Emulsified Zero-Valent Iron (EZVI): A Combination Technology for Source Zone Remediation

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EZVI - Introduction

HISTORY – Invention of EZVI

- Scientists at NASA (KSC) and UCF invented EZVI to address TCE DNAPL contamination at the Kennedy Space Center

- NASA utilized TCE as a degreaser for rocket engine parts throughout the 1960's.

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EZVI - Introduction

HISTORY – Commercialization of EZVI

- From 2003 through early 2005 a process to manufacture large quantities of reactive/stabile EZVI was developed.
- 2004 – 2005 Field Pilot projects in FL (2) & AR (1)
- 2005 First Full Scale Implementation (Patrick AFB Cape Canaveral, FL)
- 2006 – 2012 EZVI implementations conducted across the US, in Canada, Australia and Europe
- Formulation R&D continues to date

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EZVI - Introduction

HISTORY – DNAPL Remediation Issues

- Physical Chemistry:
  - Immiscible with water = **hydrophobic**
  - High density & low viscosity = **mobile**
  - Low solubility creates long term continuing source to subsurface contamination
- Location:
  - Difficult to delineate precisely
- Treatment:
  - *Difficult to contact* in the subsurface due to **hydrophobic** physical chemistry
  - Many *in-situ* remedies are aqueous solutions or suspensions of oxidizers/reducers and have a **hydrophilic** physical chemistry

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EZVI - Introduction

STRUCTURE – What is EZVI?

- Nano/micrometer sized zero-valent iron particles emplaced within a **surfactant-stabilized, biodegradable, water-in-oil emulsion.**
- EZVI is a remediation DNAPL.
- Highly effective for *in-situ* treatment of DNAPL due to matching physical chemistry and combination remedial technology (abiotic & biotic processes).

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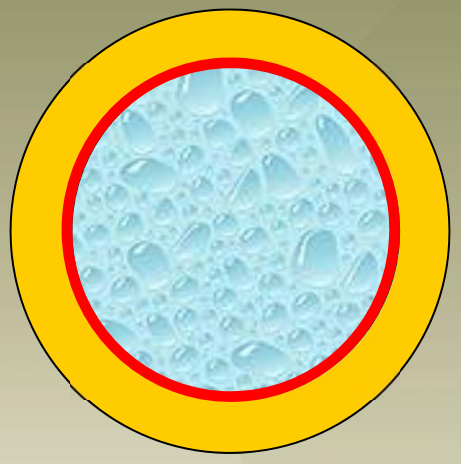
EZVI - Introduction



1) Micro Scale ZVI

2) Suspended in Water

3) Bound by a Polar Surfactant

4) Encased in Vegetal oil

- This is referred to as a micelle
- The micelle is a few to 20 microns in size

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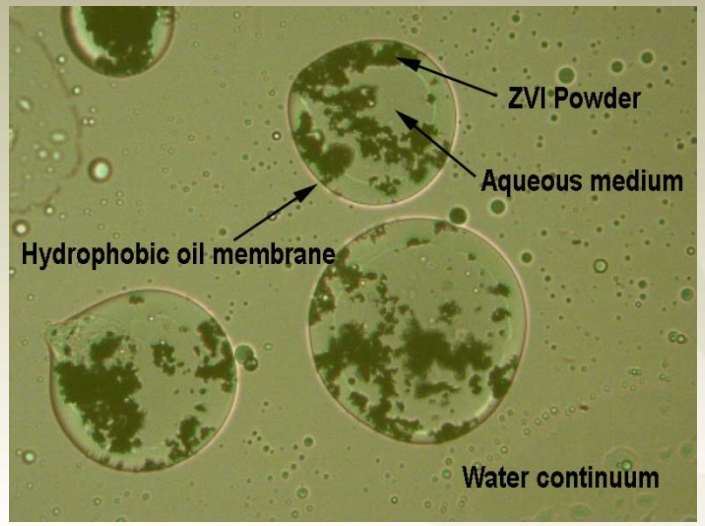
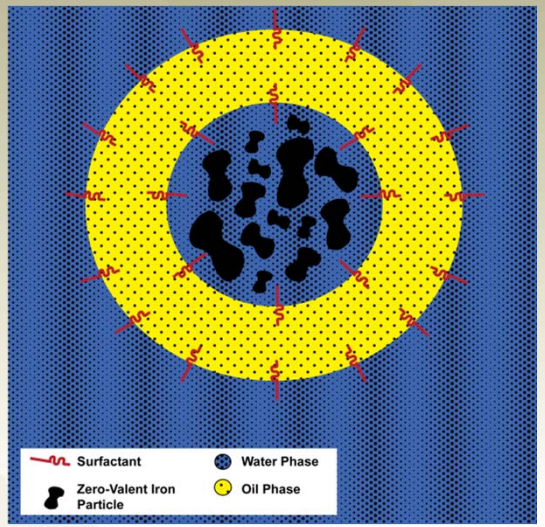
EZVI - Introduction

MECHANISMS – How does it work?

1. Sequestration
2. Dissolution
3. Reductive Dehalogenation (abiotic & biotic)





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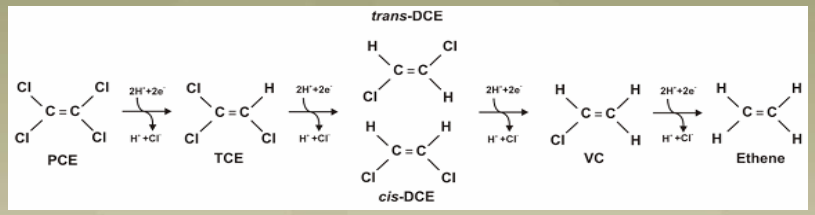
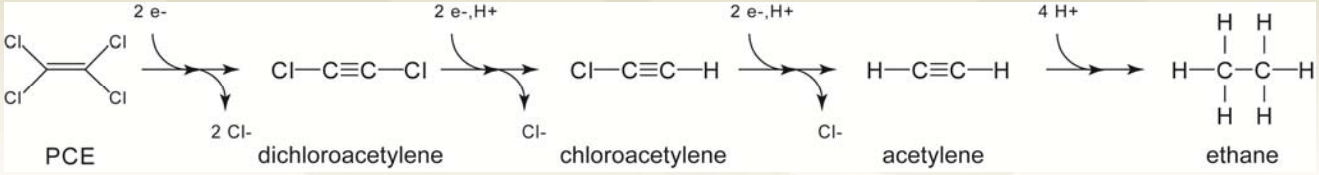
EZVI – Combination Technology

MECHANISMS – How does it work?

