Combining Remedies/ Treatment Trains for NAPL Site Remediation

Exploiting Synergies to Reduce Costs/Improve Performance/Increase Certainty

NIEHS/EPA Combined Remedies Workshop
Tufts University – June 2006

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Historical Perspective on Combining Remedies

- **Earliest – Some talk, little action (like the weather, everyone talked about it…)**
- **Early – Limited use, mostly ad hoc**
  - **Practitioners notice something 'interesting' during/after remedy implementation**
  - **EXAMPLE: Electrical Resistance Heating (ERH) to treat methylene chloride**
    - **Contaminants went away but not recovered, - ?????**
    - **Explanation: Greatly increased hydrolysis rates at 70 C**
- **More Recently (post 2003)- (Somewhat) More upfront/purposeful, but still a lot of 'dinking around…'**
- **Practice Still WAY out ahead of the Research**

Approaches

- **Temporal – Adjust/change technologies at appropriate changeover points**
- **Spatial – Treat different zones with different technology(s)**
  - **'Hot' Spots/'Warm' Spots/Dissolved Phase…**
- **'Miscellaneous' – Maximize in-situ destruction to reduce/eliminate need for off-gas treatment systems**

Expansive, Functional Definition

- "***Whatever Works…"*** – Understand/ Exploit all physical/chemical mechanisms that contribute to remedial effort
-
- ***Flexible, Adaptive Approach(es)***

Workshop Objectives

- Short-term – Elicit practical insights that can be incorporated into remedial thinking/decision making
- Medium-term – New linkages/relationships between practitioners and researchers
- Longer-term – Coherent input to federal R&D procurement mechanisms

Challenges

- Are there other examples of research collaboration at the intersection/interface between two separate/disparate knowledge domains?
- Mechanisms to foster requisite collaboration?

Concepts

‘Priming’(Front-end)

and/or

‘Polishing’
(Back-end)

‘Priming’ - Zappi et al

- **‘Chemical Oxidation *Priming* for Enhancing Pollutant Removal in Soils by Biological Treatment**’ – *ACS Nat’l Meeting, 2002*

- **‘Chemical *Primed* Enhanced Bioremediation of Petroleum Hydrocarbon Contaminated Sediments’** – *MS-AL SeaGrant Program Review Meeting U of Miss, 2002*

- **‘Integration of Chemical-Oxidation and Biotreatment for Removal of TNT’** – *Final Report to Army Research Office, 2003*

IMPORTANT NOTE: 'Polishing' Doesn't Have to Come Last

- First presentation/first day of Battelle Bio Conference, Baltimore - 2005
- Michigan PHC site
  - Combination of Chemox+Bio implemented following 12 years of MNA

Possible In Situ Technology Combinations

- Thermal + Chemical
- Thermal + Bio
- ChemOx + Bio
- Chemox + Chemox
- Surfactant/Cosolvent + Bio
- Surfactant + ChemOx
- Abiotic (Nano-Fe/ZVI) + ????
- ?
- ?

Seers…(?)

- '…it is now clear to many that chemical oxidation is best coupled with accelerated bioremediation for more successful site management.'

  – *Regenesis ReGenOx Product and Design Manual*

Seers… (cont.)

- Surfactant is very efficient when mobilizing liquids, especially liquids in the preferential flow paths in the subsurface. It is not particularly effective at increasing the water solubility of individual solute molecules, except at very high surfactant concentrations. Consequently, Surbec designed the remediation to follow the surfactant flush with a chemical oxidant injection.

. . .

- The chemical oxidation was highly effective at degrading the dissolved contaminant and at decontaminating any soil particles that had been contaminated by adsorbed contaminant. Also, chemical oxidant can diffuse into dead end pores or low permeability zones where surfactant will work much more slowly.
    - *Surbec, Bixby, Ok case study*

