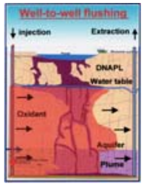

Site Remediation Using Chemical Oxidation Techniques

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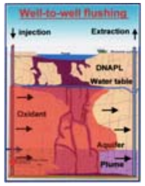
NATO/CCMS Pilot Study

"Prevention and Remediation in Selected Industrial Sectors: Small Sites in Urban Areas"

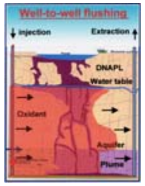
Athens, Greece

4-7 June 2006



Presentation Outline

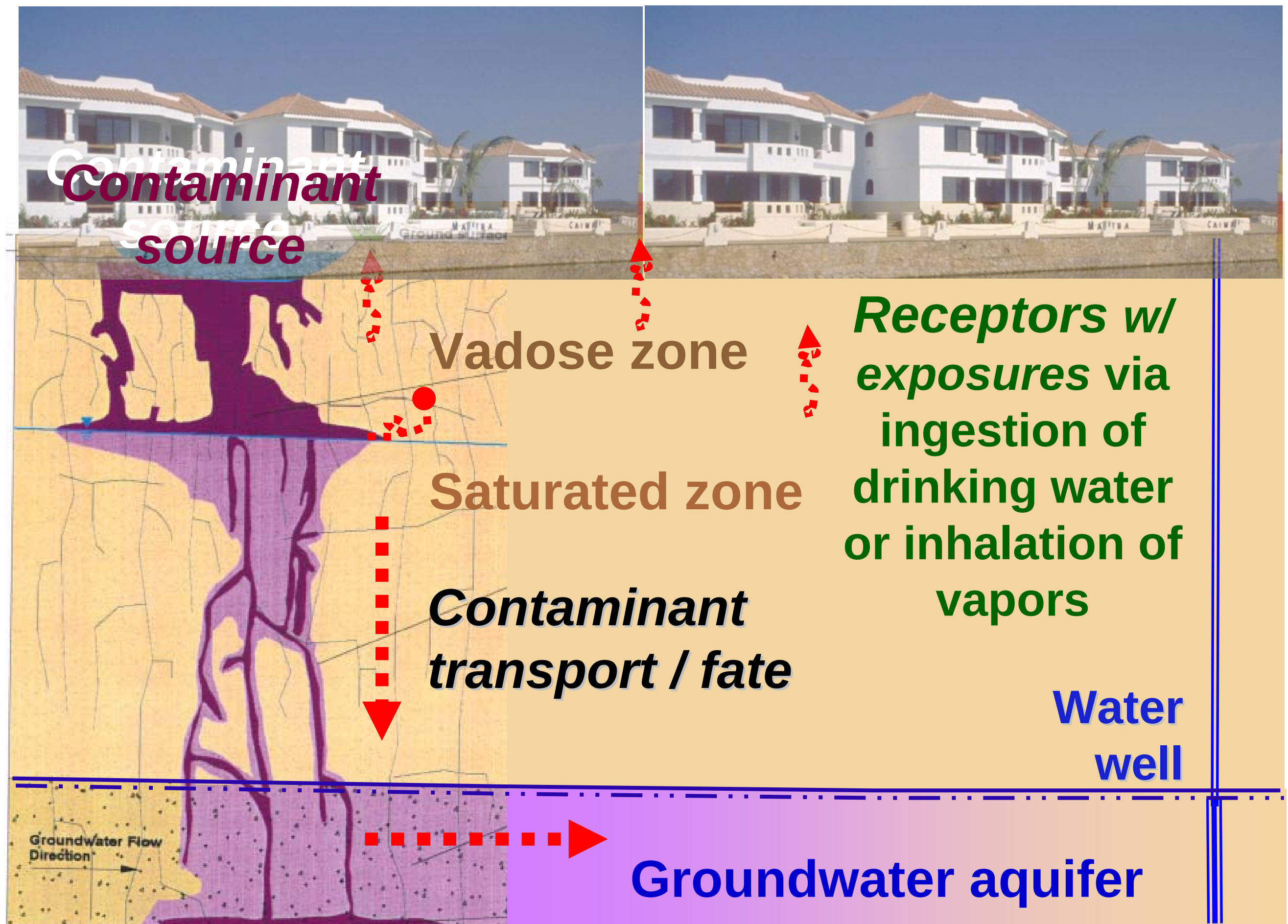
- **NATO CCMS Pilot Study - 7 June 2006**
  - **Need for and motivation to develop and use oxidation processes for site remediation**
  - **Evolution and status of chemical oxidation**
  - **Ongoing technology initiatives**
- **NATO Advanced Research Workshop - 8 June 2006**
  - **Aspects of CSM research will be covered in a companion talk during the NATO Advanced Research Workshop**
    - **Enhanced DNAPL destruction in ‘reaction clouds’**
    - **Combining oxidation with other remedies**
      - **Oxidation enhanced bioremediation (chem-bio)**
      - **Co-injection or sequential injection of oxidants with surfactants and cosolvents**
    - **Model development and application**