- ***Biotic Processes:***
  - Vegetable Oil associated with EZVI is fermented and ultimately provides H2 for biologically mediated reductive dechlorination reactions.



- ***Abiotic Process:***
  - Zero Valent Iron (ZVI) associated with EZVI is emplaced as an aqueous suspension in the interior of the emulsion. Contaminants contact the ZVI via a concentration gradient from the lipophilic membrane into the interior of the micelles.



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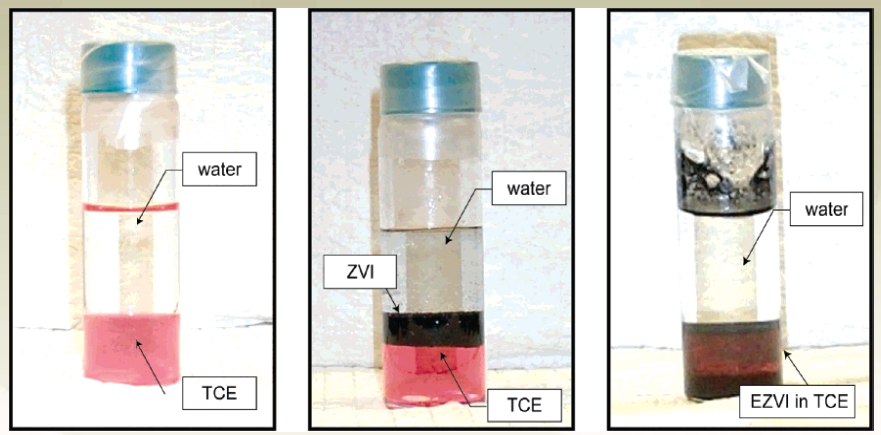
EZVI – Combination Technology

MECHANISMS – How is EZVI Unique?

- Hydrophobic exterior membrane **mimics DNAPL physical chemistry** characteristics and enables **sequestration of contaminant**
- Utilizes both **ABIOTIC** and **BIOTIC** anaerobic remediation processes
- EZVI is **MISCIBLE with DNAPLs *in-situ*** in both free phase or residual forms



Brooks, 2000 **Miscible with DNAPL**

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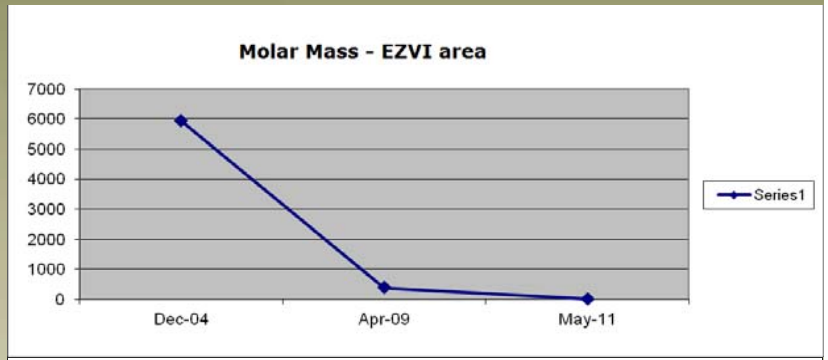
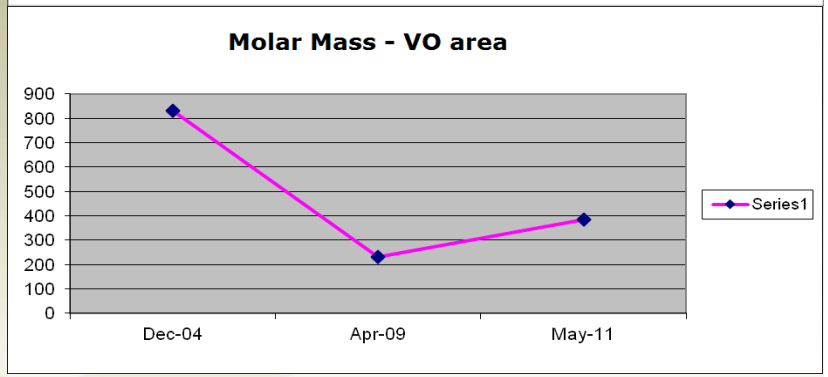
EZVI – Combination Technology

MECHANISMS – How is EZVI Unique?

EZVI vs. Veg Oil

- **EZVI** provided **99% reduction** in molar mass of TCE and degradation products **IN SOURCE AREAS**.
- 93.5% of the molar mass reduction in EZVI treated areas occurred within 4years of injection and the remainder within 3 additional years.
- During the same time period at the same site, **VO treatment** provided **54% reduction** in molar mass of TCE and degradation products **IN DISSOLVED PLUME AREAS**.





