Anaerobic Bioremediation and Aquifer pH

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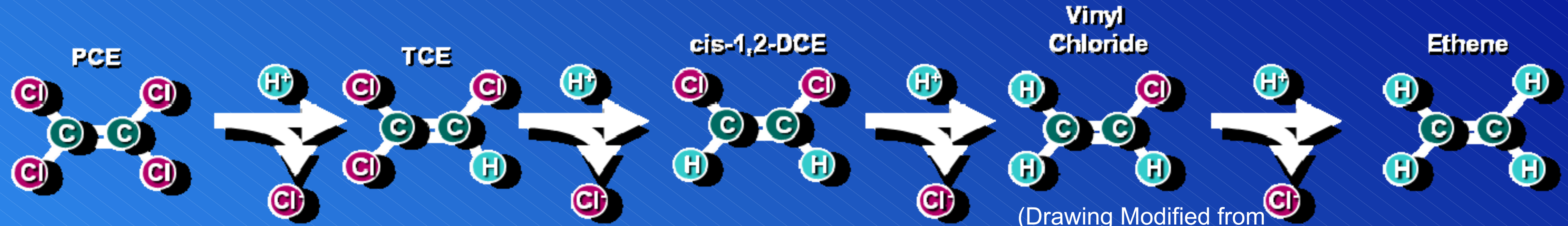
Disclaimer

- R. C. Borden is currently Professor Civil, Construction and Environmental Engineering at NCSU
- NCSU is not sponsoring or endorsing this presentation.

Outline

- Anaerobic Biodegradation and pH
  - Acidity produced during dehalogenation
  - Effect of pH on bacteria
  - Natural aquifer buffering
- Spreadsheet procedure for estimating buffer requirement
- Lessons Learned

Anaerobic Reductive Dechlorination of Chlorinated Ethenes



(Drawing Modified from AFCEE, Technology Transfer Division)

- PCE (C_2Cl_3) → DCE ($C_2H_2Cl_2$)

  $C_2Cl_4 + 2\ H_2 \rightarrow C_2H_2Cl_2 + 2\ HCl$

  $C_2Cl_4 + ½\ CH_3COOH$ (acetate) $+ 2\ H_2O \rightarrow C_2H_2Cl_2 + 2\ HCl + H_2CO_3$

- DCE ($C_2H_2Cl_2$) → Ethene (C_2H_4)

  $C_2H_2Cl_2 + 2\ H_2 \rightarrow C_2H_4 + 2\ HCl$

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Substrate Fermentation

- Lactic Acid ($C_3H_6O_3$)

$C_3H_6O_3 + 2H_2O \rightarrow 2H_2 + CH_3COOH$ (acetate) $+ H_2CO_3$

$CH_3COOH + 4H_2O \rightarrow 4H_2 + 2H_2CO_3$

$C_3H_6O_3 + 6H_2O \rightarrow 6H_2 + 3H_2CO_3$

Carbonic Acid

- Soybean Oil ($C_{56}H_{100}O_6$)

$C_{56}H_{100}O_6 + 50H_2O \rightarrow 44H_2 + 28CH_3COOH$

$28CH_3COOH + 112H_2O \rightarrow 112H_2 + 56H_2CO_3$

$C_{56}H_{100}O_6 + 162H_2O \rightarrow 156H_2 + 56H_2CO_3$

- Equations assume all H_2 eq. are eventually consumed

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Effect of pH on VC Dehalogenation

- VC → ethene
- pH= 8.5
  - Complete inhibition
- pH= 7
  - Optimum
- pH= 6.5
  - Some inhibition
- pH= 6.0
  - Strong inhibition
- pH= 5.5
  - Complete inhibition