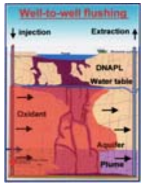


Background

- The problem…widespread contamination of soil and groundwater by organic chemicals

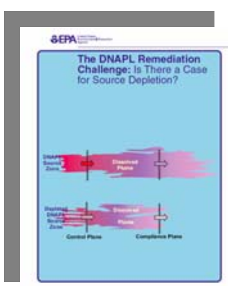
Major challenges occur at sites with dense nonaqueous phase liquids (DNAPLs) such as PCE and TCE solvents



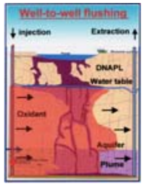


Magnitude of the problem in the U.S.

- Estimated 30,000 to 50,000 sites with groundwater contamination (excludes petrol UST sites)
  - 80% of the sites are contaminated with organic chemicals, and of these, 60% likely have DNAPLs
- Clean up costs for 15,000 to 25,000 sites with DNAPLs...?
  - Conventional groundwater pumping and treatment systems
    - Median is $180,000/year; range is $30,000 to $4,000,000/year
    - For all sites, annual costs are $2.7 to 4.5 billion/year
  - Assuming a 30-year life and a 5 to 10% interest rate, life-cycle costs of “cleanup” could range from $50 to $100 billion dollars
  - Clean up based on groundwater pump and treat is *hopeless;* Alternative technologies and approaches are needed…..

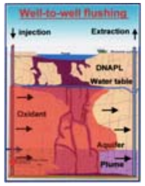


Source: USEPA (2003). www.epa.gov/ada/download/reports/600R03143/600R03143.pdf

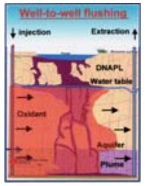


❑ In Situ Chemical Oxidation (ISCO) for remediation

- ISCO involves delivery of oxidants into soil and groundwater to destroy organic chemical contamination
- Several different chemical oxidants can be used for ISCO:
  - Catalyzed hydrogen peroxide (H_2O_2) (modified Fenton's)
  - Activated sodium persulfate ($Na_2S_2O_8$)
  - Potassium or sodium permanganate ($KMnO_4$, $NaMnO_4$)
  - Ozone (O_3)
- These oxidants can rapidly destroy many contaminants (e.g., > 99% destruction in minutes)
  - Oxidants can mineralize chlorinated hydrocarbons, PAHs, BTEX, MTBE, phenols, PCBs, TNT, Lindane, and others
  - Reaction stoichiometries, pathways, and kinetics are generally well-established for a wide range of contaminants

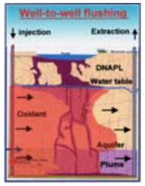


- **But,… successful use of ISCO for site clean up requires system engineering that must address:**
  - **Oxidant type and concentration to be used**
    - **Natural oxidant demand (NOD) of subsurface media**
    - **Contaminant type, mass level, and architecture**
    - **Subsurface and surface site conditions**
  - **Method and mode of oxidant delivery to soil or groundwater**
    - **Wells vs. probes vs. mixing etc. and One vs. many doses**
    - **Hydraulic control and fugitive emissions control**
    - **Maintain permeability in injection wells and/or the aquifer**
    - **Prevention of groundwater quality impacts**
  - **Synergy of ISCO with pre- and post-ISCO methods**
  - **Methods for process monitoring and performance validation**
  - **Health and safety controls**



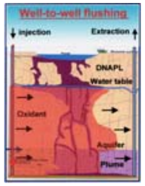
- For clean up of small sites, ISCO can be very attractive
  - Small sites often have contaminants that ISCO can treat
    - For example: dry cleaners, machining and metal working, vehicle repair, chemical factories, testing labs, etcetera
  - At small sites, ISCO can be relatively easy to use - why?

