

Combining Remedies/ Treatment Trains for NAPL Site Remediation

Exploiting Synergies to Reduce Costs/Improve
Performance/Increase Certainty

**Federal Remediation Technologies Roundtable
May 2007**

Jim Cummings
TIFSD/OSWER/USEPA

Historical Perspective on Combining Remedies

- Earliest – Some talk, little action (like the weather, everyone talked about ‘treatment trains...’)
- Early – Limited use, mostly *ad hoc*
 - Practitioners noticed 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
- Practice Still WAY out ahead of the Research (SERDP/ESTCP to the rescue...)

Combinations

- Temporal – Adjust/change technologies at appropriate changeover points
- Spatial – Treat different zones with different technology(s)
 - ‘Hot Spots’/’Warm Spots’/Dissolved Phase
- ‘Misc.’ – E.G., Maximize in-situ destruction (hydrolysis) to reduce/eliminate need for off-gas treatment systems

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

- Michigan PHC site
 - Combination of Chemox+Bio implemented following 12 years of MNA
 - BTEX plume shrank, but zone still > RAO's
 - Trimethylbenzene recalcitrant to Bio alone

Possible In Situ Technology Combinations

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

Seers...(?)

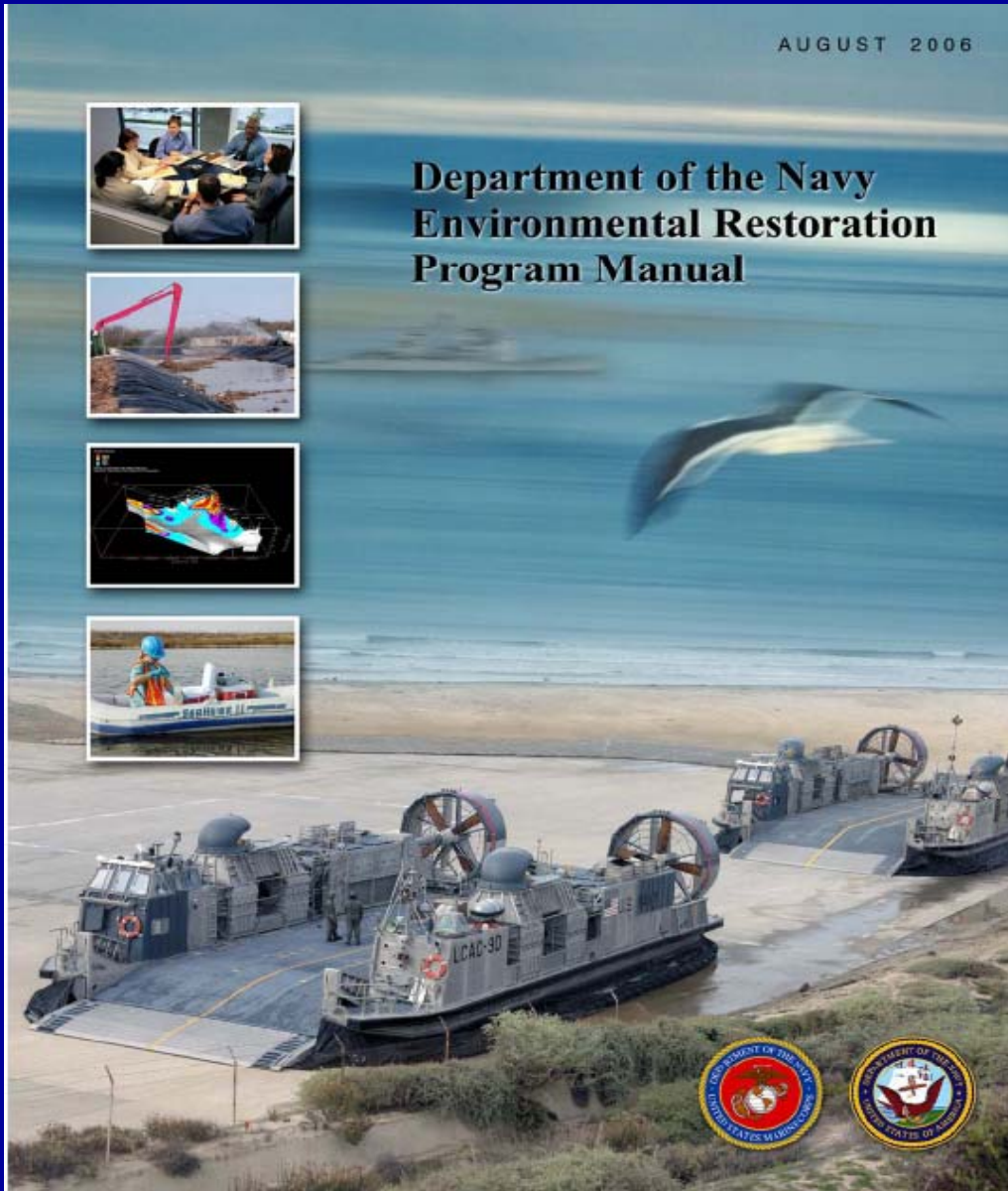
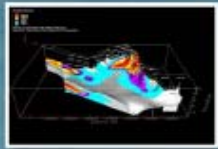
- **‘...it is now clear to many that chemical oxidation is best coupled with accelerated bioremediation for more successful site management.’**

– Regenesis ReGenOx Product and Design Manual

Seers... (cont..)

