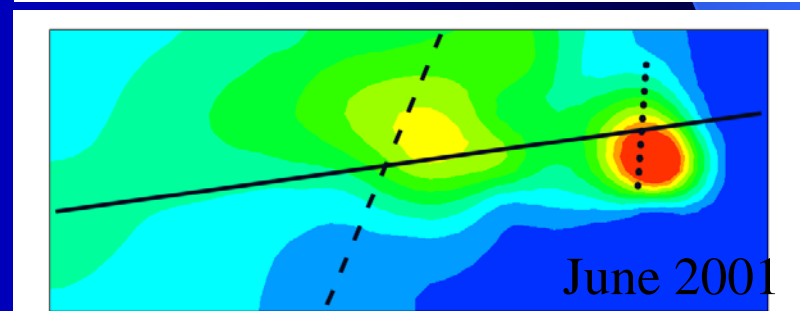
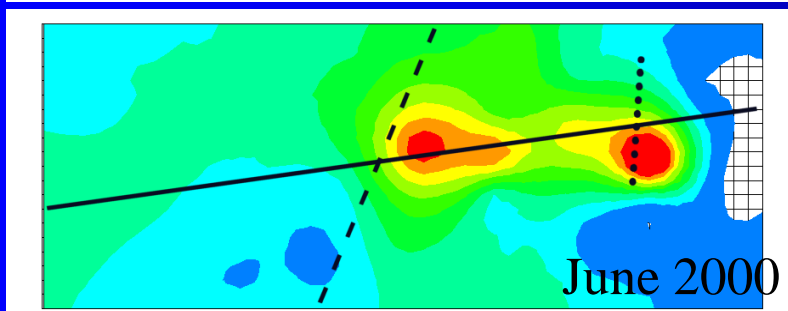
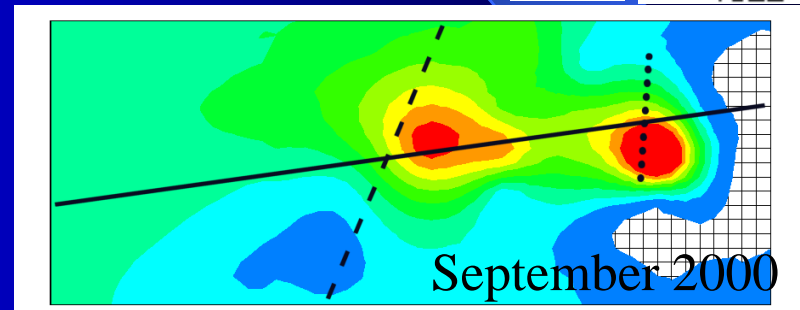
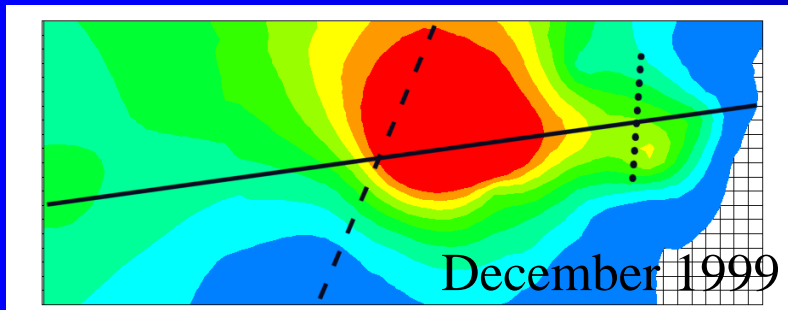
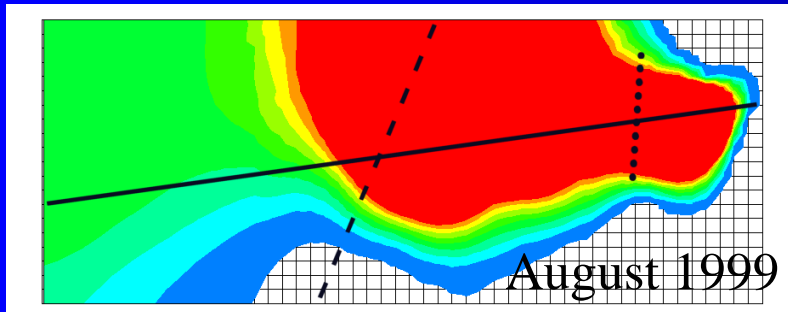
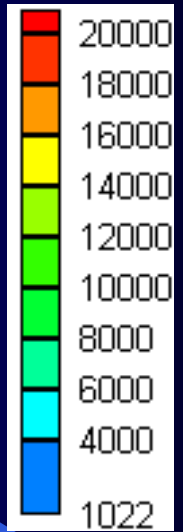
Concentrations at average aquitard depth



