Mistakes or Learning Experiences?

Evolution of Chlorinated Solvents Remediation in Brownfields

XCG Environmental Engineers & Scientists

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Outline

- Chlorinated Solvents
- Evolution of Remediation Tools
- Case Studies
- Summary of Costs Implications to Projects
- Lessons Learned
- Project Updates

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Chlorinated Solvents

- Widely used chemical compounds containing chlorine
  - Methanes, Ethanes, and Ethenes
    - PCE, TCE, DCE, VC
- Not particularly soluble
  - Solubility > established drinking water standards
- Dense non-aqueous phase liquids (DNAPLs)
  - Tend to sink resulting in complex dispersal patterns

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Chlorinated Solvents

- Most commonly used as cleaning and degreasing agents in industrial and dry cleaning operations
- Widespread groundwater contamination
  - Poor disposal practices, leaking storage containers, uncontrolled discharge

– Colourless, volatile, and serious risk to human health

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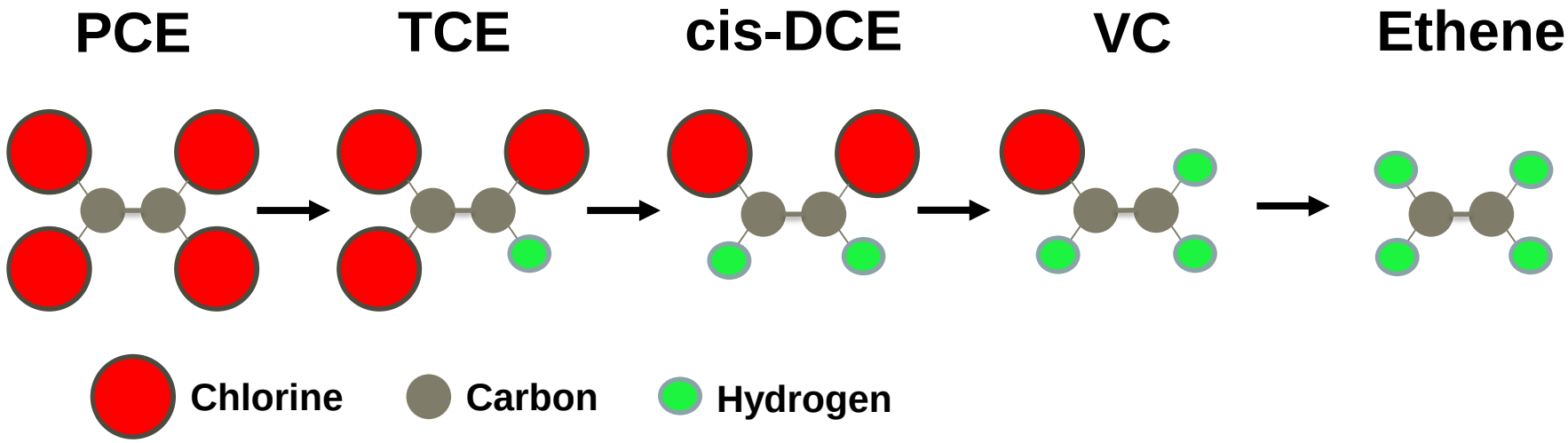
Chlorinated Solvents

Chlorinated Ethenes Degradation



- All chlorinated ethenes are toxic
  - Complete conversion from chlorinated ethenes to benign ethene is critical for detoxification

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Evolution of Remediation

- In-Situ Chemical Oxidation (ISCO)
  - Oxidant injected directly into contaminated medium
  - Introduced into subsurface using direct push method as a water based solution
  - Can be applied under pressure
  - Propagated by water current and gravity
  - Type of contaminant
  - Soil conditions / hydrogeology

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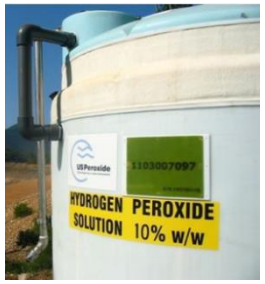
Evolution of Remediation

- Fenton's Reagent
  - Hydrogen peroxide catalyzed with iron
  - Low chemical cost
  - Rapid reaction process
  - Chlorinated and non-chlorinated solvents, PAH, VOC, BTEX
  - Requires low pH, difficult to transport



- Permanganate
  - Sodium or potassium permanganate
  - Treats organic compounds with carbon-carbon double bonds
  - Wider pH range
  - Reacts slowly in subsurface
  - Compound can move further and oxidize more contaminants
  - Cost effective