AUGUST 2006

Department of the Navy Environmental Restoration Program Manual



Navy ERP Manual

- **9.2.3 Flexible ROD**
- The goal of a flexible ROD...is to allow modifications in the remedial approach... These are often required to address ***uncertainties and changing site conditions that typically are encountered during implementation of a remedy as additional site and performance data are collected***

Navy ERP Manual (cont.)

- It is important that the language used in the remedy description allows for ***flexibility in technology transition and unit process selection***
- The remedy should also address the treatment train planned for remedial technologies, such as a transition from contaminant source area treatment to MNA for the dissolved phase plume



NAVFAC
Naval Facilities Engineering Command

ENGINEERING SERVICE CENTER
Port Hueneme, California 93043-4370

TECHNICAL REPORT
TR-2279-ENV

**FINAL REPORT – COST AND PERFORMANCE REVIEW OF
ELECTRICAL RESISTANCE HEATING (ERH) FOR
SOURCE TREATMENT**

Prepared by
Arun Gavaskar, Battelle
Mohit Bhargava, Battelle
Wendy Condit, Battelle

Prepared for
Naval Facilities Engineering Service Center

March 2007

Approved for public release; distribution is unlimited.

Excerpt from NAVFAC Report Executive Summary

- **“In addition to volatilization and steam stripping, enhanced biodegradation and other abiotic reactions at elevated temperatures were an active mechanism at all five sites.**
- **Degradation of some components of organic matter at elevated temperatures and the consequent increase in the availability of a carbon source is advantageous for bioremediation.” (i.e., beneficial downgradient effects)**

Charleston Navy Facility ERH Performance

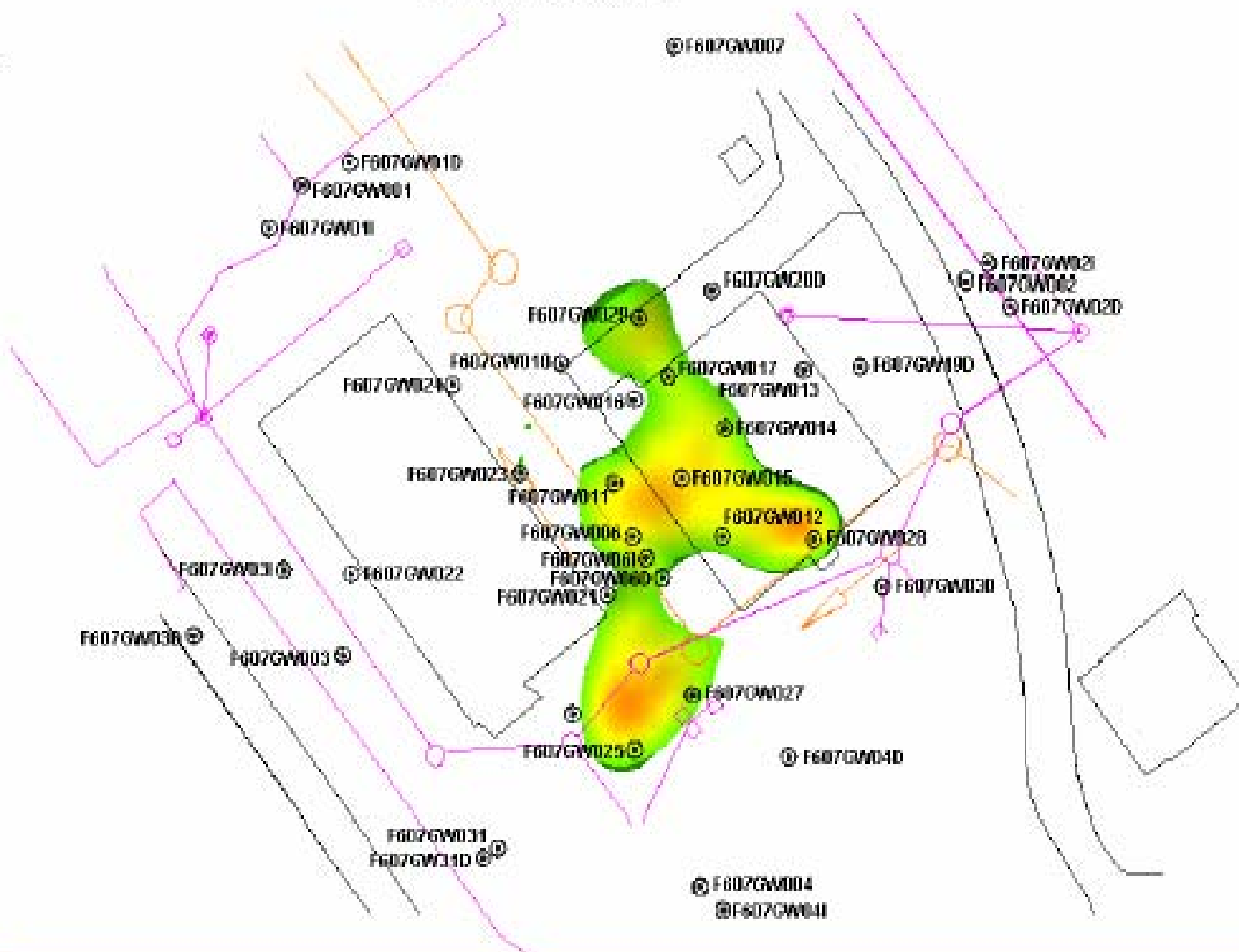
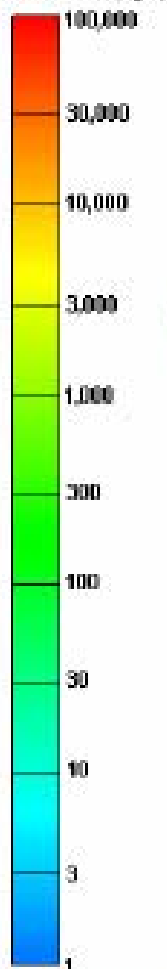
- **Initial Results - 79% VOC reduction (dissolved phase) versus 95% target**
 - **Electrode spacing an issue, also soil drying, acetone generation**
- **Subsequent monitoring data shows continued reduction in contaminant levels**