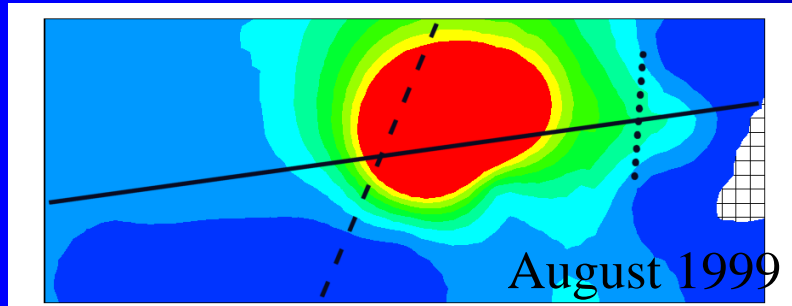
# cis-DCE Contours

Concentrations at average aquitard depth

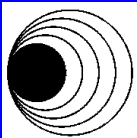
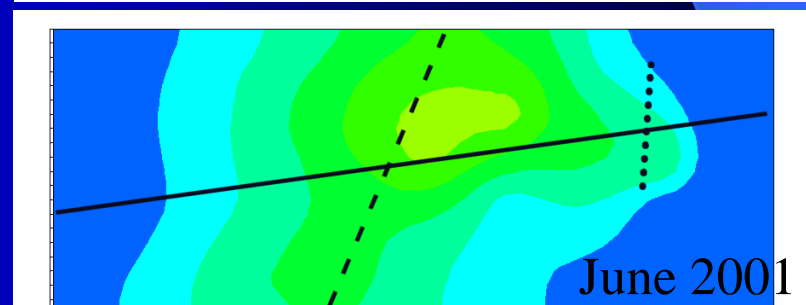
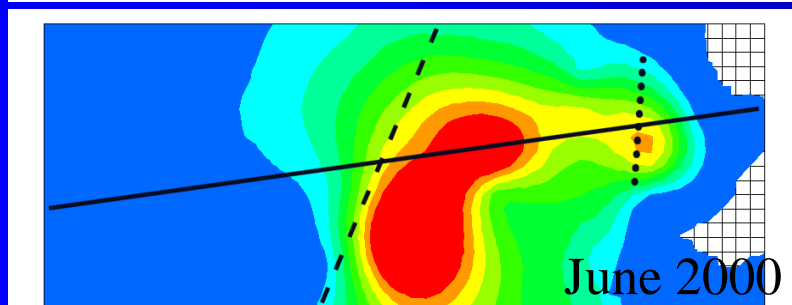
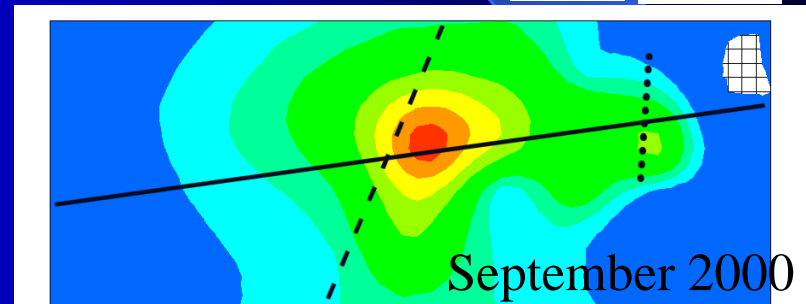
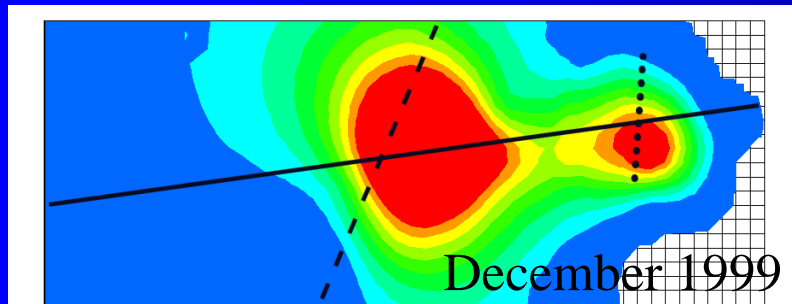
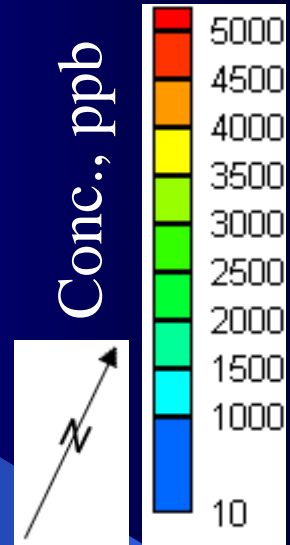
Conc., ppb