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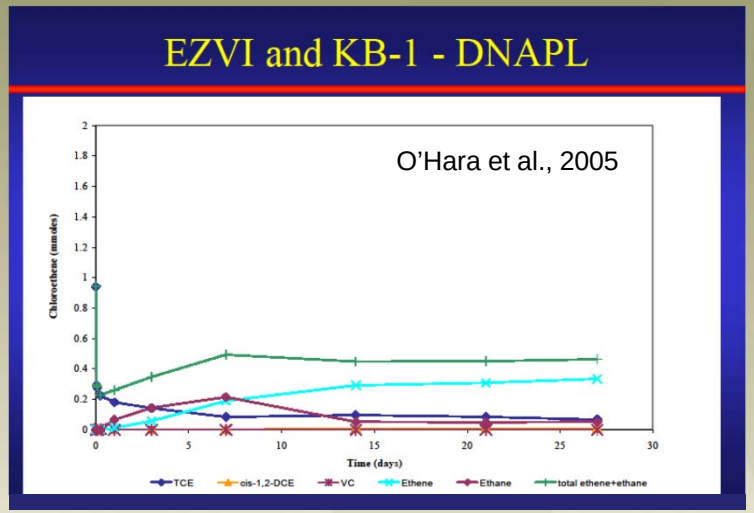
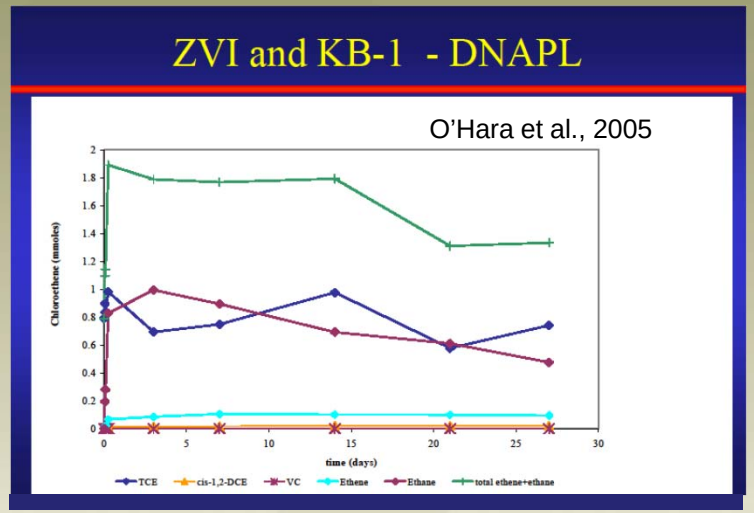
EZVI – Combination Technology

MECHANISMS – How is EZVI Unique?

EZVI vs. ZVI





- EZVI provides **reduced Mass Flux** of DNAPL due to sequestration
- EZVI provides more **efficient use of ZVI** due to hydrophobic membrane

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EZVI – COCs

- **Zero Valent Iron (ZVI)**

Tetrachloroethene (PCE)
Trichloroethene (TCE)
cis 1,2-Dichloroethene (cDCE)
trans 1,2-Dichloroethene (tDCE)
1,1-Dichloroethene (11DCE)
Vinyl Chloride (VC)
Hexachloroethane (HCA)
1,1,2,2-Tetrachloroethane (1122TeCA)
1,1,1,2-Tetrachloroethane (1112TeCA)
1,1,1-Trichloroethane (111TCA)
1,1,2-Trichloroethane (112TCA)

1,1-Dichloroethane (11DCA)
Carbon Tetrachloride (CT)
Trichloromethane (TCM)
Tribromomethane (TBM)
1,2-Dibromoethane (12EDB)
Trichlorotrifluoroethane (Freon 113)
Trichlorofluoromethane (Freon 11)
1,2,3-Trichloropropane (123TCP)
1,2-Dichloropropane (12DCP)
Lindane
Hexachlorobutadiene (HCBD)
N-nitrosodimethylamine (NDMA)

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EZVI Implementation

- Engineered as an *in-situ* source treatment technology
- Delivered into subsurface soil/groundwater zones that are contaminated with source material(s) (DNAPL)
- Is effective in **vadose soils**, as well as **saline** and **aerobic** saturated environments
- Has been implemented at highly active military and commercial manufacturing sites

Pilot Scale

Full Scale

EZVI and VO staged for field implementation

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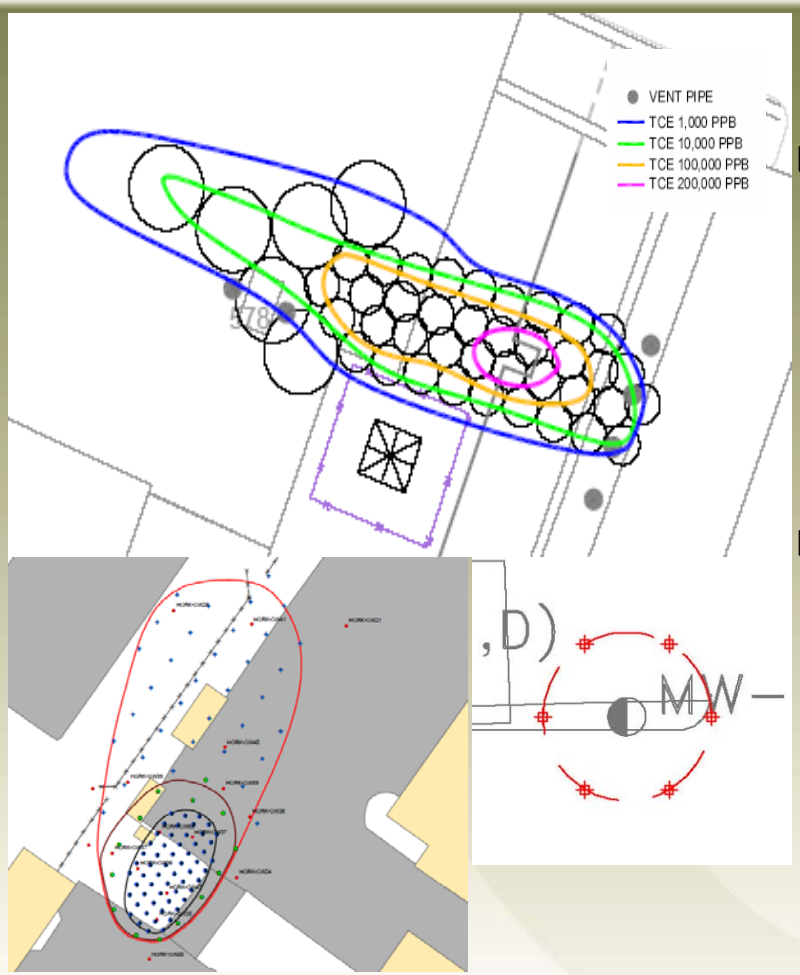
EZVI Delivery