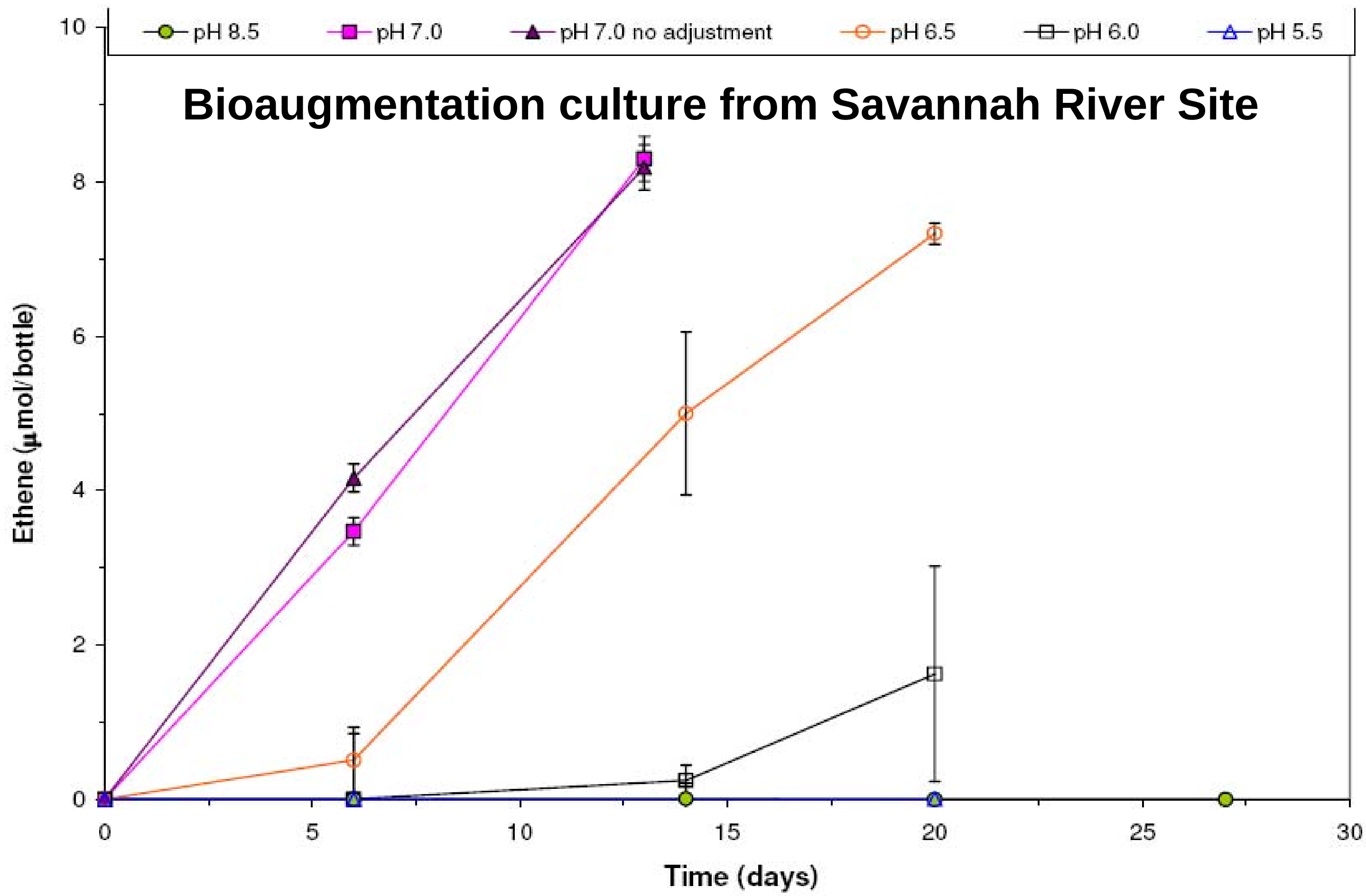

Figure 4.172 Comparison of pH effect on ethene production based on the first PCE and TCE addition at all pH levels (averages of triplicates). Error bars represent ± one standard deviation.

Ashley Eaddy, 2008. *Scale-Up and Characterization of an Enrichment Culture for Bioaugmentation of the P-Area Chlorinated Ethene Plume at the Savannah River Site*. M.S. Thesis, Clemson University, under the direction of David Freedman.