    - Engineers are 'comfortable' with chemical oxidation based on training and experience (e.g., with waste treatment)
    - ISCO can be designed and implemented with widely available materials and equipment
    - ISCO does not require large or highly specialized equipment
    - ISCO does not have unusual power requirements or other utility needs
    - ISCO can be done relatively quickly (days to a few weeks)
    - ISCO does not have major patent limitations

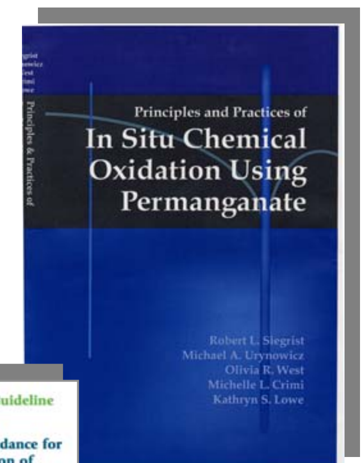


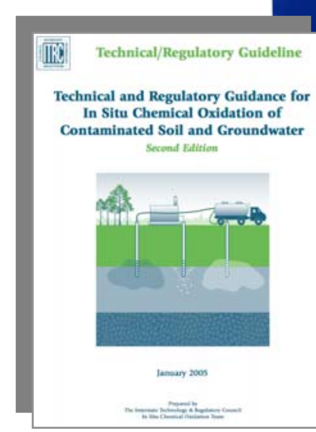
Technology Status

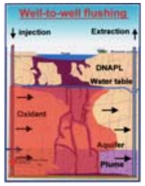
- **ISCO has 'matured' since the early 1990's**
  - **Laboratory research increased the fundamental understanding of chemical oxidation, including:**
    - **Reaction chemistry for organics in aqueous systems**
    - **Transport processes affecting oxidant delivery**
    - **Oxidant interactions with soil or aquifer media**
  - **Pilot-scale studies helped advance the engineering of ISCO for common types of contaminated sites, including:**
    - **Sites with dissolved and sorbed phase levels of organic chemicals in soil and groundwater plumes**
    - **To a lesser degree, sites with DNAPL source zones**
      - **DNAPL residuals suspended in homogeneous media**
      - **DNAPL pools resting on a low permeability layer**



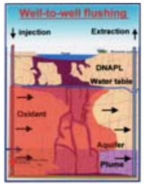
- **Based on the results of R&D and pilot-scale studies, guidance documents were produced in the late 1990's and early 2000's, including:**
  - **Project case study reviews**
    - **e.g., USEPA 1998, ESTCP 1999**
  - **Technical reference book**
    - **e.g., Siegrist *et al.* 2001**
  - **Technical and regulatory guidance**
    - **e.g., ITRC 2001, 2005**
    - **www.itrcweb.org/gd_ISCO.asp**



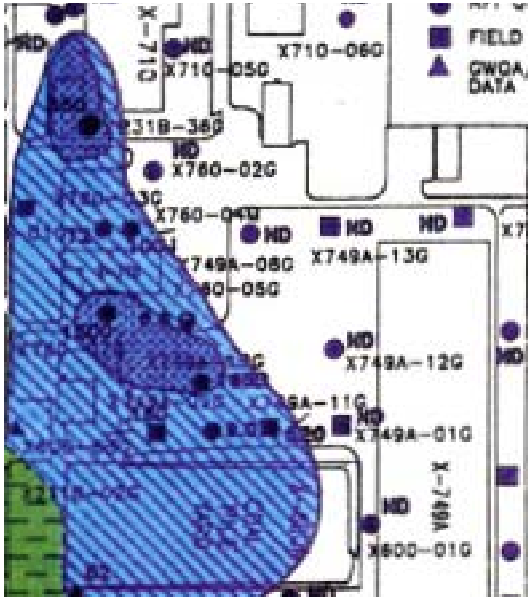




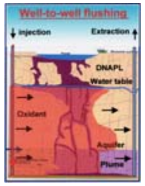
- During the late 1990's, engineers and consultants increasingly used ISCO for site remediation
  - Different oxidants have been used alone or combined
    - H_2O_2, $Na_2S_2O_8$, $NaMnO_4$, $KMnO_4$, O_3
  - Optional subsurface delivery methods have been used
    - Direct-push probes, drilled wells, or specialized injectors, with some use of fracturing techniques
    - Reactive barriers, recirculation schemes, multiple delivery modes, or other strategies
  - Cleanup goals have varied, for example:
    - Reduce the concentration or mass by some % (e.g., >90%)
    - Achieve a final soil concentration (e.g., 1 mg/kg or less)
    - Achieve a concentration in a plume at some compliance plane downgradient from a DNAPL source zone