- EZVI injections performed using:
  - Fracturing methods
  - KAPSDIDS method
  - Direct Push method
  - Soil Mixing (LDA method)
- Injection pattern typically "outside-in" and "bottom-up"

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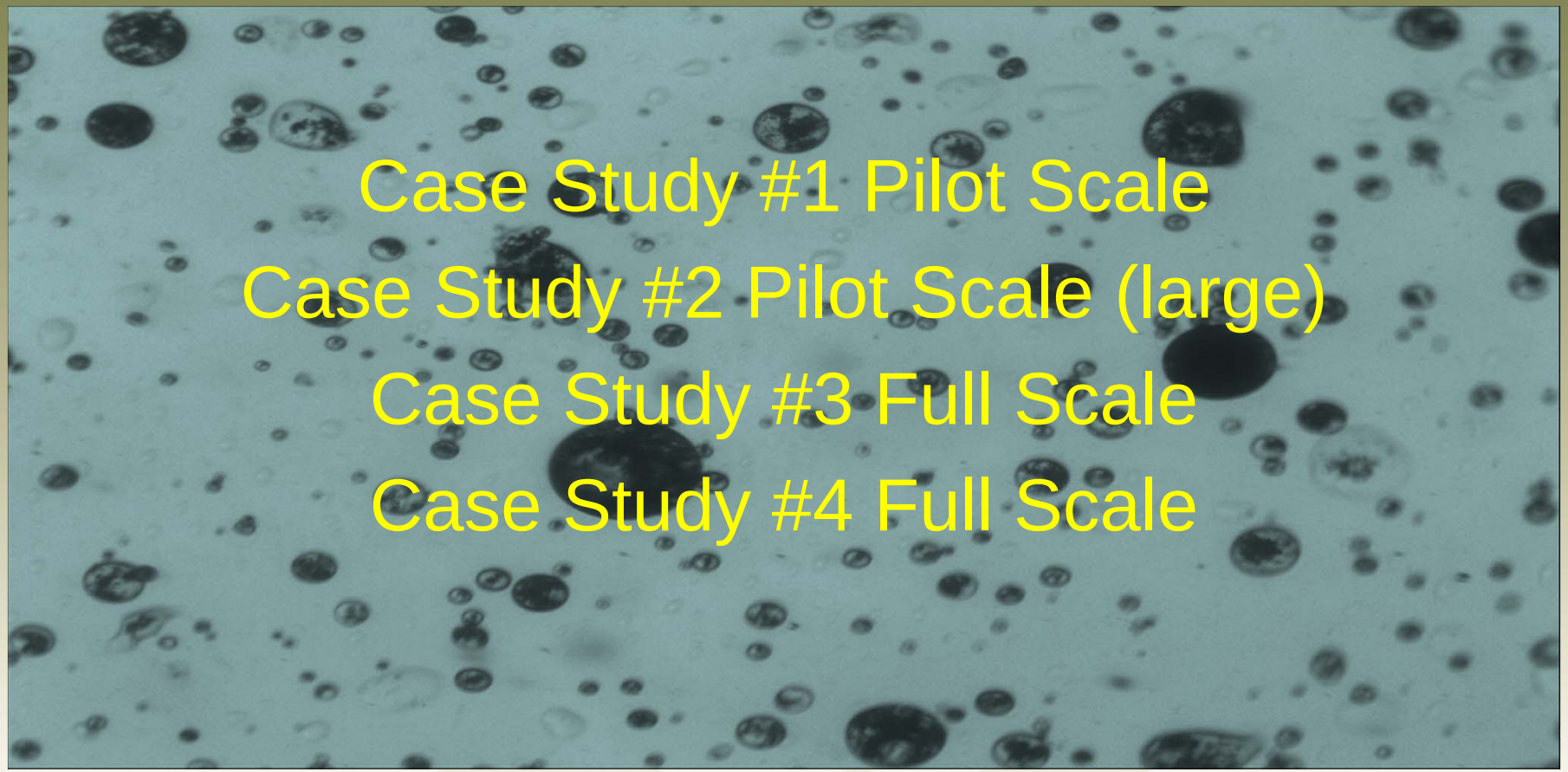
Case Study Examples



Case Study #1 Pilot Scale

Case Study #2 Pilot Scale (large)

Case Study #3 Full Scale

Case Study #4 Full Scale

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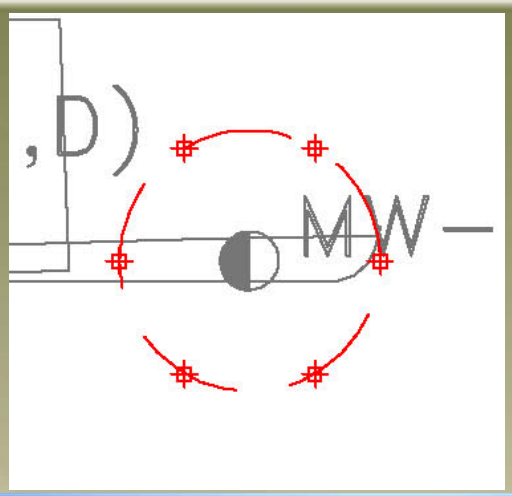
Case Study #1-Pilot Scale

Private Client in Central Florida

- Trichloroethylene (TCE), cis-1,2-DCE, trans-1,2-DCE, and vinyl chloride
- About 1,000 liters of 10% EZVI was injected in a 11m radius around a former UST/sump location.
- Injections targeted a 3 m thick subsurface zone.
- Vegetable oil was injected above the area treated with EZVI and down gradient of the former source area as a carbon source to stimulate naturally-occurring biodegradation of the dissolved phase plume.