Thought Experiment…

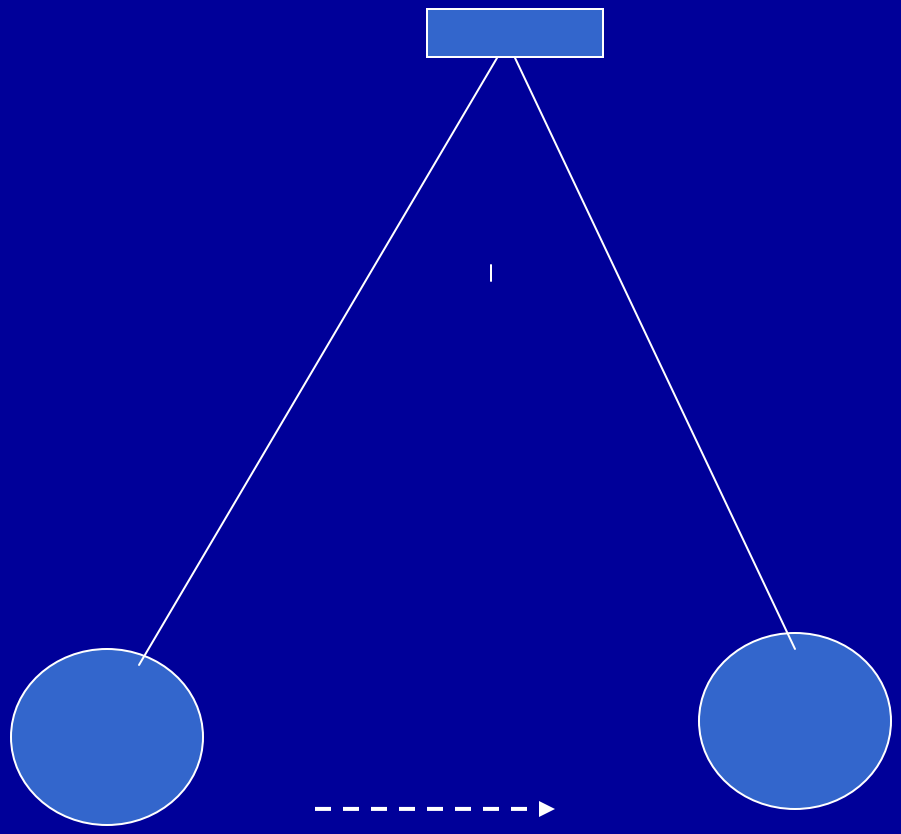
- Might there be situations/conditions where you don't want too much initial contaminant reduction – i.e., are there optimum mass flux levels for purposes of subsequent (enhanced) bioremediation and eventual, maximum mass reduction?

  – *Conversation w/ Suresh Rao, Purdue Univ.*

Additional Thought Experiment

- What would a regulatory framework look like that put a number on ‘reasonable time frame…’ (e.g. 30 years), and allowed consultants to design treatment trains to meet that timeframe?