(Courtesy Dean Williamson, CH2M Hill)

Baseline PCE > 500 ug/L at AOC 607

Tetrachloroethene in Groundwater Above 500 ug/L
AOC 607, Charleston Naval Complex
Baseline Event (2001)

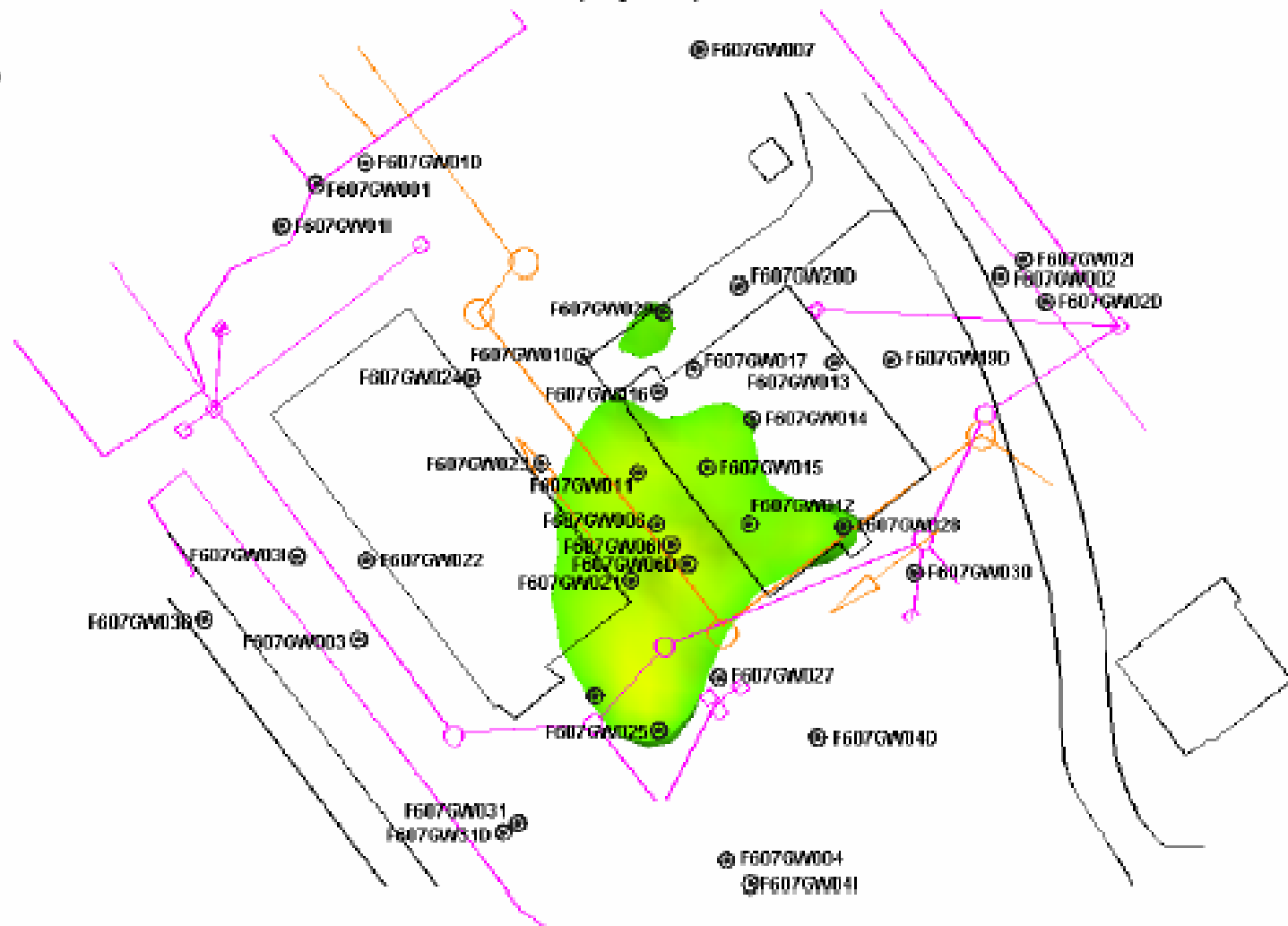
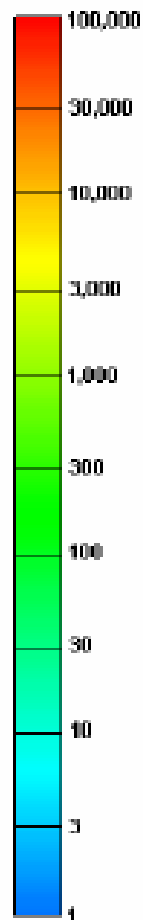
Groundwater
Concentration (ug/L)