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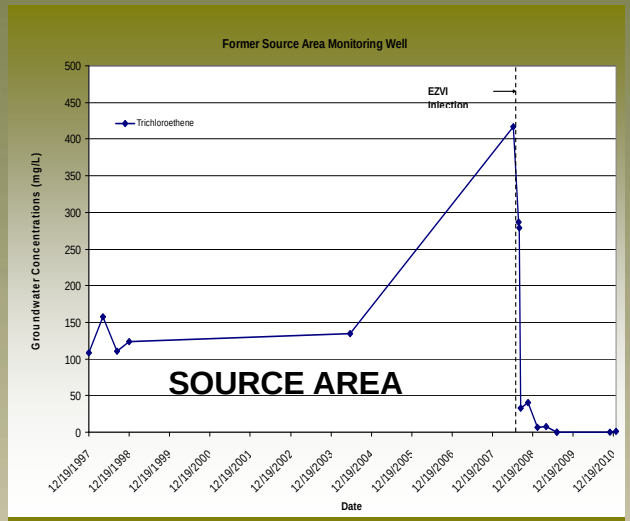
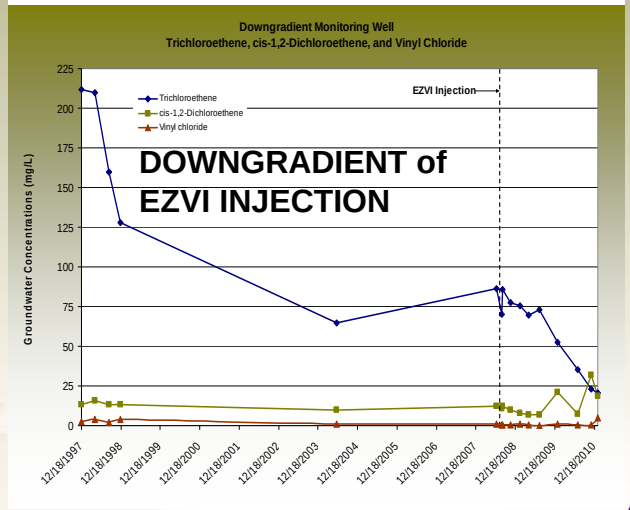
Results of Case Study #1

- Source area results: TCE groundwater concentrations from 417 mg/L (baseline results) to 6.88 mg/L after six months and non-detect within twelve months.
- Dissolved TCE concentrations adjacent to and above the EZVI injection zone decreased from 3.25 mg/L (baseline results) to <0.002 mg/L.
- Source Area [TCE] remained at non-detect levels for ~ 3 years post EZVI injection.





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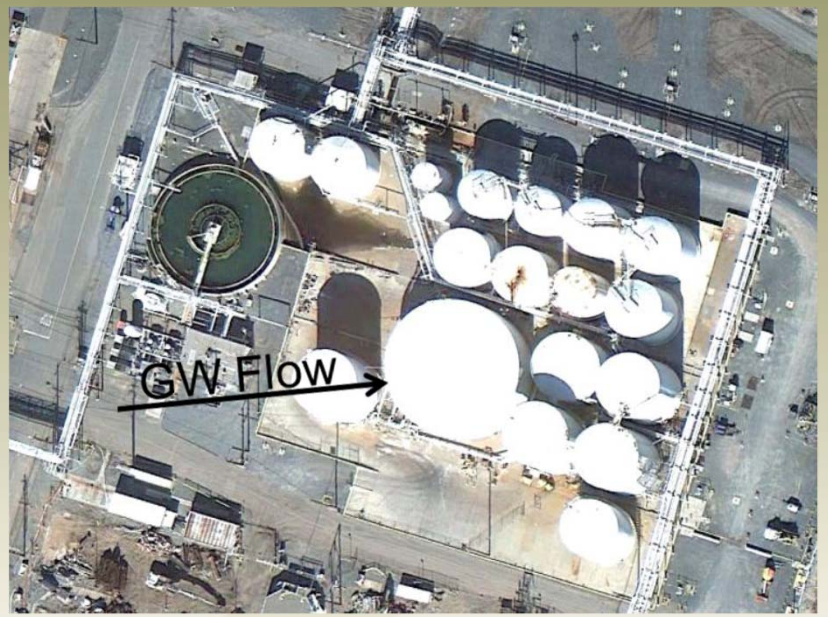
Case Study #2-Pilot Scale

Private Client in Western U.S.

- PCE/CT source area beneath a tank farm in an active chemical facility, with a depth of contamination to 30 m
- **MIP survey** conducted to identify location/depths of injection points
- About 110 m^3 of 10% EZVI were injected using the **KAPSDIDS technology**
- Injection design and monitoring program limited due to active tank farm