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Microbial Summary

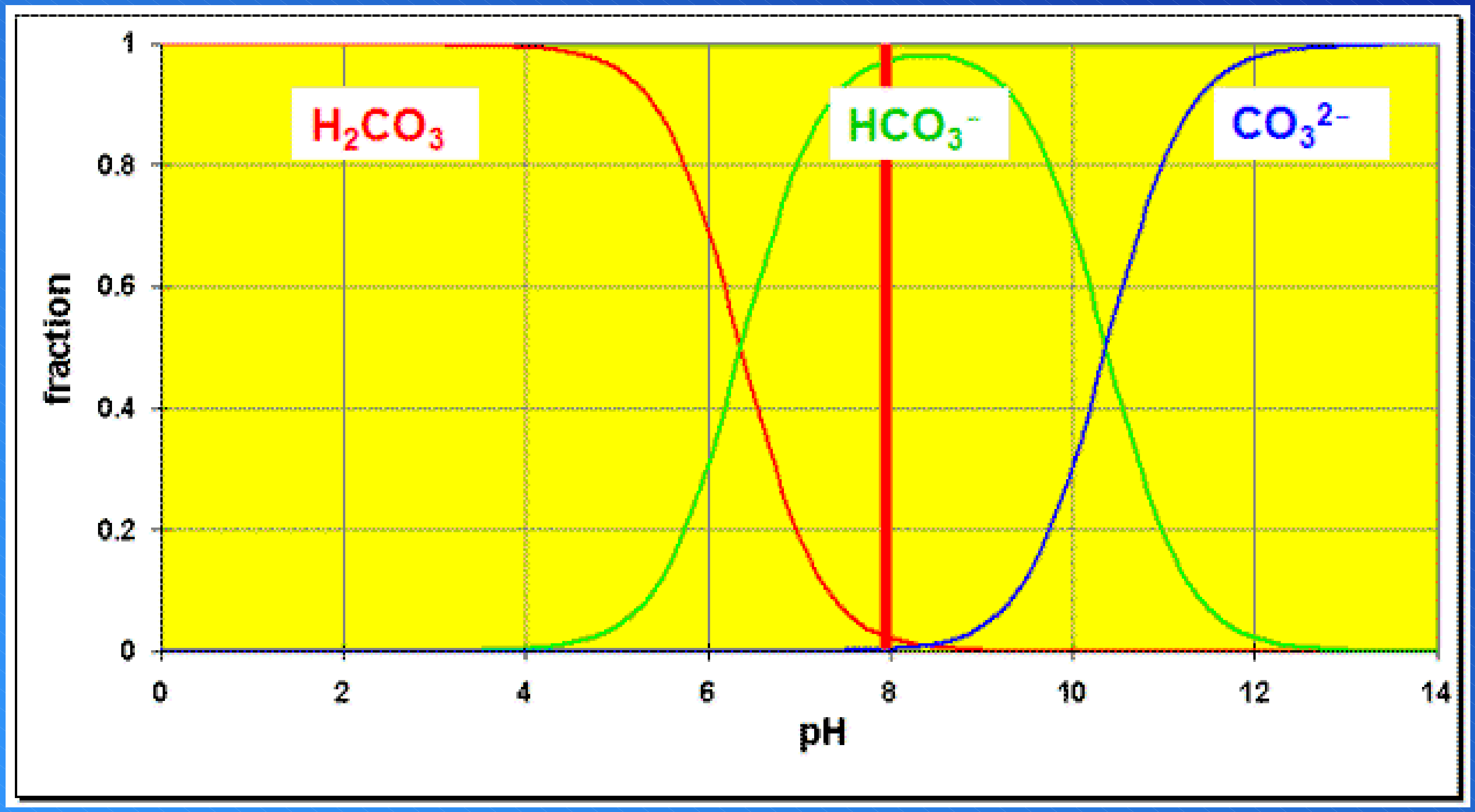
- Fermentation produces lots of VFAs and H_2CO_3 → lower pH
- Reductive dechlorination produces HCl → lower pH
- If pH drops too low
  - VFAs build up → low pH
  - Dechlorination is inhibited
  - VC → ethene is probably most pH sensitive

pH Buffering in Aquifers

- Naturally Occurring Processes
  - Carbonate dissolution
  - Proton exchange with clays
  - NO_3^-, $Fe(OH)_3$, HCO_3^- reduction
- Buffer Addition

Carbonate System and pH

$$CO_2(g) + H_2O \Leftrightarrow H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \Leftrightarrow 2\,H^+ + CO_3^{2-}$$



Dr. Micheal J. Mombourquette, Queens University, Class Notes for Chem 112
www.chem.queensu.ca/people/faculty/mombourquette/FirstYrChem/solubility/index.htm

$NaHCO_3$ Addition

- Open Systems (vadose zone)