The Bio-Augmentation Pendulum



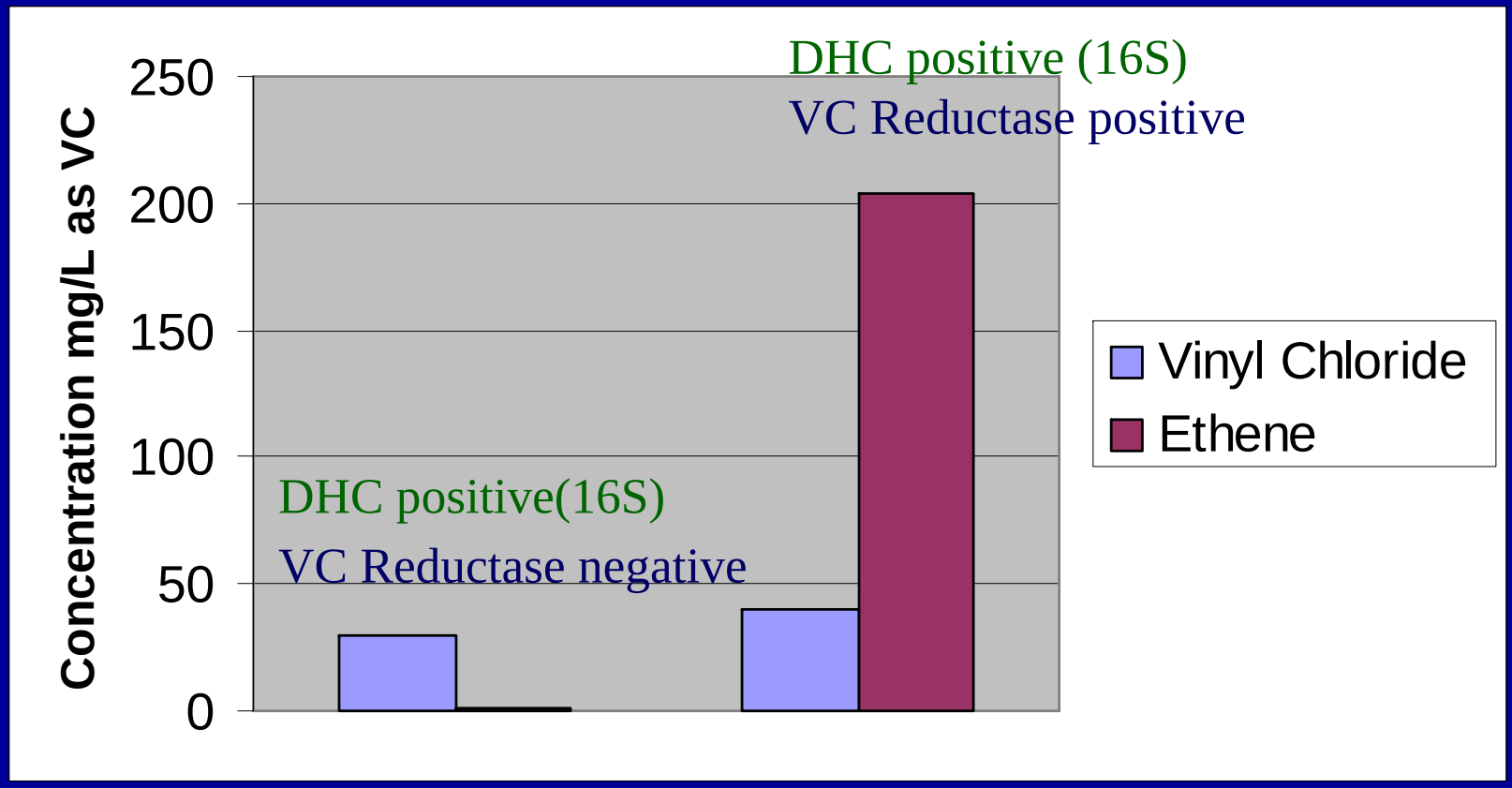
1995 – No Way, Jose…

- Predation, etc, etc.

2005 – Why Not?

- “It’s so cheap…”

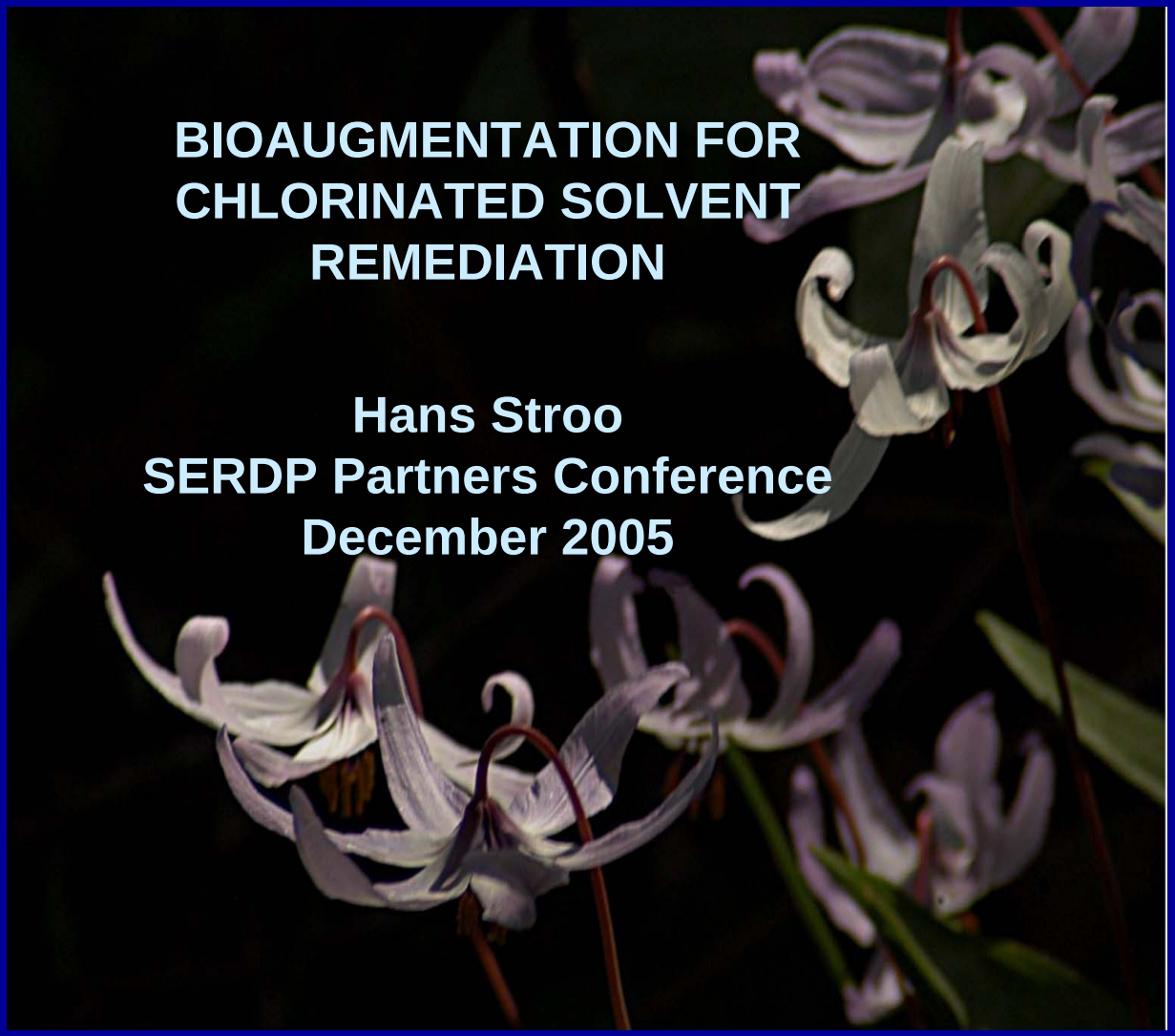
NASA LC-34



Pre-bioaugmentation
VC to ethene ratio - 30:1

5 months post-bioaugmentation
VC to ethene ratio - 1:5

(Highly) ‘Recommended Reading’:



Issues

- **Impact of Active Agents – Heat/Oxidants on Mico-organisms**
  - **Within limits, effects seem tolerable/reversible**
  - **Downgradient zones are not affected – In fact, appear to benefit (e.g, Ft Lewis, Wash.)**
- **Effects of Oxidants on Thermal System Components**
  - **May require corrosion resistant materials**
- **Whether costs will be synergistic or additive? – especially with multiple vendors**

Issues

- **Presumption of Certainty in Decision documents for sites subject to fed'l/state oversight**
  - **But NOTE: Trend toward more flexible, adaptive approaches and combined remedy specifications in RODs**

Issues (cont.)

- **Combined Remedies may be particularly suitable for early-/mid-90's RODs specifying Pump and Treat at site w/ likely NAPL contamination (??)**
  - Need to overcome institutional inertia

‘Icebreakers’ - Recent NPL Site Combined Remedy RODs

- **Brunswick Wood site ROD**
  - Stabilization/Solidification, Slurry Walls, and In-situ Chemical Oxidation
- **TEXWOOD site ROD**
  - insitu S/S, open slurry walls, In-situ Chemical Oxidation, and MNA

Combined Remedy RODs (cont.)

- **Pemaco NPL (solvent) site, Maywood, Ca**
  - Electrical Resistance Heating (ERH) in hot spot at 35-95’ bgs
  - Possible use of In Situ ChemOx, Enhanced Bio, MNA in downgradient zones

Challenges

- Convincing clients that ‘combined remedies’ is not a euphemism for ‘blank check’
- Whether single technologies or combinations, we still have work to do in the area of in situ process control

Desired End State/Least Cost Solutions

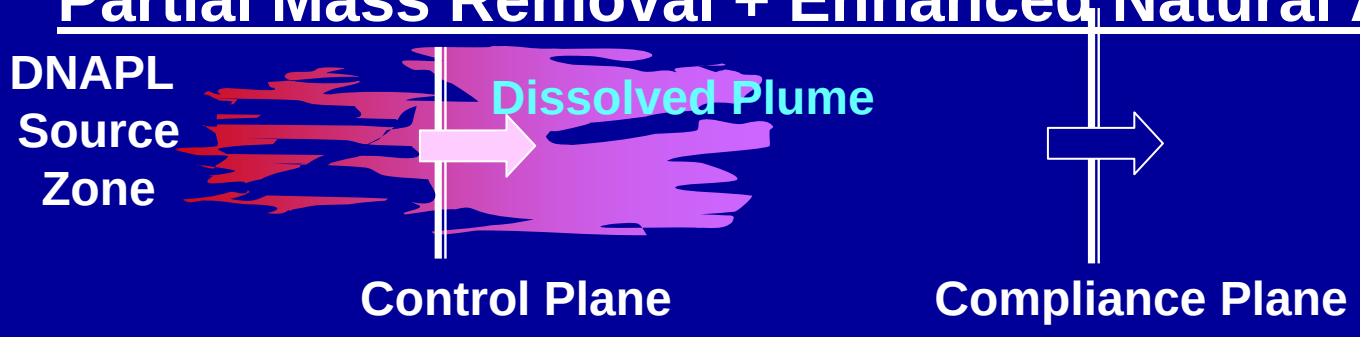
- **Adequate Use of Robust Source Term Removal Technologies**
- **Timely transition to cost-effective 'polishing' step(s)**
- **Reduce/Eliminate Need for Pump and Treat**
- **Appropriate Reliance on Monitored Natural Attenuation (MNA)**

PLUME RESPONSE

Pre-Remediation:

Partial Mass Removal:

Partial Mass Removal + Enhanced Natural Attenuation:



Thermal + Bio

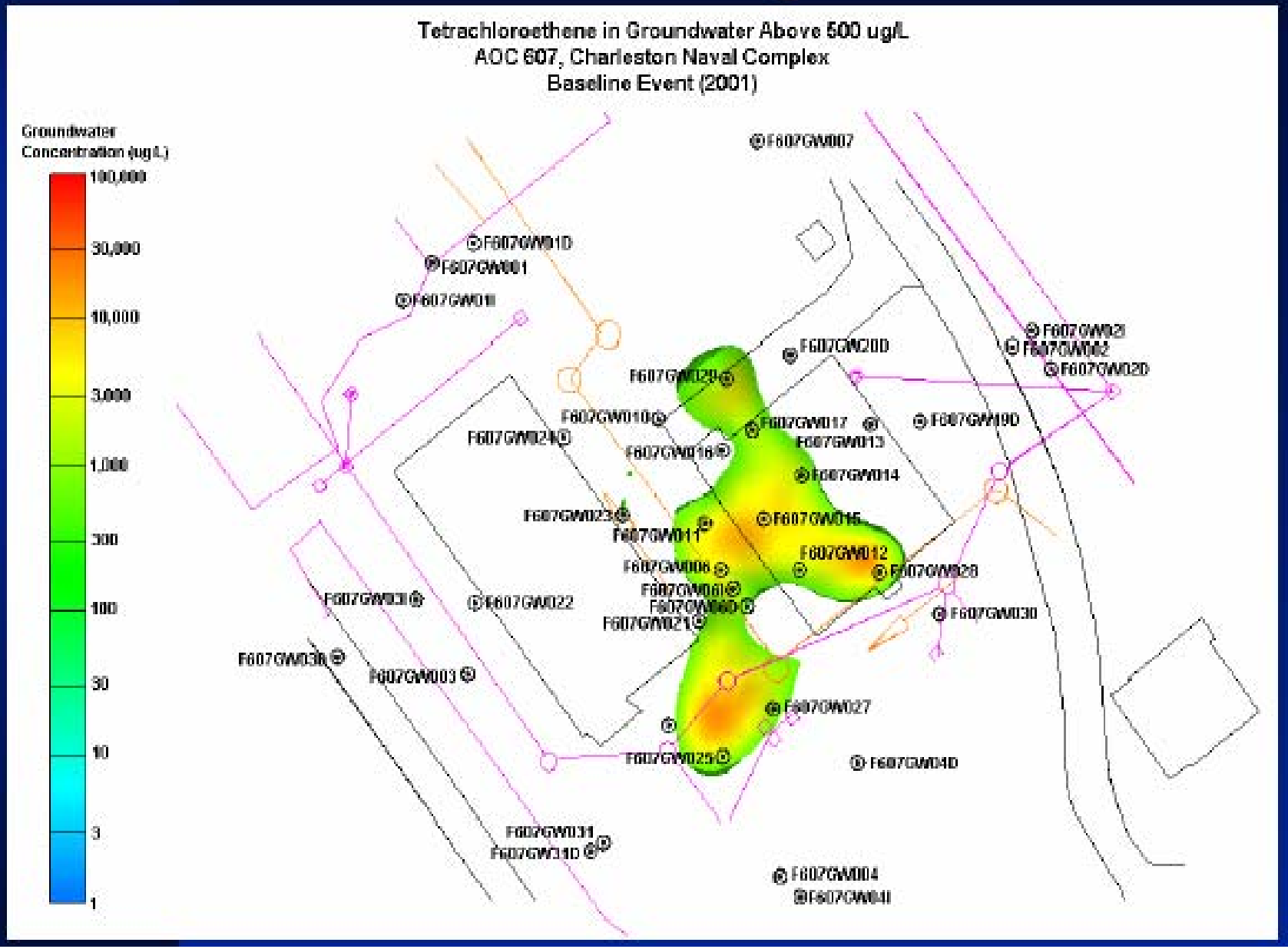
- **Evidence of biodegradation following Electrical Resistance Heating (ERH) at Charleston Navy Facility Dry Cleaner**
- **Downgradient reduction trends also partly attributable to (slow) flow of clean groundwater through treated zone**