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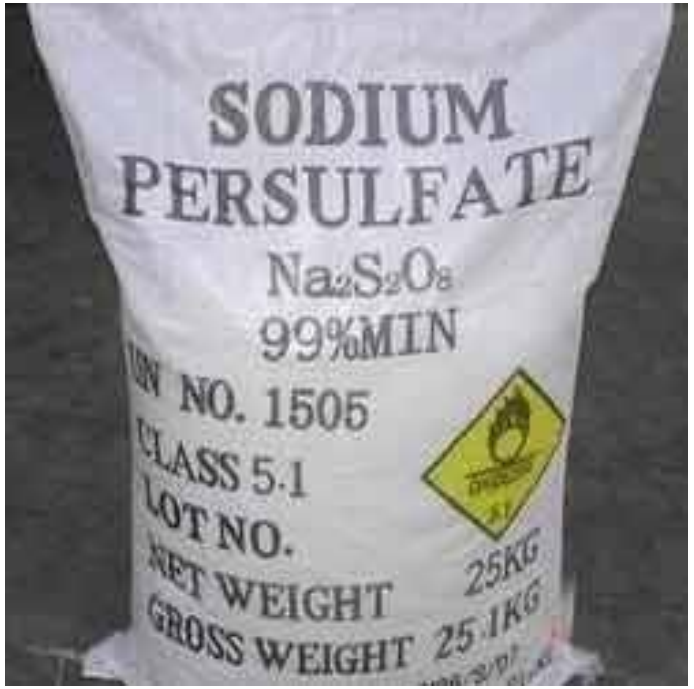
Evolution of Remediation

- Persulfate
  - Development in late 1990s
  - Addresses limitations of previous technologies
  - More stable/does not react quickly
  - Fewer transportation limitations
  - Highest water solubility and leaves least harmful by-products



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Evolution of Remediation

- In-Situ Chemical Reduction(ISCR)
  - Opposite of ISCO
  - Reductant or reductant generating material injected into subsurface
  - Zero valent iron and carbon amendments
  - Anaerobic bioremediation
  - Contaminants converted into less toxic compounds

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- Bioremediation/Bioaugmentation
  - Adding or fostering existing microbial strains capable of degrading contaminants
  - Typically requires carbon-based amendments
  - Most sites lack sufficient organic carbon to promote microbial respiration
  - Dehalococcoides – capable of final stages of chlorinated solvent degradation

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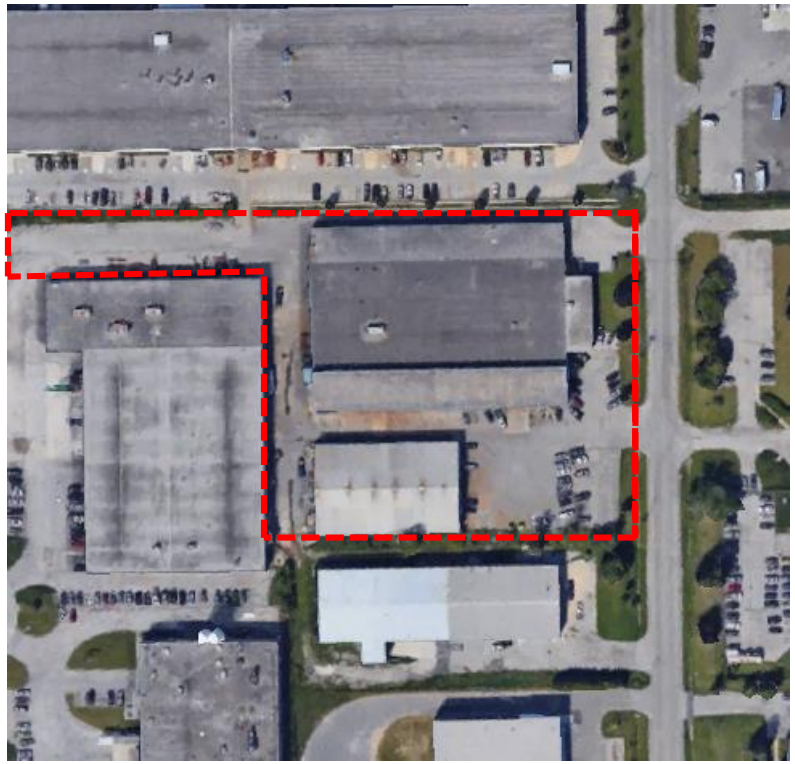
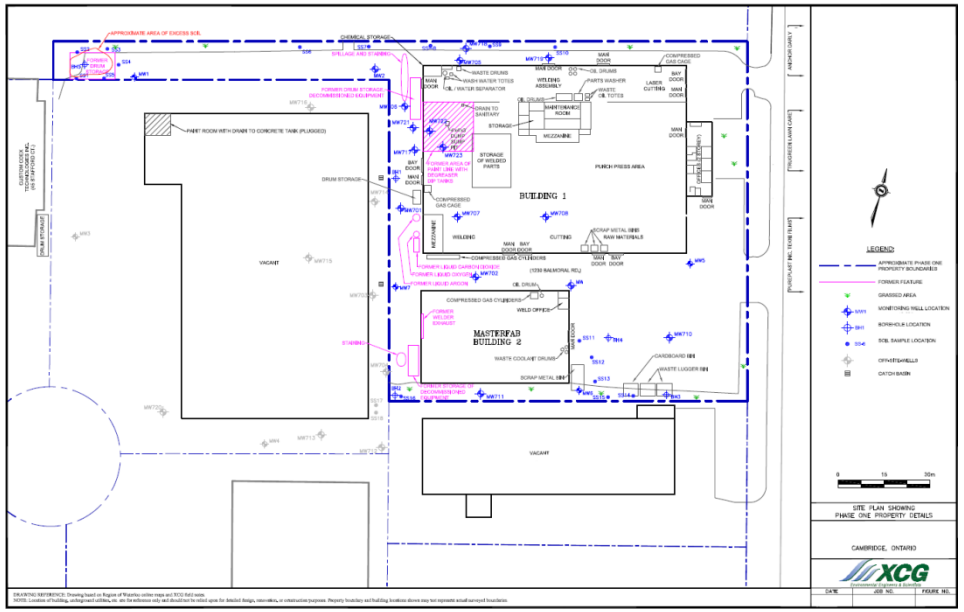
Case Studies