  $NaHCO_3 + H^+ \rightarrow Na^+ + H_2CO_3$

  $H_2CO_3 \rightarrow H_2O + CO_2(g)\uparrow$

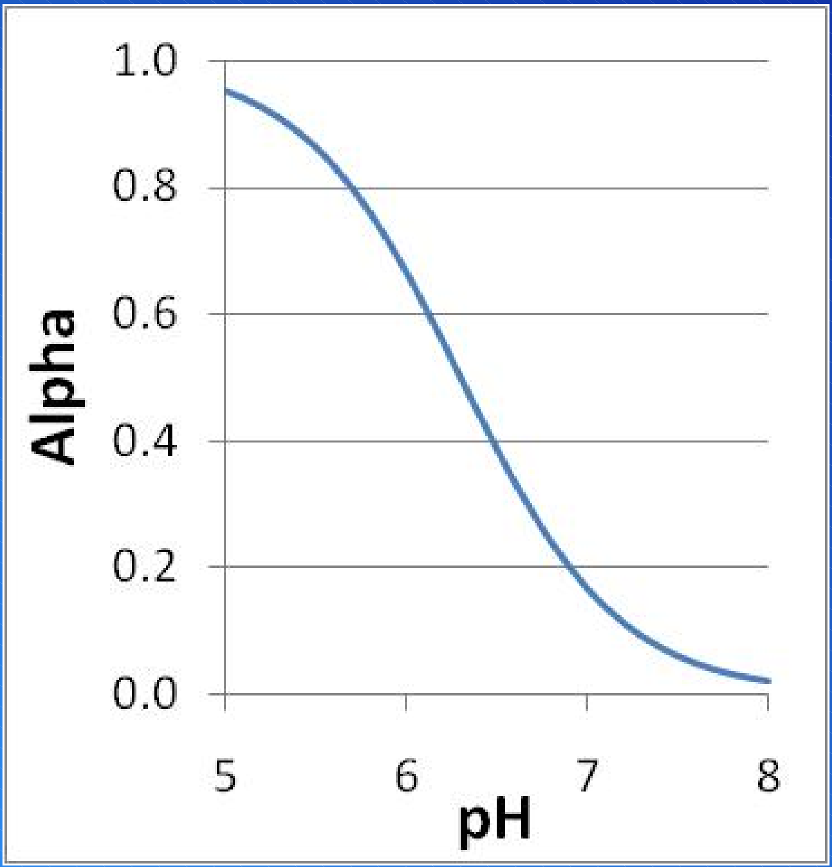
  $NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2(g)\uparrow$

  - Closed Systems (below water table)

    $NaHCO_3 + \alpha H^+ \rightarrow$

    $\rightarrow Na^+ + \alpha H_2CO_3 + (1-\alpha)HCO_3^-$

    α = H^+ consumed per mole $NaHCO_3$



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Carbonate Mineral Buffering

- Carbonate Dissolution

  $CaCO_3(s) + H^+ \Leftrightarrow Ca^{+2} + HCO_3^-$

  Only effective as buffer when $CaCO_3$ dissolves

  $CaCO_3$ is not very soluble

- Carbonic Acid (H_2CO_3)

  $H_2CO_3 + CaCO_3 \Leftrightarrow Ca^{+2} + 2HCO_3^-$

$$K_{eq} = \frac{[Ca^{2+}]\,[HCO_3^-]^2}{[H_2CO_3]}$$

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Cation Exchange on Clay Surfaces