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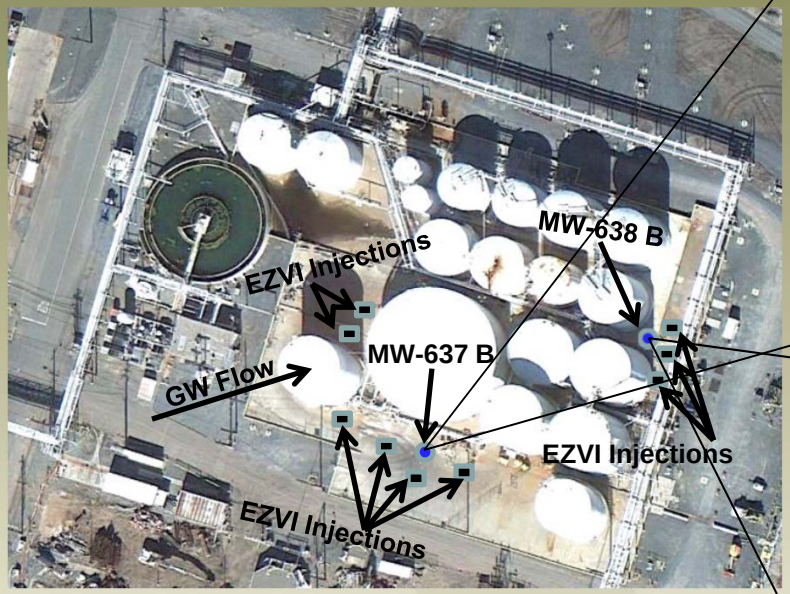
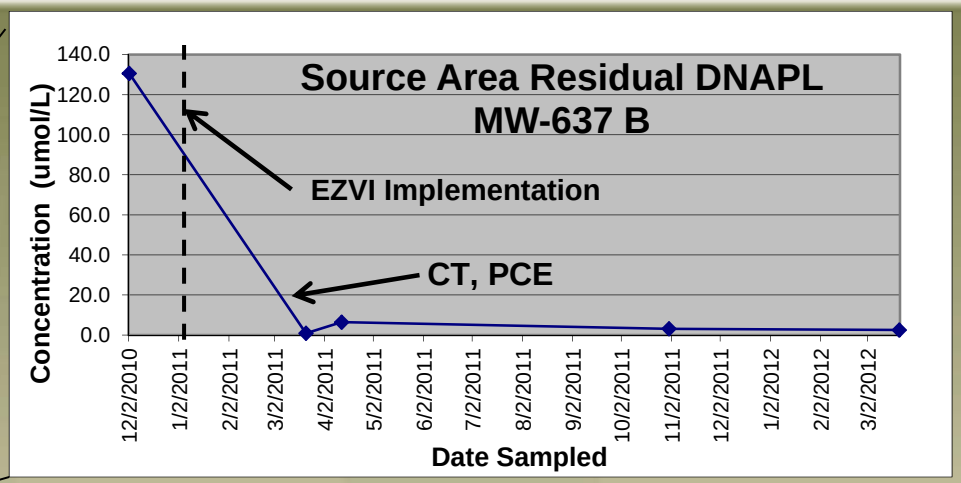
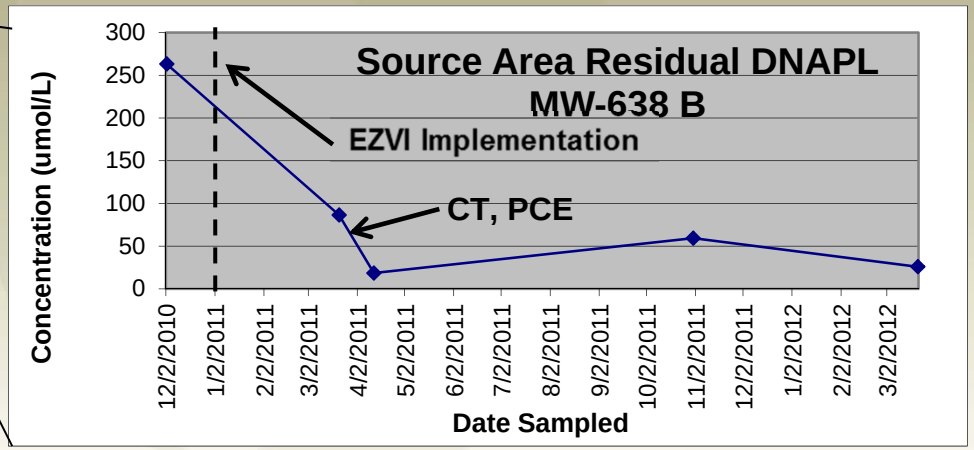
Results of Case Study #2







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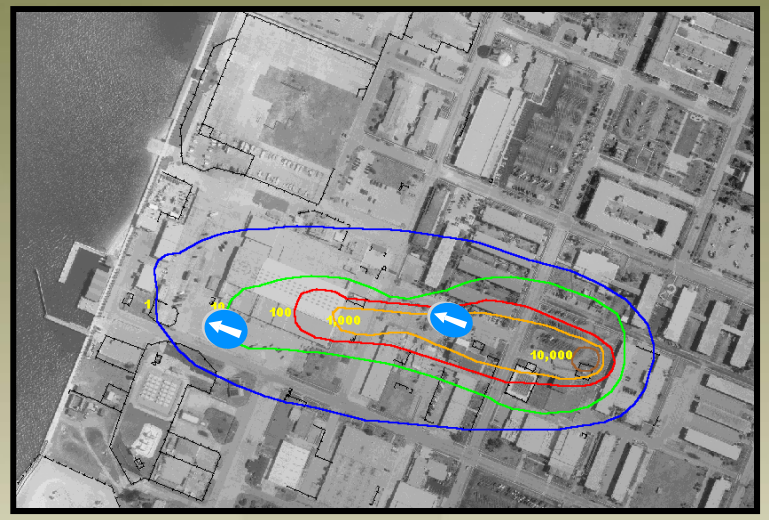
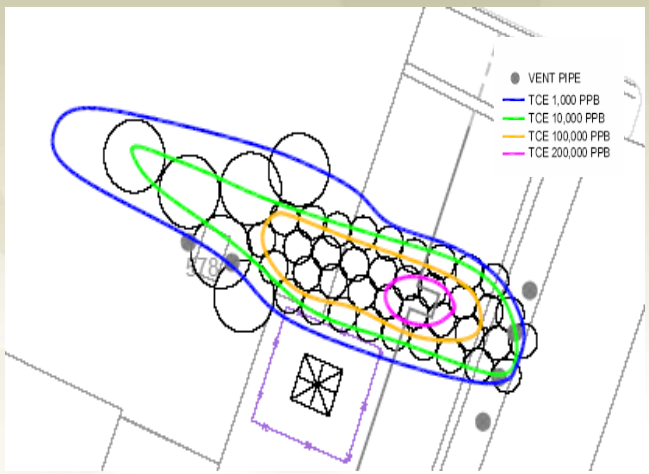
Case Study #3-Full Scale

Federal Client in Central Florida

- TCE source area was 25x50 m long with a depth of contamination to 15 m
- 20 hectares dissolved plume
- 230 m^3 of 10% EZVI were injected using pneumatic fracturing technology
- Vegetable oil and KB-1 were also injected in the downgradient plume areas.