- Cambridge, Ontario



Overview:

- PCE & TCE impacts
- Former paint and degreaser dip tanks
- Fine sand and gravel aquifer
- Water table at ~ 18m
- Direct push injections – low pressure



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Case Studies

- Cambridge, Ontario
  - Oxidation to Reductive Environment
    - Potassium Permanganate injections 2010 - 2013
      - PCE concentrations <100 µg/l
      - High oxidation-reduction potential in groundwater (+200 mV)
    - Bioaugmentation 2015 - present
      - Reverse conditions from highly-oxidizing to reducing (negative ORP values)
      - Initial amendment → Emulsified vegetable oil as food source (carbon donor)
      - Groundwater monitoring
      - Additional amendment → Anaerobic water and dehalococcoides (bioaugmentation cultures) to accelerate remedial process

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Case Studies

- Cambridge, Ontario

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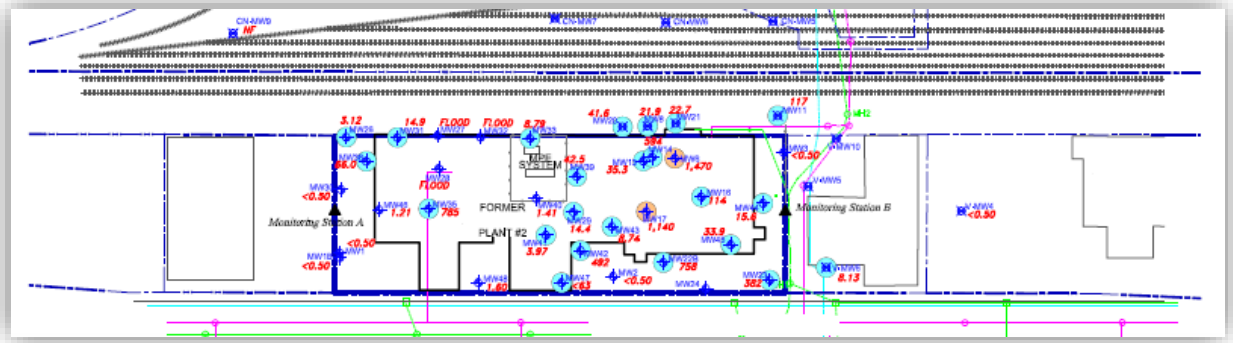
Case Studies

- Kitchener, Ontario



Overview:

- TCE plus degradation products (cis-1,2 DCE, VC) (shallow and intermediate aquifer)
- Former degreasing operations
- Complex Geology - Sand and gravel aquifer
- Shallow and intermediate water bearing units
- Water table at ~6m and 25m
- Dedicated injection wells

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Case Studies

- 2003 – 2008
  - Manual application and pressurized injections of potassium permanganate
- 2009 – Present
  - Reductive approach
    - Ceased injections in mid-2009 to allow ORP to return to reducing conditions
    - Widespread reduction in ORP in 2011, increase in 2012
      - significant rebound of chlorinated solvent concentrations
      - Increased concentration of degradation products suggest anaerobic reductive de-chlorination
    - Initial amendment (Sept 2017) → diluted molasses as food source (carbon donor) and recirculation of amended groundwater