PCE > 500 ug/L at ERH Shutdown

Tetrachloroethene in Groundwater Above 500 ug/L
AOC 607, Charleston Naval Complex
Post-Treatment (July 2002)

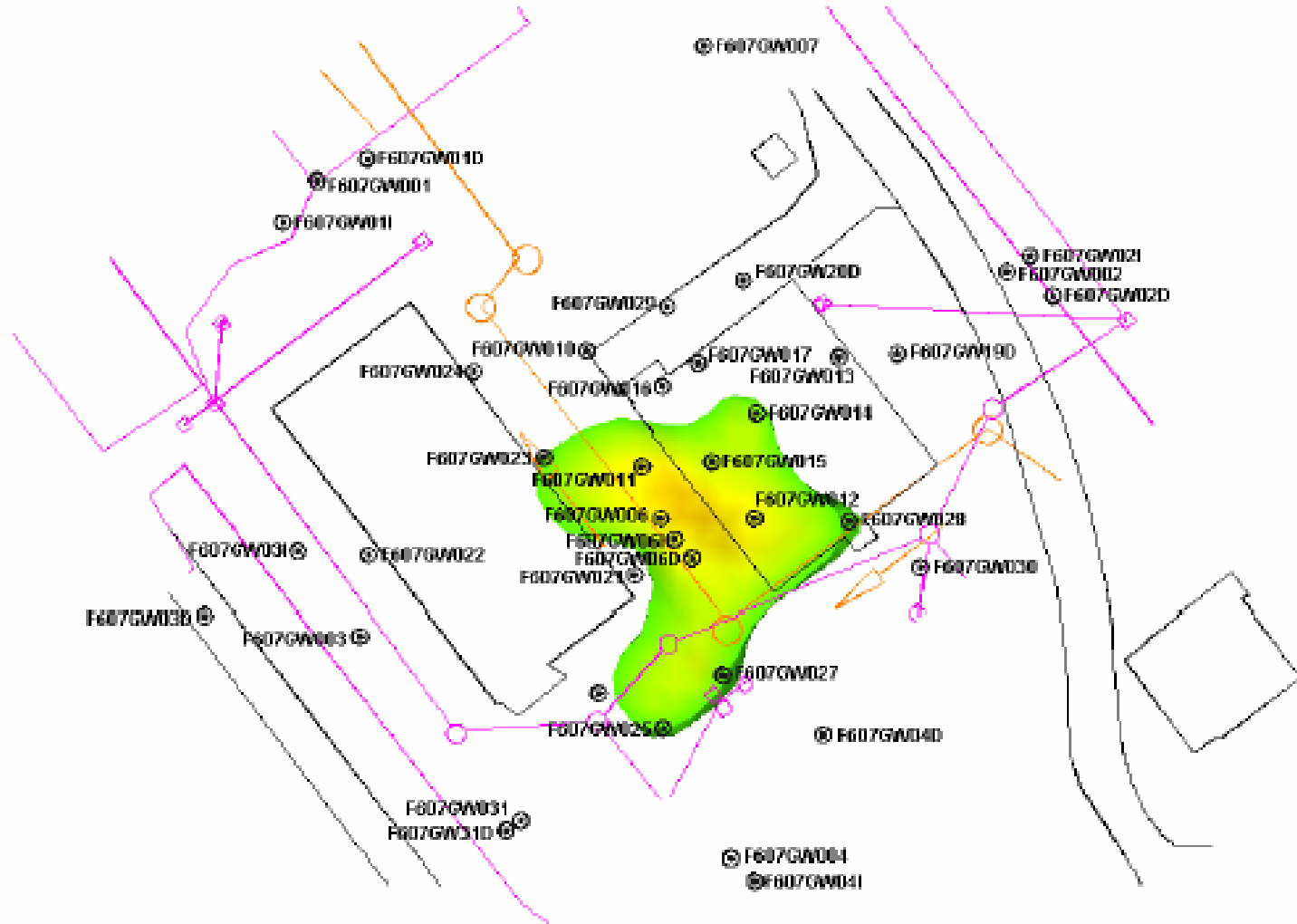
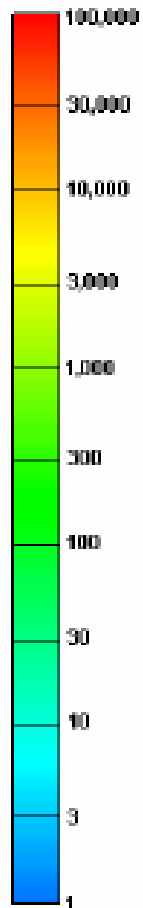
Groundwater
Concentration (ug/L)