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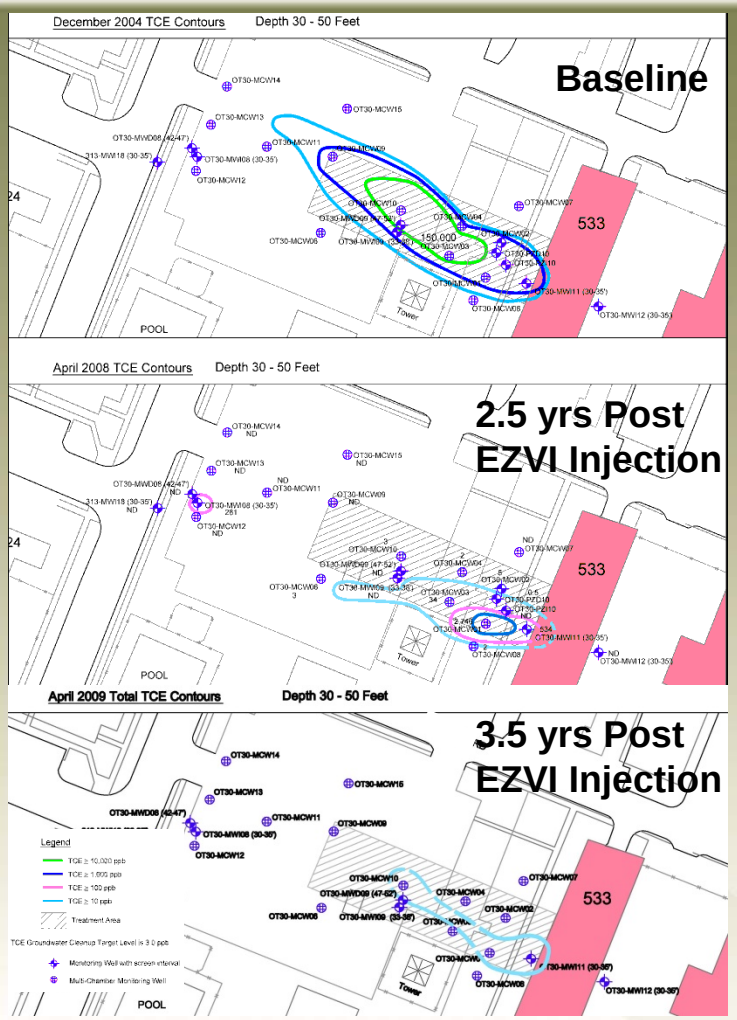
SOURCE AREA Results
Case Study #3



- Baseline samples from TCE source zone up to **350 ppm** in groundwater samples
- One EZVI injection event
- ~90% destruction of source area TCE within one year
- >99% destruction of source area TCE to date
- **Prior to EZVI injection-** Estimated to take ~**250 yrs**. to remediate site via MNA
- **Post EZVI injection-** Estimated to attain remediation goals within < **80 yrs**.

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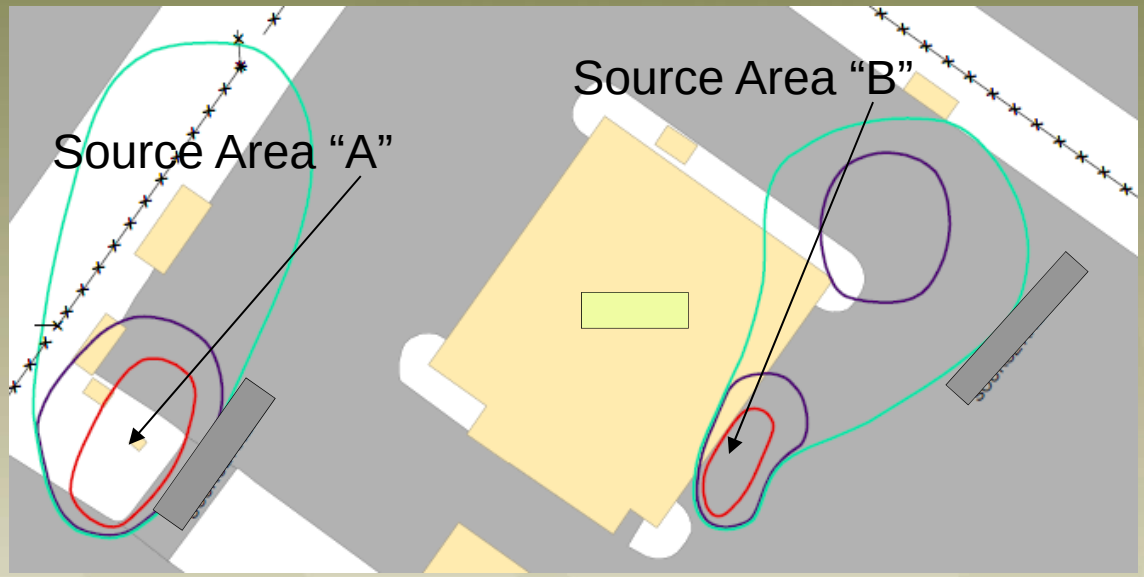
Case Study #4-Full Scale

Federal Client in Central Florida



- TCE source area "A" was ~ 15 x 30 m; while source area "B" was 7 x 20 m; both with a depth of contamination to 15 m
- 140 m^3 of 10% EZVI were injected into the two source areas using the KAPSDIDS technology