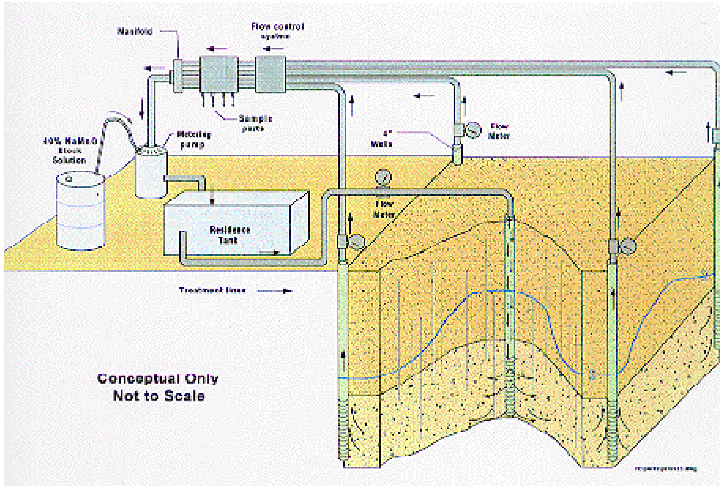
- **A few examples help illustrate the features of ISCO remediation projects**
  - **Vertical well-to-well recirculation of $NaMnO_4$ in Ohio**
    - **ISCO treatment of the source of a TCE groundwater plume in an industrial area**
      - **1.5 to 2.0 mg/L TCE in sandy gravel aquifer zone at 7.9- to 10.4-m depth bgs (Ksat ~ 7.9 to >90 m/d)**
    - **Treatment goal**
      - **Reduce the mass of TCE in the source zone causing the groundwater plume and prevent the plume from growing**

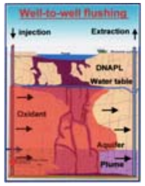


Source: Lowe, K.S., F.G. Gardner, and R.L. Siegrist (2003). *Ground Water Monitoring and Remediation*. Winter issue.

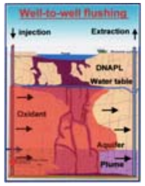


- System design and implementation
  - Lab tests, modeling, hydraulic control tracer test
  - Full-scale system included 1 center injection well and 4 perimeter extraction wells at 13.7-m radius
  - Extraction of groundwater, amendment with ~250 mg/L $NaMnO_4$, flow-through reactor, inline filter, and re-injection
  - Injection/extraction rate was 68 Lpm yielding 3 pore volumes throughput in a 380 m^2 treatment zone in ~10 days
  - Oxidant used = 162 kg (295 L) of 40 wt.% $NaMnO_4$ solution