PCE > 500 ug/L 6 Months After ERH Shutdown

Tetrachloroethene in Groundwater Above 500 ug/L
AOC 607, Charleston Naval Complex
Post-Treatment (January 2003)

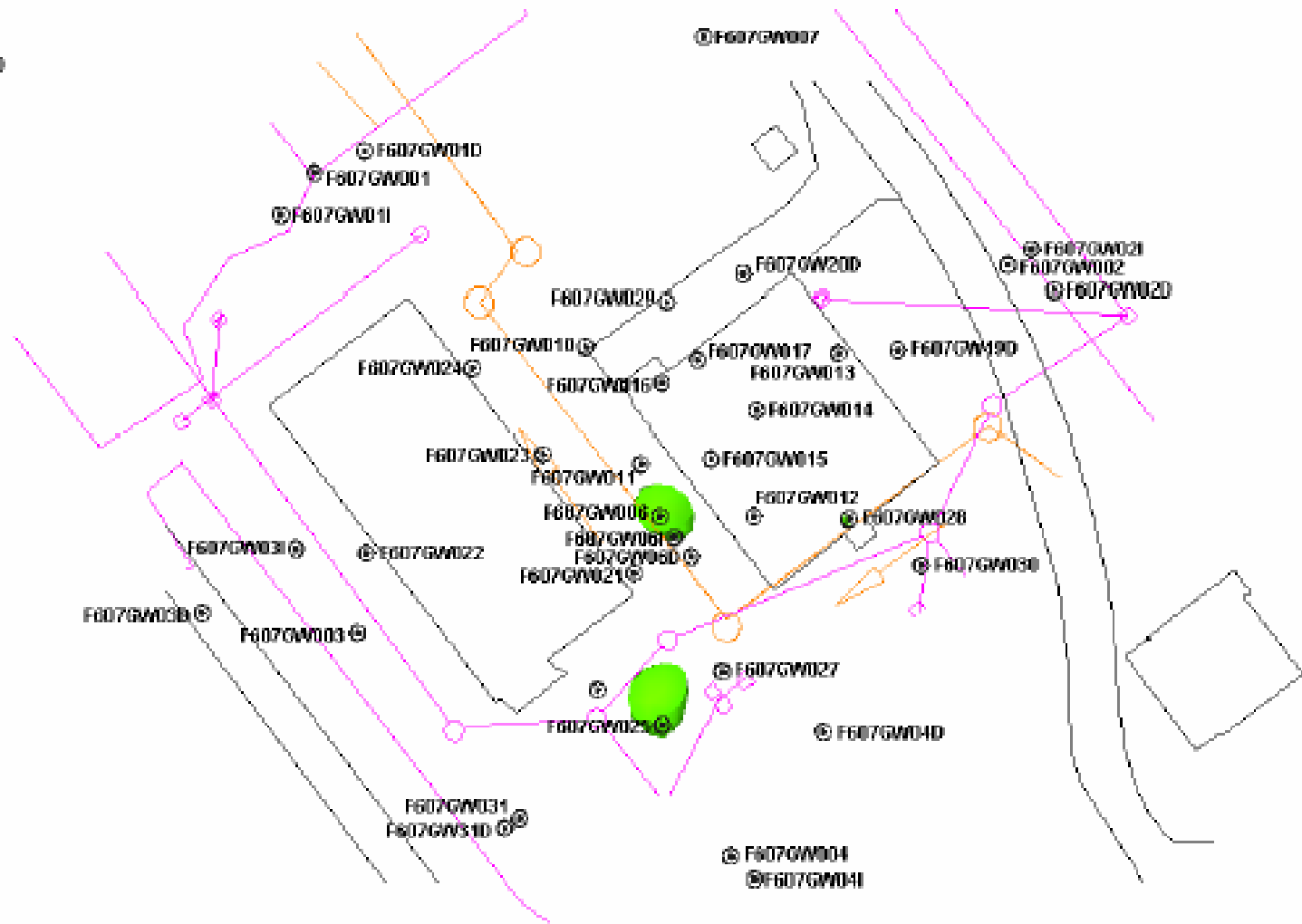
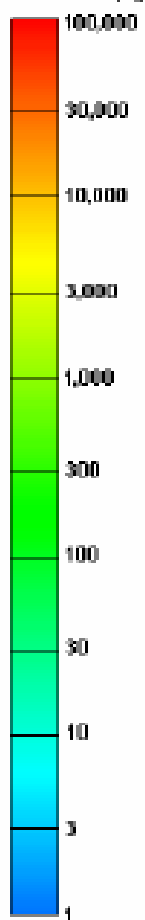
Groundwater
Concentration (ug/L)