- Proton Exchange

  A^- = exchange site on clay surface, Na^+ = typical cation

  $H^+ + NaA \Leftrightarrow HA + Na^+$

  At low pH, large amounts of H^+ are exchanged on clay surfaces

  Typical Cation Exchange Capacities: 0.05 – 1.0 eq/Kg of clay

- Effect of Carbonic Acid (H_2CO_3) Addition

  $H_2CO_3 + NaA \Leftrightarrow HA + HCO_3^- + Na^+$

  H^+ attachment to clay surfaces will limit pH drop from CO_2 production

- Effect of Sodium Hydroxide (NaOH) Addition

  $NaOH + HA \Leftrightarrow NaA + H_2O$

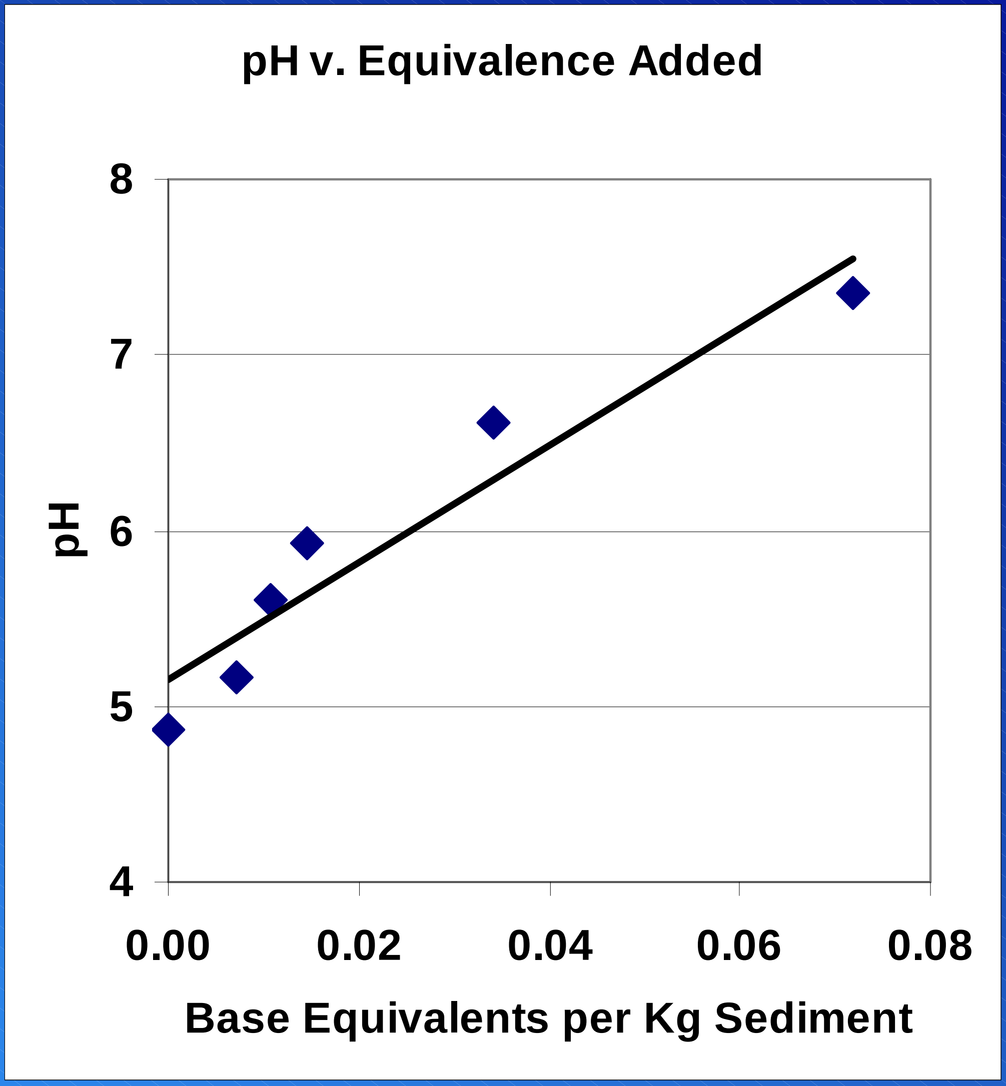
  H^+ release from clay surfaces will limit pH increase from NaOH addition

Acid Demand of Low pH Aquifer

- Aquifer material from Charleston NWS
  - Add varying amounts of base
  - Equilibrate and measure pH

- Base required to increase pH to 6.5
  - Volume
    = 3 m thick x 15 m x 15 m
    = 1.2 x 10^6 Kg
  - Base required (0.04 eq/Kg)
    = 48,000 eq
    = 10,400 Kg $NaHCO_3$
    = 1,900 Kg pure NaOH