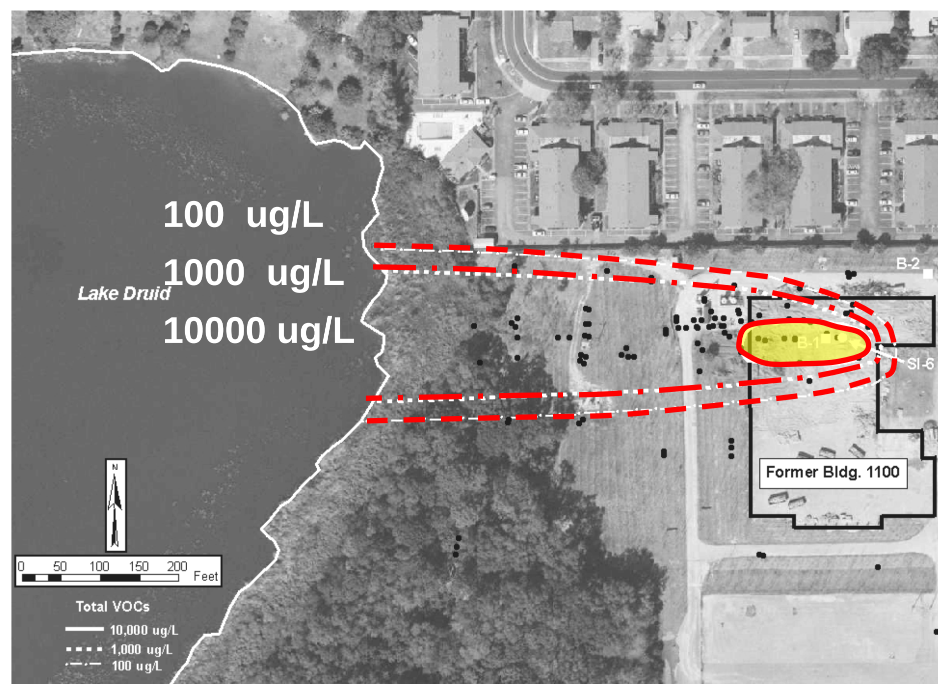




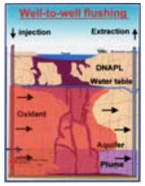
- **Performance observations**
  - **Effective hydraulic control was quickly accomplished**
  - **Monitoring revealed TCE reduction of >97%**
    - **After 30 days, concentrations remained < 20 ug/L**
  - **Oxidant depletion**
    - **To <20 mg/L at 2 weeks**
    - **To <1 mg/L at 4 weeks**
  - **No loss in hydraulic conductivity within the treated zone**
  - **No biotoxicity measured by Microtox assays**



- **Vertical well-to-well flushing of $KMnO_4$ in Florida**
  - **ISCO treatment of the source of a PCE plume in groundwater**
    - **PCE plume (10,000 ug/L near the source) located in shallow (0 to 25 ft) and deep (25 to 60 ft) sandy zones**
    - **The plume was estimated to be approximately 100 ft wide, 500 ft long, and 60 ft deep**
  - **Treatment goal**
    - **Reduce the PCE mass in the source zone and enhance the effectiveness of bioremediation and phytoremediation in the downgradient plume**

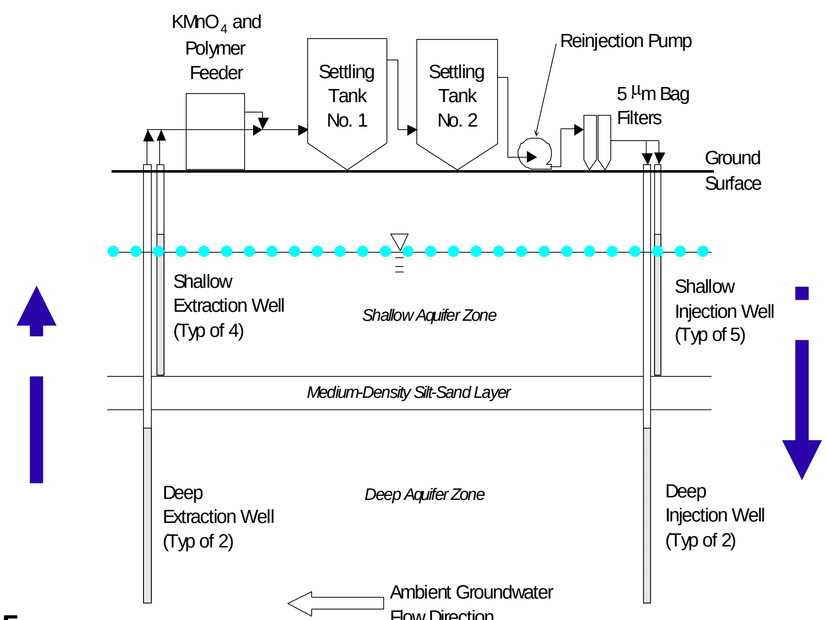


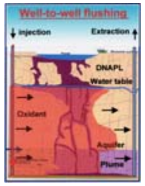
Source: Crimi and Siegrist (2003). *J. Ground Water;* Singletary *et al.* *(2006). Battelle Recalcitrant Organics Conf*.



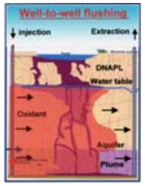
❖ **System design and implementation**

- **Lab tests, field pilot test, and flow modeling were done**
- **The full-scale system included a vertical well network with $KMnO_4$ flushing of shallow and deeper aquifer zones**
  - **Groundwater was extracted and processed in a treatment system prior to re-injection at a design rate of 57 Lpm (6.4 to 9.5 Lpm per well) and concentration of 1000 mg/L $KMnO_4$**