PCE > 500 ug/L 22 Months After ERH Shutdown

Tetrachloroethene in Groundwater Above 500 ug/L
AOC 607, Charleston Naval Complex
Post-Treatment (March 2004)

Groundwater
Concentration (ug/L)



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**

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-Activated Persulfate Field Results

Chlorinated Solvents

<u>Location</u>	<u>1,1 DCE (ug/l)</u>	<u>1,1,1 TCA (ug/l)</u>
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

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
- **Polishing:** 0.4 wt% Fenton's Reagent, 130,000 gallons over 6 days

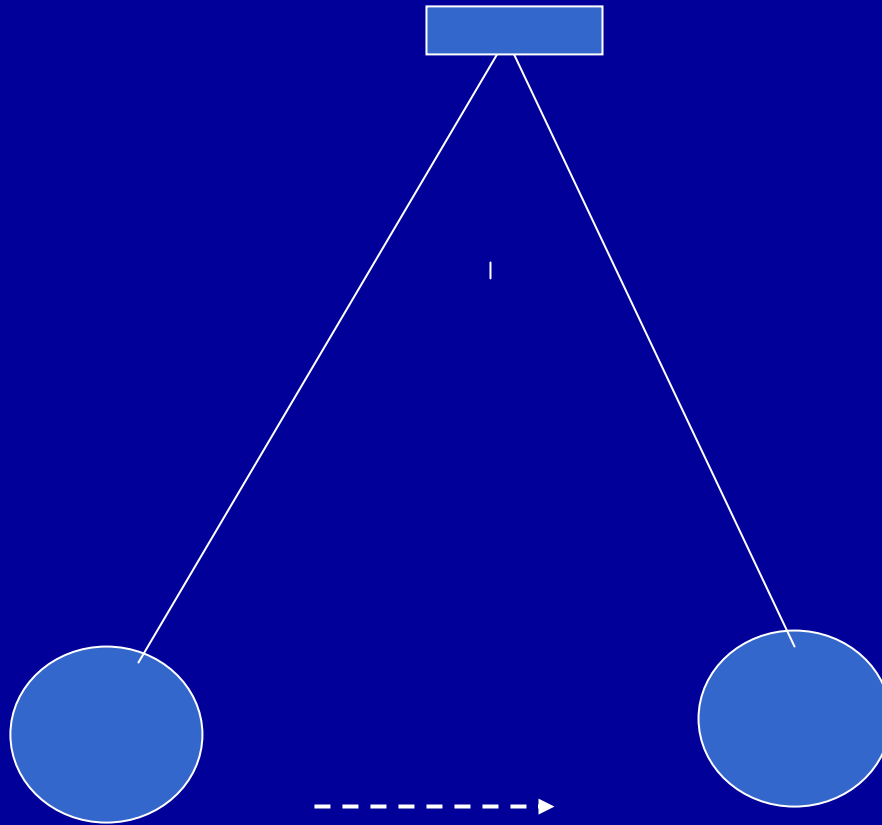


Bixby UST Site

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

The Bio-Augmentation Pendulum



1995 – No Way ...

- Predation, etc, etc.

2005 – Why Not?

- “It’s so cheap...”

Bioaugmentation

- **Some vendors report bio-augmenting as a matter of course – i.e., without even looking for *Dehalococoides Ethogenes (DHE)***

(Highly) 'Recommended Reading':

**BIOAUGMENTATION FOR
CHLORINATED SOLVENT
REMEDICATION**

**Hans Stroo
SERDP Partners Conference
December 2005**



Enhanced Reductive Dechlorination

- **There are a variety of possible electron donors – vegetable oil, molasses, whey, beer wastes, chitin, HRC**
- **Electron Donor appropriateness appears to be site specific**

DESIGN CONSIDERATIONS FOR REMEDIATION BY STEAM AND IRON ENHANCED IN-SITU SOIL MIXING



The 5th International
Conference on
Remediation of
Chlorinated and
Recalcitrant
Compounds