Aquifer Material



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Electron Acceptor Reduction

- Aerobic Respiration

  $O_2 + 2\ H_2 \rightarrow 2\ H_2O$

- Nitrate-Reduction

  $NO_3^- + 2\frac{1}{2}\ H_2 \rightarrow 2\ H_2O + \frac{1}{2}\ N_2 + OH^-$

- Iron-Reduction

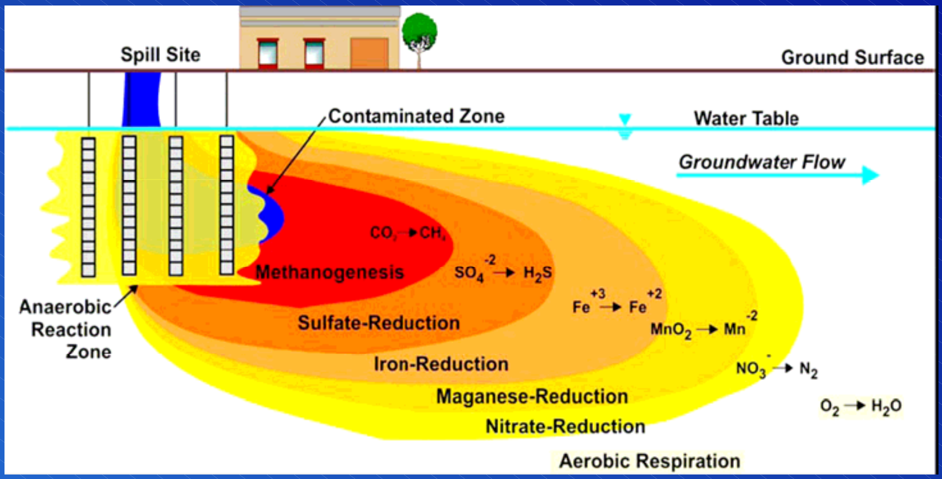
  $Fe(OH)_3 + \frac{1}{2}\ H_2 \rightarrow Fe^{2+} + H_2O + 2\ OH^-$

- Sulfate-Reduction

  $SO_4^{2-} + 4\ H_2 + Fe^{2+} \rightarrow Fe^{2+} + H_2S + 2\ H_2O + 2\ OH^- \rightarrow FeS_2 + 4\ H_2O$

- Methanogenesis

  $HCO_3^- + 4\ H_2 \rightarrow CH_4 + 2\ H_2O + OH^-$



Source: AFCEE, Principles and Practices of Enhanced Anaerobic Bioremediation of Chlorinated Solvents, August 2004

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Geochemistry Summary

- Carbonate Dissolution
  - $CaCO_3$ must dissolve to be effective
  - Moderately effective pH buffer
- Proton Exchange on Clays
  - Strong buffer in many aquifers
  - Will poise pH close to ambient
  - Lots of base required to increase pH above ambient
- Reduction of NO_3^-, $Fe(OH)_3$, and HCO_3^-
  - Releases OH^- → higher pH

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How Much Base is Needed?

- Geochemical Modeling
  - PHREEQC

- Stoichiometric (Spreadsheet) Procedure
  - Acidity of soil and groundwater
    - Depends on background pH and CEC of soil
  - HCl produced from dechlorination
  - H_2CO_3 produced from substrate oxidation
  - Steady-state pool level of acetate
  - OH^- released from NO_3^-, $Fe(OH)_3$ and HCO_3^- reduction

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Example Site

➢ Treatment Conditions

- Duration = 3 years
- Volume = 3 m thick x 15 m x 15 m (1.2 x 10^6 Kg)
- GW velocity = 30 m/yr → 1.2 x 10^6 L of water / 3 yr
- Target pH = initial pH = 6.5