# VC Contours



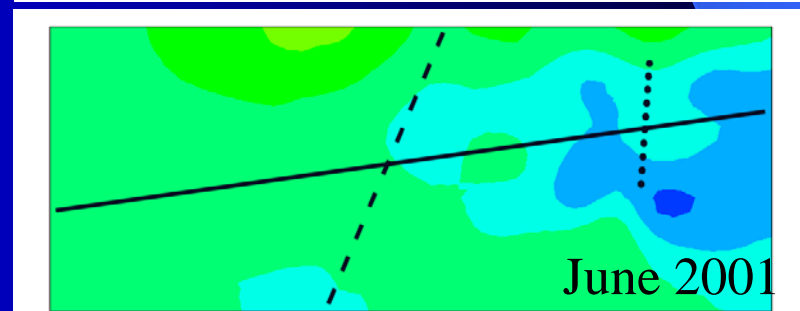
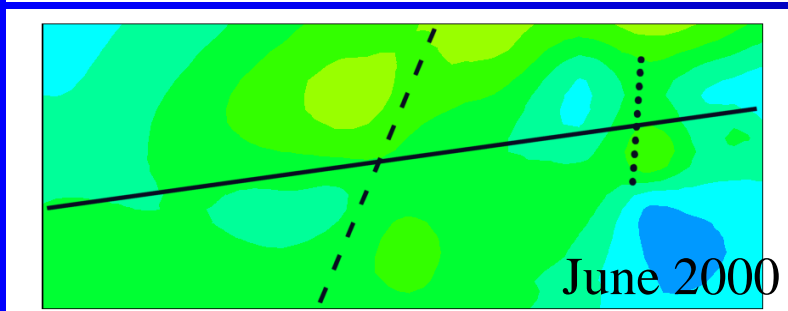
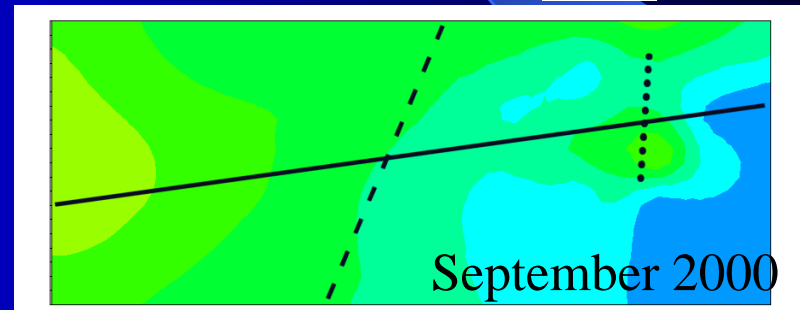
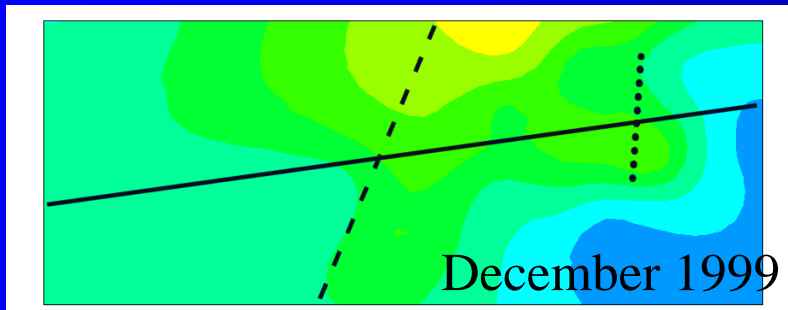
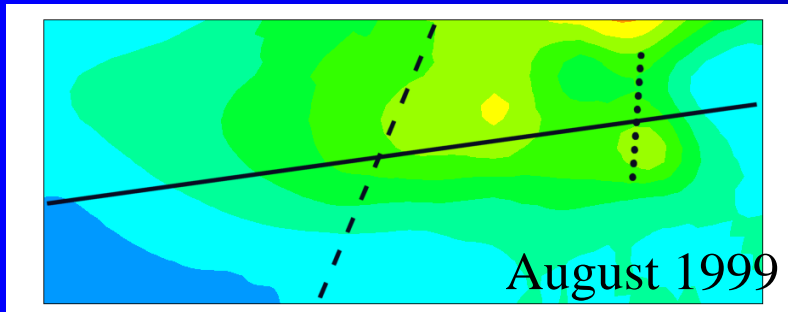
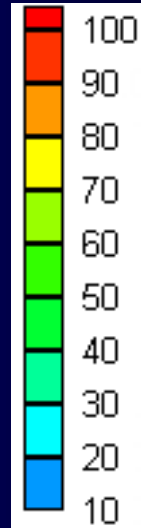
Concentrations at average aquitard depth