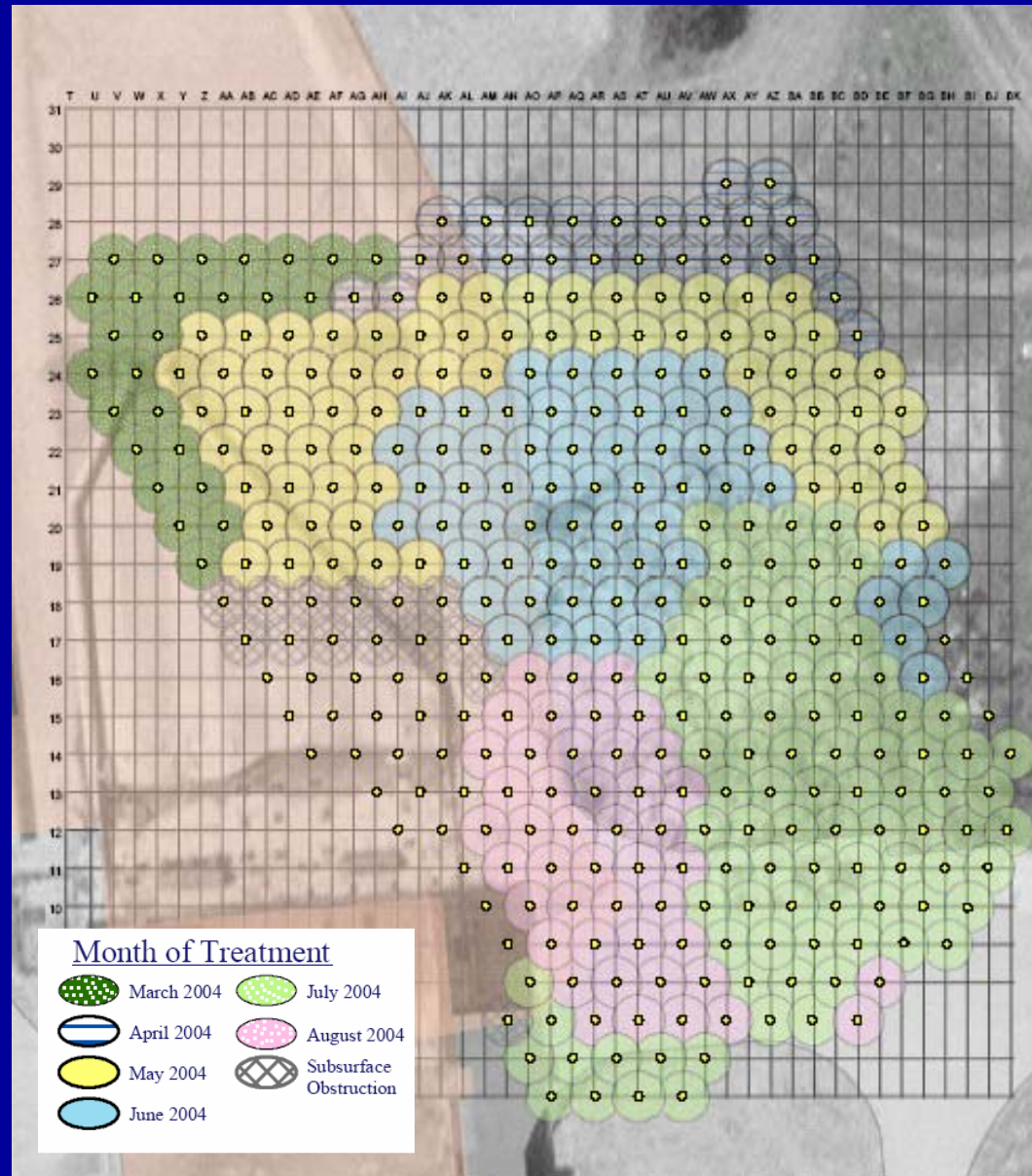
25 May 2006
Monterey, CA

John P. Matthews
Patrick AFB, FL

SPACE LAUNCH COMPLEX 15

Launch Stand Treatment

- 313 treatment cells
- 20 ft to 55 ft bgs
- 1 March – 3 October 2004
- Estimated TCE Mass Removed: 3,800 – 6,100 lb
- Estimated VOC Mass Removed: 9,700 – 12,600 lb
- Does not include in-situ breakdown with ZVI
- Estimated Treatment Volume: 26,500 cubic yards (minus overlap)



LESSONS LEARNED & FUTURE SITES

- **Lessons Learned from Space Launch Complex 15**

- **Change from 10 foot auger to 8 foot auger**
- **Upgrade data acquisition system**
- **Increase number of gas chromatographs – run continuously**
- **Work outer ring first – then step out from “hot” cells**
- **Mix zero-valent iron slurry to lowest depth along outer ring**
- **Tweaked treatment protocol to spend more time on high-contaminated cells and less time on low-concentration cells**



- **Future Cape Canaveral AFS Sites**

- **Security Police Confidence Course (145 cells)**
- **Facility 1381 (892 cells)**

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'I/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**

Combined Remedy RODs

- **Pemaco NPL (solvent) site, Maywood, Ca – STATUS; Installation underway**
 - Electrical Resistance Heating (ERH) in hot spot at 35-95' bgs
 - Enhanced vacuum extraction in vadose zone
 - Possible use of In Situ ChemOx, Enhanced Bio, MNA in downgradient zones

Addtl 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

Grants, NM Solvent NPL site ROD

PROBLEM COMPONENT

REMEDY

Vapor Intrusion

Mitigation

Source Areas

In Situ Thermal Treatment

Shallow Plume Core and Hot Spot

ISCO + followon ERD

Shallow GW Plume periphery

ERD Bio-Barrier

Deeper GW Plume

ERD Bio-barrier

Grants NM ROD (cont.)