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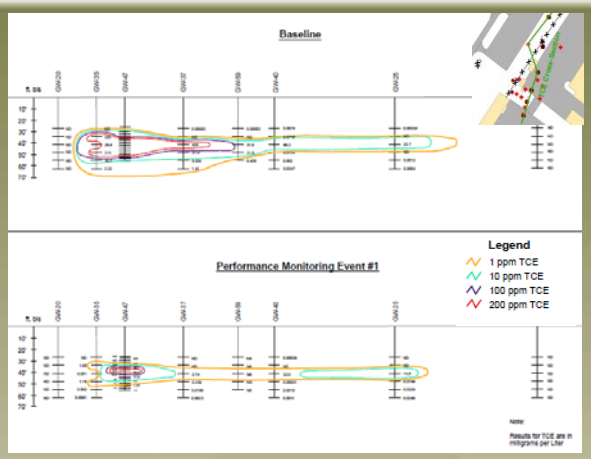
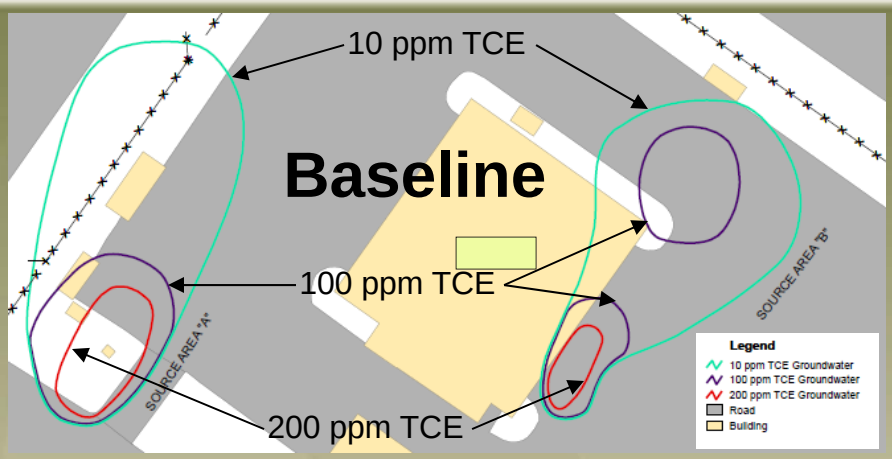
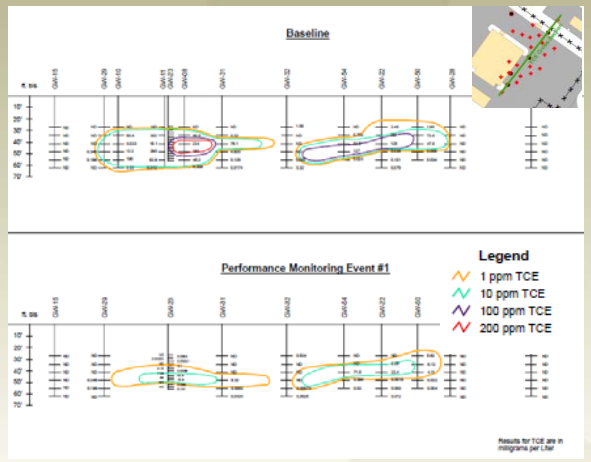
SOURCE AREA Results
Case Study #4

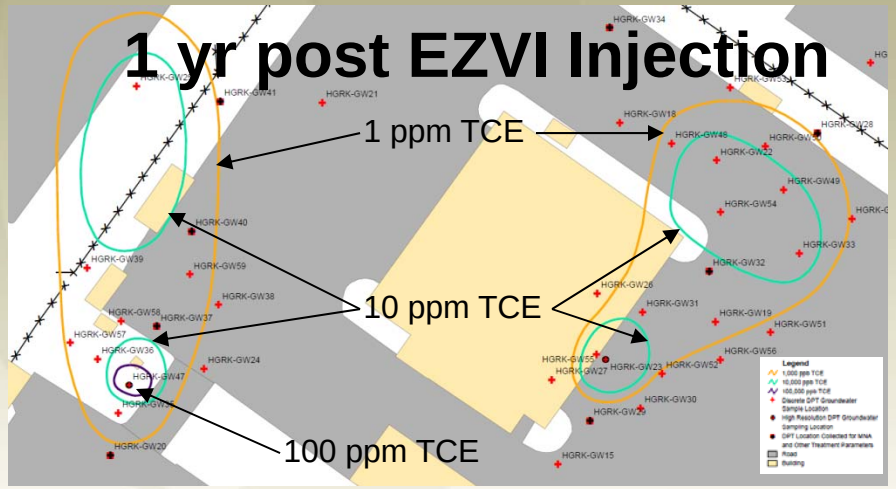
Source Area A





Source Area B





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EZVI Performance & Cost

- **Contaminant Reduction**
  - Typical source area VOC concentration reduction of 80 - 95% within <1 year
- **Timeframe of Reactivity**
  - EZVI has been shown to be effective in the subsurface for periods exceeding 2.5 years
- **Source Area Effects**
  - Directly destroys source material
- **Plume Effects**
  - *Adjacent to source area:* Fermentation reactions provide hydrogen for biotic transformations or "polishing" adjacent to injection area
  - *Downgradient:* Eliminates on-going source for downgradient areas
- **EZVI Material Costing**
  - Volume dependent range is 4 to 6 euro/l for 10% formula

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Why EZVI?

Benefits

- Directly treats contaminant source
- Biostimulation for dissolved phase treatment
- Requires less treatment time
- Cost competitive
- Green & Sustainable (GSR) approach
- Effective in oxidative or saline environments
- Effective in vadose soils

Success Highlights

- Field-tested by the U.S. EPA under the SITE Program
- Used at commercial and government sites to treat CVOCs (e.g. PCE, TCE, CT)
- Applied in multiple locations, including; FL, AR, NC, TN, IL, OH, TX, LA,WV, MA, NJ & Canada!
- 2005 **Award for Excellence** in Technology Transfer by the Federal Laboratory Consortium
- 2005 NASA Government **Invention of the Year**
- 2006 NASA **Commercialization Invention of the Year**
- 2007 NASA **" Space Technology Hall of Fame"** Inductee

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Questions

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