# Cl- Contours

Concentrations at average aquitard depth

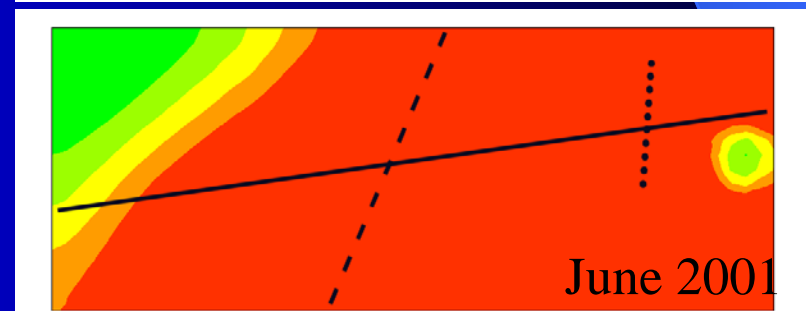
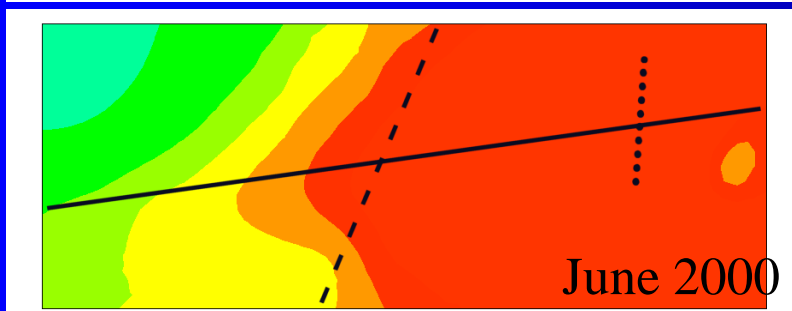
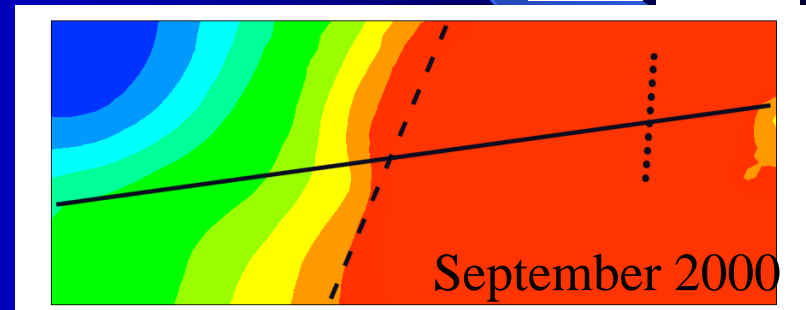
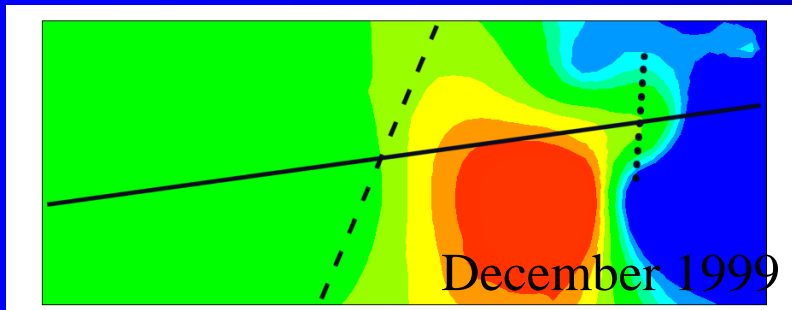
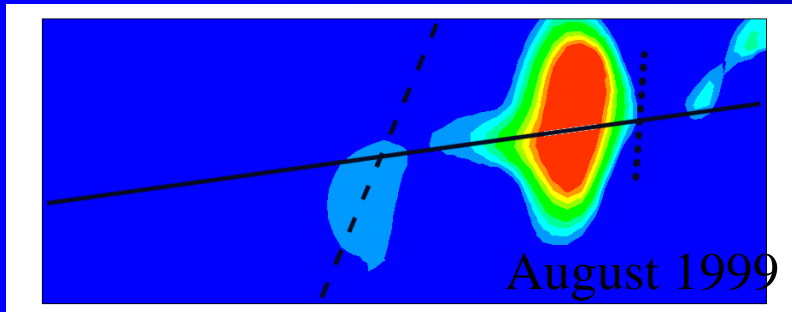
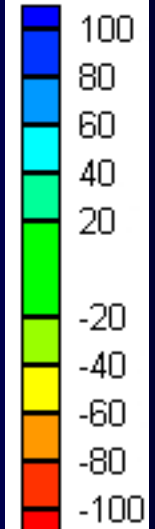
Conc., ppm



# ORP Contours

ORP values at average aquitard depth

ORP, mV

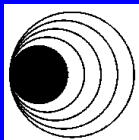


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# Chloride Mass Balance

- Cl<sup>-</sup> is the end product of CVOC mineralization & reductive dechlorination
- Cl<sup>-</sup> mass balance after adjusting for influx and outflux
- ~2,060 Kg of eq. TCE degraded from Aug-99 - Sept-00

<b>Duration</b>	<b>Cl<sup>-</sup> produced (Kg)</b>	<b>Equivalent TCE (Kg)</b>
Dec-98 to Aug-99	660	815
Aug-99 to Dec-99	217	267
Dec-99 to Mar-00	903	1115
Mar-00 to Jun-00	0	0
Jun-00 to Sept-00	549	678





# Additional Investigation Results

Location	H <sub>2</sub> , nM/L	SO <sub>4</sub> <sup>2-</sup> , mg/L	Field Fe <sup>2+</sup> , mg/L
CW13	1.55	430	1.4
CW15	1.36	156	0.3
CW16	1.69	277	1.2

- PLFA:

- Gram Negative type of bacteria (including sulfate-reducing bacteria) present at CW13 and CW15
- Sulfate-reducing bacteria biomarkers present at CW13 and CW16



# Conclusion

Enhanced reductive dechlorination was observed following chemox activities

- Cl<sup>-</sup> mass balance and daughter/parent ratios
- Making the CVOCs more bioavailable by reducing sorption sites
- Providing simple organic carbon (a food source) for bacteria by degrading naturally occurring complex organic carbon
- Enhancing sulfate reducing bacteria growth