➢ Changes in Soil Chemistry

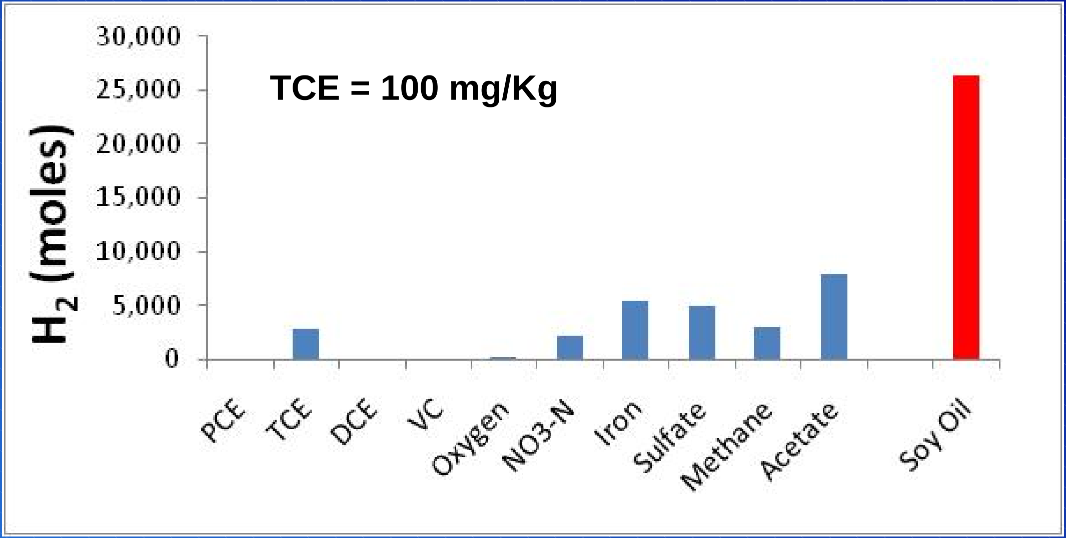
- TCE: 100 mg/Kg → 0 mg/Kg
- Fe 500 mg/kg Fe(III) → Fe(II)

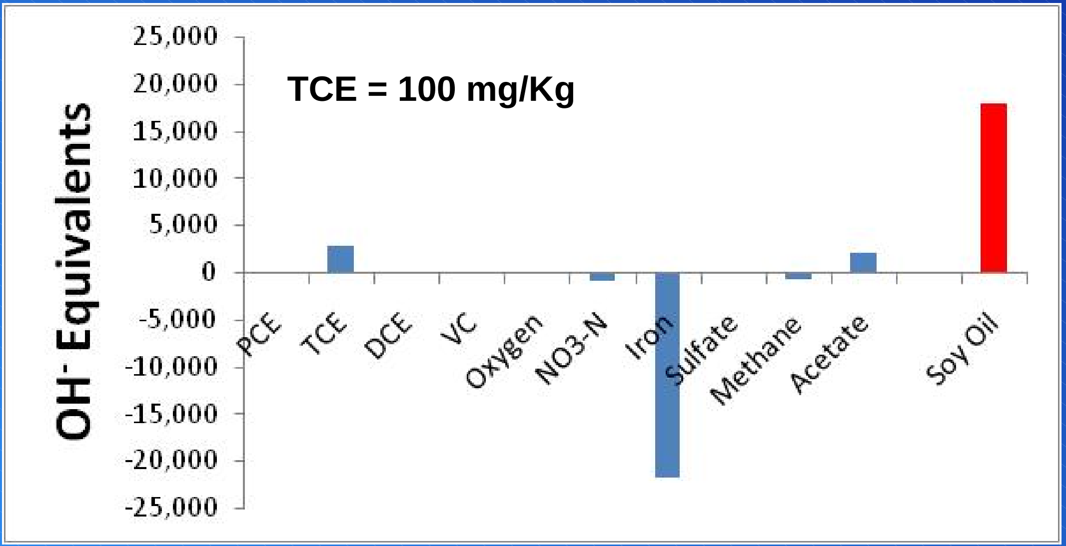
➢ Changes in Water Chemistry

- O_2: 3 → 0 mg/L
- NO_3-N: 10 mg/L → 0 mg/L
- SO_4: 100 mg/L → 0 mg/L
- Acetate: 0 mg/L → 100 mg/L
- CH_4: 0 mg/L → 10 mg/L

H_2 and OH^- Required

- For moderate TCE Conc. (~ 100 mg/Kg)
  - H_2 demand dominated by background demand
  - Large amounts of OH^- released by Fe(III) reduction
- No additional buffer required