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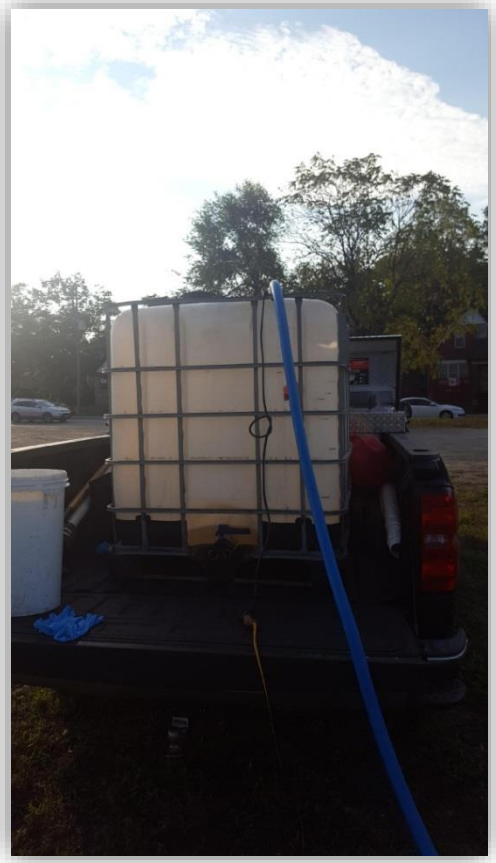
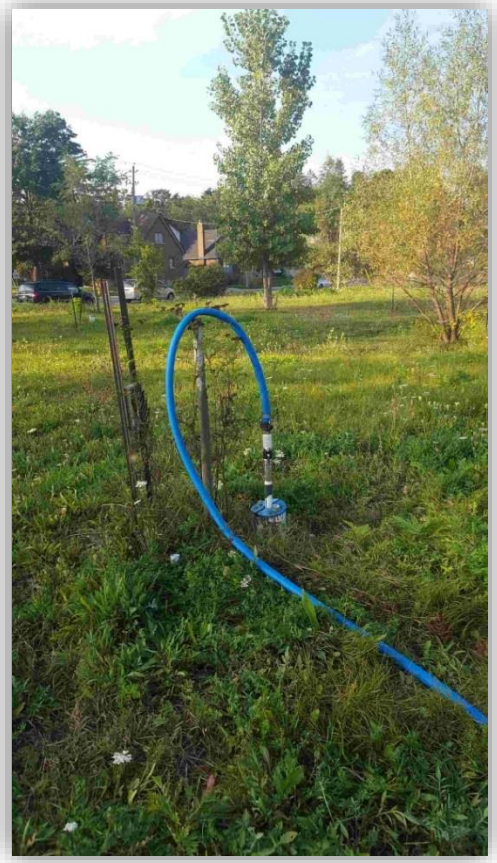
Case Studies

- Kitchener, Ontario





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Summary of Cost Implications to Projects

Cambridge

- Initial Oxidation Method
  - 3 years → ~$235,000
    - Chemical costs ($KMnO_4$)
    - Drilling
    - Pressurized injections (6 events)
    - Groundwater monitoring (before & after)

Kitchener

- Initial Oxidation Method
  - 5 years → ~$231,000
    - Chemical costs ($KMnO_4$)
    - Drilling
    - Pressurized injections (monthly, 4 years)
    - Groundwater monitoring (before & after)

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Summary of Cost Implications to Projects

Cambridge

- Reductive Method (Bioaugmentation)
  - 1 ½ years → ~$150,000
    - Reversing oxidizing conditions (3 years)
    - Chemical costs (EOS-100, KB-1, micro-ZVI)
    - Drilling and injection services (3 events)
    - Groundwater monitoring before, during, and after

Kitchener

- Reductive Method
  - time frame and cost → TBD
    - Naturally reversing oxidizing conditions (7 years)
    - Chemical costs (diluted Molasses)
    - Injection services (1 event)
    - Groundwater monitoring before and after

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Project Updates

- Cambridge
  - Amendments and switch of state has been completed
  - Introduced high-concentration microbes to actively bio-remediate
  - Budget and time-frame met for this process, continue verifying conditions
- Kitchener
  - Observed naturally occurring decrease in ORP
  - Late Sept 2017 commenced with carbon-source amendments
  - Monitor conditions

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Lessons Learned

- There is no “silver-bullet” method
- Methods and products used with high-success in many situations don’t fit all
- Time = money
- Technological advancements continue to become commercially available
- Better understanding, trusted advisors, additional opinions
- Brownfield Redevelopment and time commitments don’t always provide for experimentation, pilot-testing, delays

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Remtech 2017

Questions and Thank you

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