Charleston Navy Facility ERH Performance

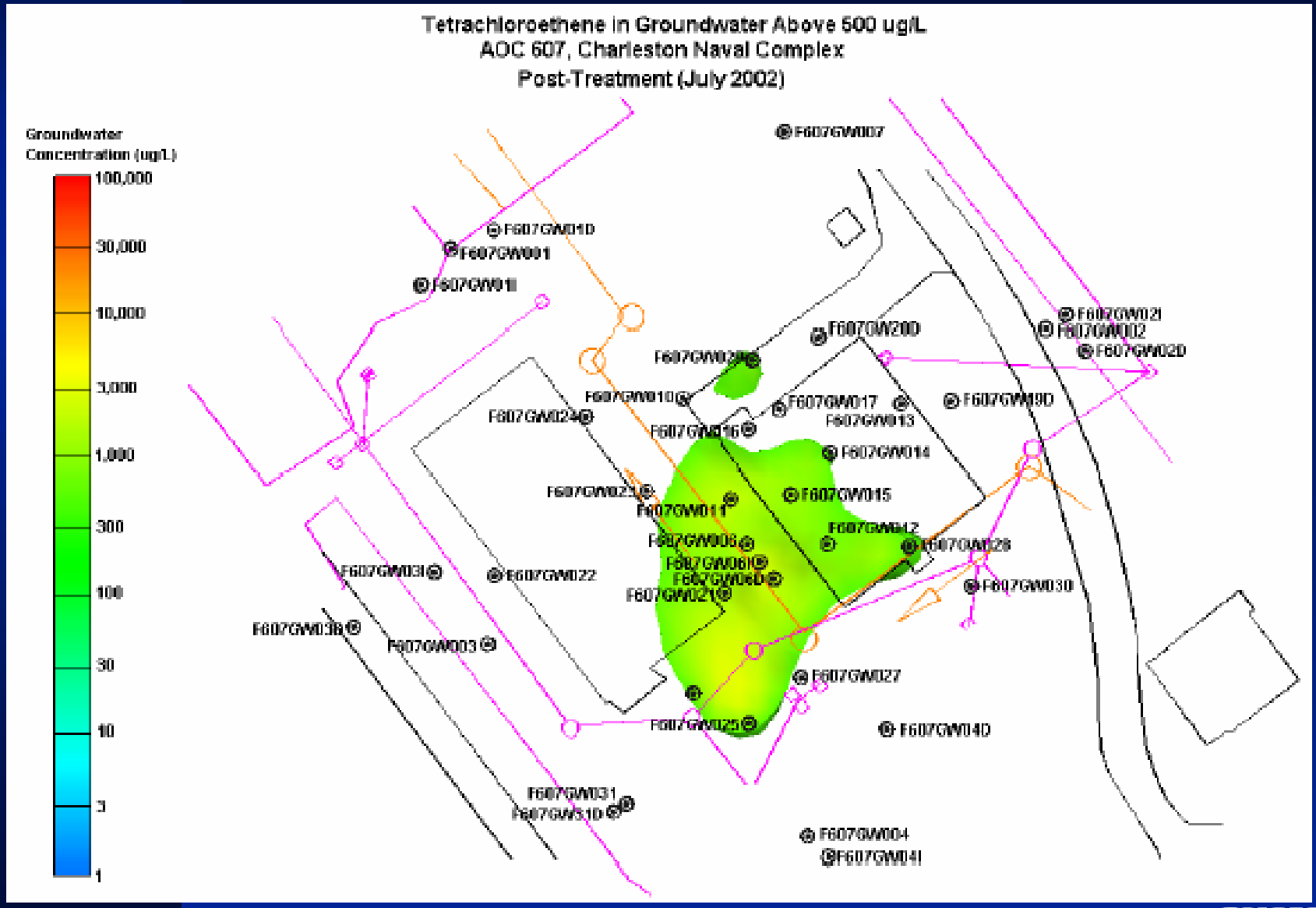
- **Initial Results - 79% VOC reduction (dissolved phase) versus 95% target**
  - **Electrode spacing an issue, also soil drying, acetone generation**
- **Subsequent monitoring data shows continued reduction in contaminant levels**

(Courtesy Dean Williamson, CH2M Hill)