- Remedial Flexibility
 - “EPA will evaluate the site conditions to determine if MNA is a viable remedial alternative after the first 5-year review and after source control has been established in the source area and the shallow GW plume...”

Challenges

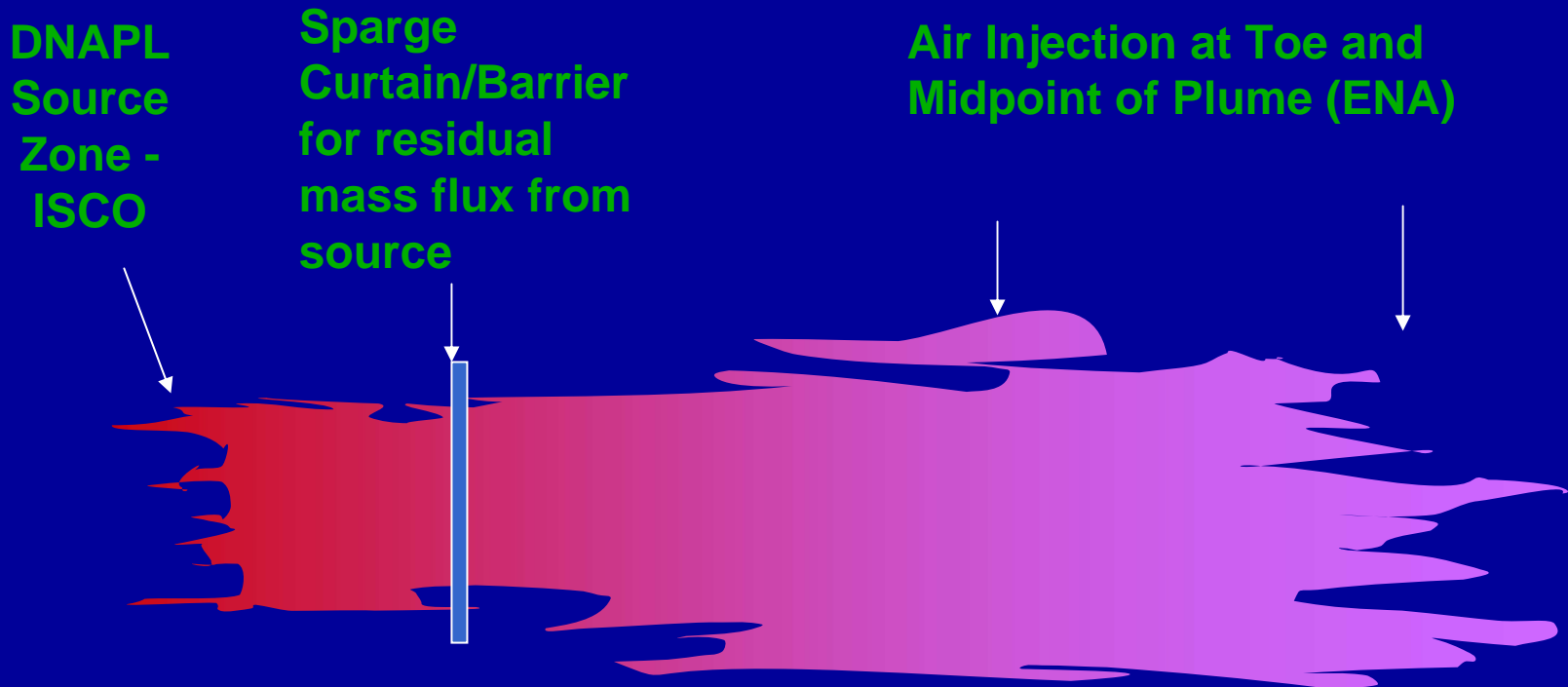
- **Convincing decision-makers that ‘combined remedies’ is not a euphemism for ‘blank check’**
- **Whether single technologies or combinations, we still have work to do in the area of in situ process control**

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)

'Holistic' Remedy: Partial Mass Removal via In Situ ChemOx (ISCO) + Enhanced Natural Attenuation

Northeast US former Manufactured Gas Plant(MGP)



- NOTES:
- 1) Plume mgmt necessary because contamination has reached residential wells
 - 2) ISCO pilot completed. Consultant analyzing results

Combined Remedies - Closing Thoughts

- Flexible, Adaptive Implementation is a Crucial Component of Combining Remedies For NAPL Sites

Combined Remedies - Closing Thoughts (Cont.)

- **System installation and operation can provide valuable information on actual subsurface conditions and contaminant distribution**
 - “RD/RA - Just the next phase of Site Characterization...”
 - “NAPL sources begin to reveal themselves as the remediation progresses...”

- *Consultant at Pittsburgh
Envl Restoration Conference*

Another Way of Thinking About 'Performance-Based' ...

- What would a regulatory framework look like that put a number on 'reasonable time frame...' as envisioned by the NCP (e.g. 30 years), and allowed consultants to design treatment trains to meet that timeframe?**
- Hint: Tools like 'Natural Attenuation Software' will be part of the package**