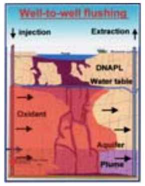


- **Performance observations**
  - **During the initial months of operation the delivery and distribution of $KMnO_4$ in the subsurface was much more limited than anticipated**
  - **The system was shutdown and CSM studies were done**
  - **Characterization studies revealed:**
    - **Very fine uniform sands (small d_{10} and very low U.C.)**
    - **High organic carbon content and high NOD**
    - **High groundwater dissolved solids level**
    - **These conditions caused injection well permeability loss and an inability to achieve the design oxidant injection flow rate and limited the actual oxidant distribution at the site**
  - **Flow-through column tests and modeling studies using a new CSM model, CORT3D revealed:**
    - **Oxidant distribution could be improved by using a lower concentration at a faster injection rate for more pore volumes**



- **In situ soil blending using $Na_2S_2O_8$ in New Jersey**
  - **Treatment of VOC contaminated soil and groundwater**
    - **Depth to groundwater = 0.3 m**
    - **Treatment interval = 0.3 to 3.3 m depth bgs**
  - **System design and implementation**
    - **In situ blending using base-catalyzed persulfate (Klozur)**
      - **Applied 10 Klozur grams per kilogram of soil**
      - **Applied 1 gram hydrated lime per kilogram of soil**

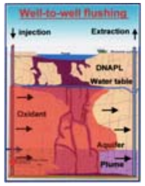
Source: Dr. John Haselow (2006). Redox Tech, LLC. http://redox-tech.com/



- **Performance observations**
  - **Treated approximately 5000 tons in 2 days**
  - **Concentrations dropped from 100 – 200 ppm total VOCS (TCE plus daughters) in groundwater to < 0.1 ppm in 1 week**

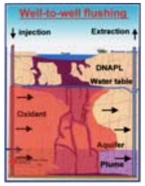

Product of the Month

In Situ Soil Blending



ISCO performance - design vs. outcomes…?

- At some sites, clean up goals have been met in a predictable, cost-effective and timely manner using ISCO
- At other sites, ISCO performance has not met expectations
  - Examples of deficiencies have included:
    - Inability to achieve site cleanup goals based on predictions for the ISCO system that was designed and implemented
    - So-called “rebound” in groundwater concentrations following the end of active ISCO operations
  - Poor performance is often attributed to:
    - Site heterogeneities and low permeability zones
    - Excessive oxidant consumption by soil and aquifer media
    - Presence of large masses of contaminants (e.g., DNAPLs)



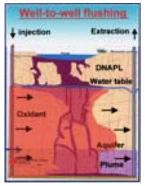
ISCO R&D at CSM

- CSM has been working along with others to help improve ISCO system design and performance
- Several major projects are in progress at CSM
  - "Reaction and transport processes controlling in situ chemical oxidation of DNAPLs" ~ 2002 to 2005
    - Oxidants: Catalyzed H_2O_2, $NaMnO_4$, $KMnO_4$
    - Contaminants: Varied levels of PCE and TCE
    - Processes: Interphase mass transfer and oxidative degradation
    - Delivery: advection and diffusion transport processes
    - Coupling: oxidant enhanced bio, or surfactant flushing
    - Modeling: analytical and numerical methods

DoD EPA DOE SERDP Strategic Environmental Research and Development Program



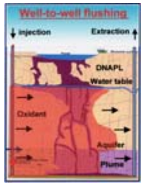




- **"In Situ Chemical Oxidation for Groundwater Remediation - Technology Practices Manual" ~ 2006 to 2008**
  - **New project being completed by a team from CSM, with CH2M Hill and the Navy**
  - **The goal is to advance the standard-of-practice and enable more predictable, cost-effective application of ISCO by providing engineering guidance and decision-support tools**

ESTCP — CH2MHILL — NAVFAC Naval Facilities Engineering Command SOUTHERN DIVISION

Task 1. *ISCO Protocol development*	***Task 2.*** *Test Protocol against case studies*	***Task 3.*** *Select DoD sites for Protocol application*	***Task 4.*** *Apply ISCO Protocol to selected DoD sites*	***Task 5.*** *Refine the ISCO Protocol and tools*	***Task 6.*** *Produce an ISCO Technology Practices Manual and FAQ guide*



Closing Remarks

- **Acknowledgements**
  - **CSM team members for their contributions**
    - **Drs. Michelle Crimi, Tissa Illangasekare, Junko Munakata-Marr**
    - **Jeff Heiderscheidt, Pamela Dugan, Ben Petri, Sarah Seitz, Jason Sahl, Shannon Jackson, Kathryn Lowe**
  - **DoD SERDP/ESTCP for CSM research funding**
  - **Dr. John Haselow (Redox Tech LLC) for case study slides**

- **Thank you for listening…**

Questions…?