Baseline PCE > 500 ug/L at AOC 607

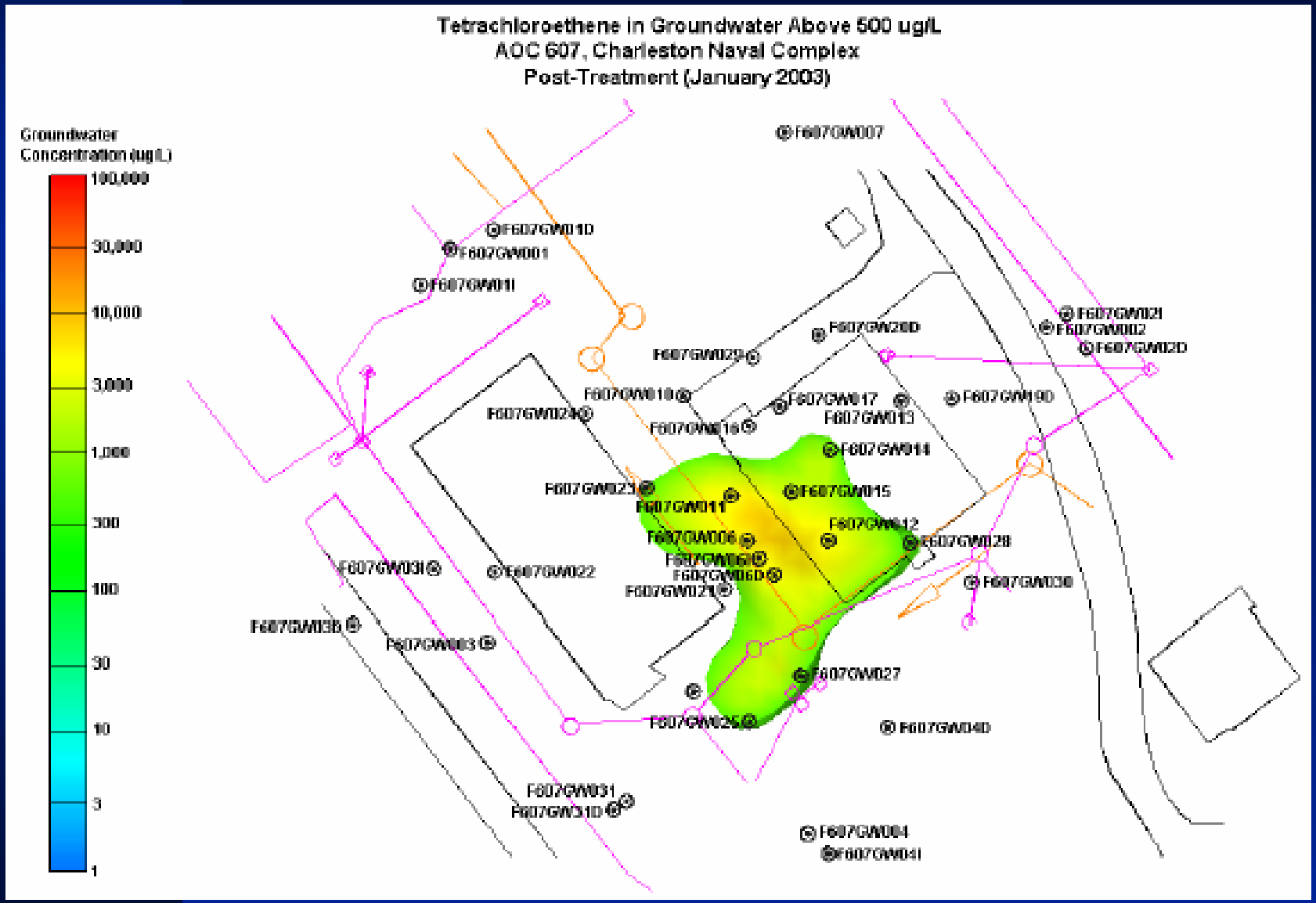


PCE > 500 ug/L at ERH Shutdown



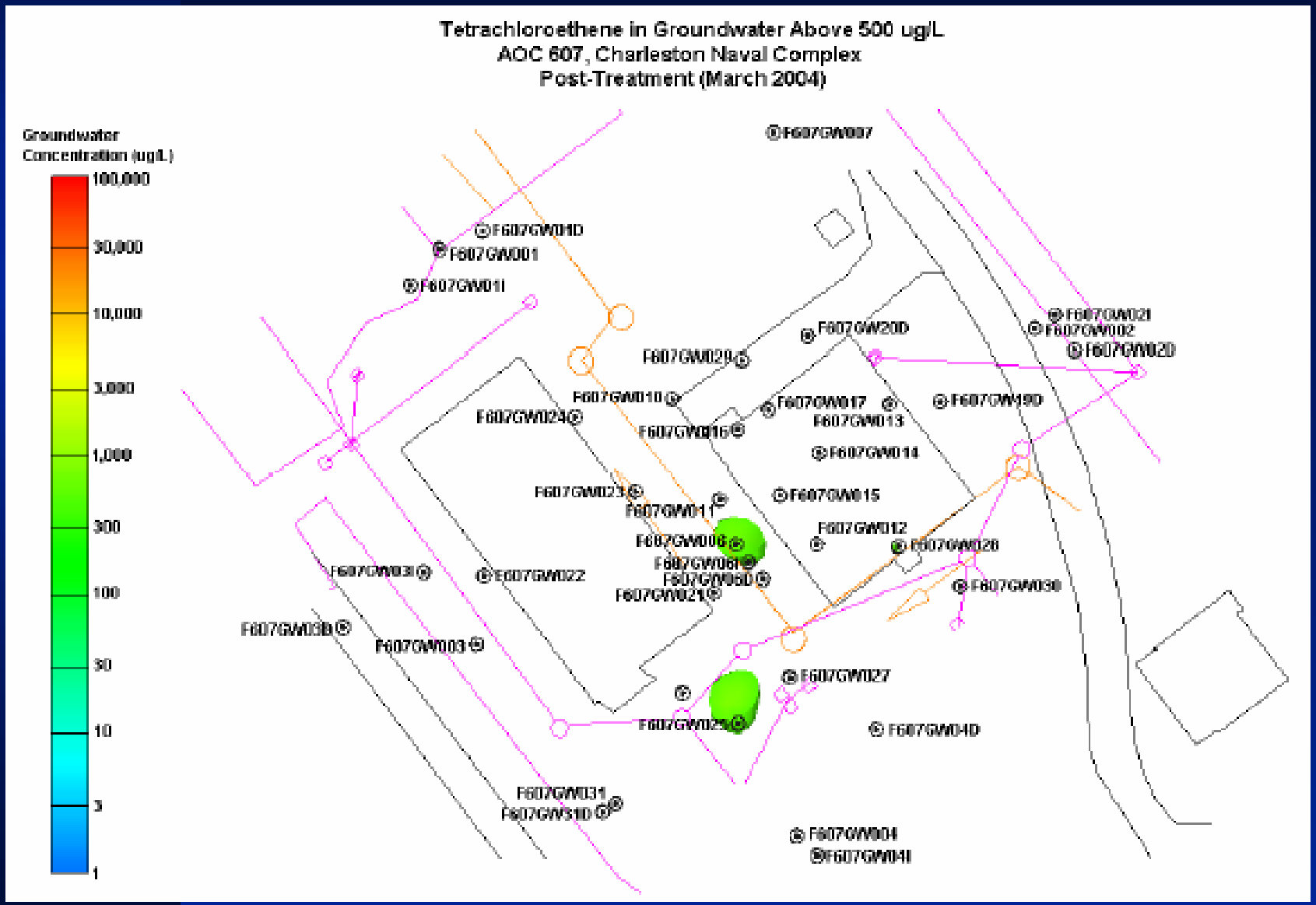
CH2MHILL

PCE > 500 ug/L 6 Months After ERH Shutdown



CH2MHILL

PCE > 500 ug/L 22 Months After ERH Shutdown



CH2MHILL

Changes in VOC Concentrations 22 Months After ERH Shutdown; Well F607GW011, Charleston Naval Complex

	Prior to ERH (ug/L) 7/2001	After ERH (ug/L) 3/2004	% change
PCE	5600	283	-95%
TCE	430	520	+20
Cis-DCE	440	1060	+140
VC	<250	6.3	
Total VOC	6470	1066	-83%

Thermal + Chemical

- **Dozens of Steam-activated Persulfate Cleanups**
- **Cost Information:**
  - steam subsurface to 65 deg C = $22/cu yd
  - steam subsurface to 45 deg C = $13/ cu yd
  - persulfate @ 1g/kg ox demand = $19/cu yd
  - persulfate @ 2 g/kg ox demand = $28/ cu yd

Steam-ActivatedPersulfate Field Results

Chlorinated Solvents

Location	1,1 DCE (ug/l)	1,1,1 TCA (ug/l)
Scotland Neck, NC	230,000/460	390,000/68,000
Garner, NC	81,700/0.8	73,000/987

Location	PCE (mg/kg)	TCE (mg/kg)
Cobb County, GA	5,100/<2.6	3.2/<0.05

Petroleum

Location	Benzene (ug/l)	MTBE (ug/l)
Blackstone, VA	1600/78	1300/360
Clayton, DE	519/7.4	16,100/233

Location	xylene (ug/l)	naphthalene (ug/l)
Hagaman, NY	2,778/22	
Lexington, NC		>1,000,000/<1,000

Combined Surfactant/Chemical Oxidation

LNAPL Contamination (Petroleum Hydrocarbons)

Bixby Underground Storage Tank Site, Bixby, OK (LNAPL)

- NAPL: mixed gasoline and kerosene
- Geology: fine sand
- Free product: 0.5 to 2.2 ft, extent 120 ft x 85 ft
- **Surfactant flushing: Mobilization**, 0.94 wt%, 120,000 gallons (1.5 PV) over 13 days
- **Chemox Polishing: 0.4 wt% Fenton's Reagent,** 130,000 gallons over 6 days

Bixby UST Site

SURBEC ENVIRONMENTAL LLC

Bixby UST Site (cont.)

- No free product observed after surfactant flushing
- Post surfactant flushing: GW Benzene conc. 50 ug/L to 20 mg/L
- Post chem ox polishing: GW Benzene conc. ND to 1.8 mg/L (SSTL 5.6 mg/L)
- Project completed in 2.5 months

SURBEC ENVIRONMENTAL LLC

Florida Dept of Transportation Underground Storage Tank site

- **Progressive, Adaptive Implementation of Multiple Remedies**

- Dual Phase Extraction

- Source Removal

- Soil Vapor Extraction

- **- Bioremediation Stimulated by**
- **Oxygen Injection**

Floral City Groundwater Results

Groundwater Cleanup Target Level			1	40	30	20	14	5,000
Natural Attenuation Default Concentration			100	400	300	200	140	50,000
Sample Location	**Sample Date**	**Purpose**	**Benzene**	**Toluene**	**Ethylbenzene**	**Xylenes**	**Naphthalene**	**TRPH**
MW-1R	01/18/05	Baseline	**1.26**	1.01	< 1.00	< 3.00	< 5.00	< 400
	04/15/05	First Quarter	< 1.00	< 1.00	< 1.00	< 3.00	< 5.00	< 400
	07/28/05	Second Quarter	< 1.00	< 1.00	< 1.00	< 3.00	< 5.00	< 400
MW 8DR	01/18/05	Baseline	255	17.6	**132**	**33.6**	**30.2**	2,040
	04/15/05	First Quarter	**88.7**	8.89	**52.1**	16.7	**14.6**	580
	07/28/05	Second Quarter	< 1.00	< 1.00	< 1.00	< 3.00	< 5.00	< 400

Combined Remedies - Closing Thoughts

- **Flexible, Adaptive Implementation is a Crucial Component of Combining Remedies**

- **System installation and operation can provide valuable information on actual subsurface conditions and contaminant distribution – Pay Attention!!**
  - ***"RD/RA is just the next phase of Site Characterization"***

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Key Words:
Environment
Remediation
Chlorinated Solvents

Retention:
Permanent

ENHANCED ATTENUATION: A REFERENCE GUIDE ON APPROACHES TO INCREASE THE NATURAL TREATMENT CAPACITY OF A SYSTEM

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