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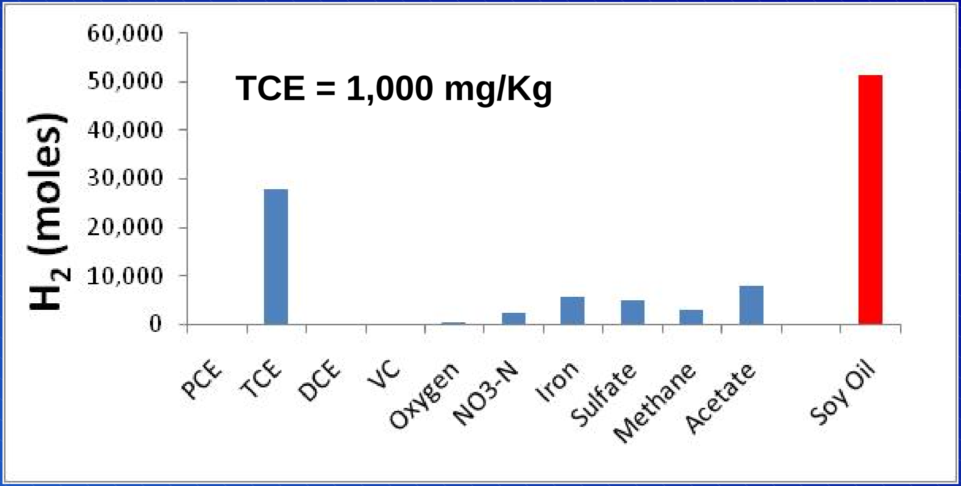
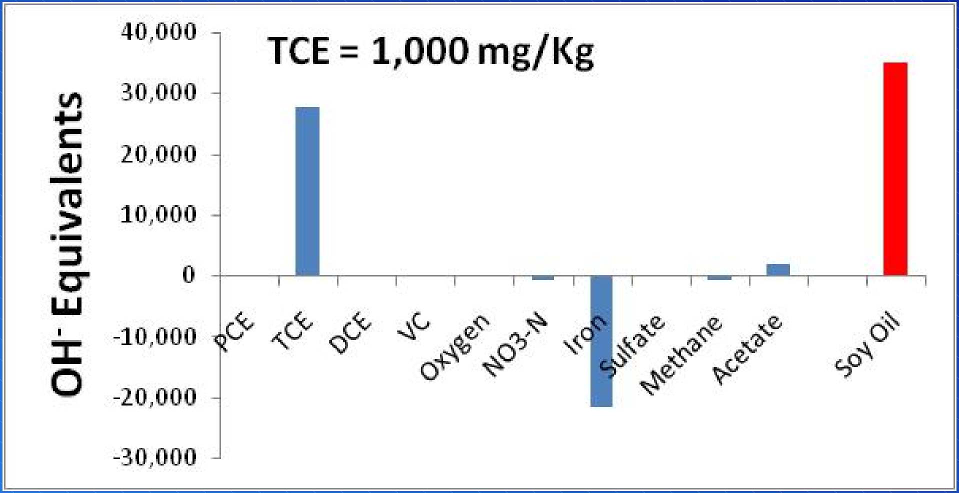
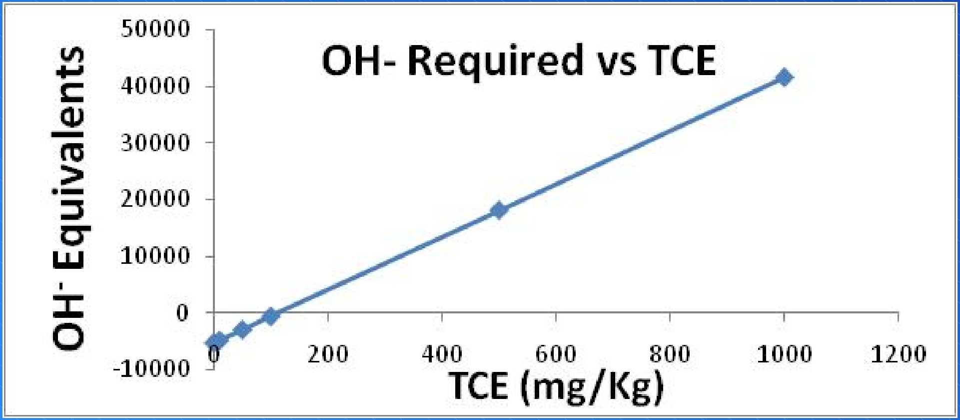
H_2 and OH^- Required

- For high TCE Concentrations (~ 1000 mg/Kg)
  - Primary H_2 demand → TCE
  - Primary OH^- demand
    - HCL from TCE
    - H_2CO_3 from soy oil
  - OH^- released by Fe(III) reduction not sufficient to buffer pH
  - External buffer required







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Substrate and Buffer Requirements

- Moderate TCE (100 mg/Kg)
  - H_2 demand = 26,300 moles H_2 → 147 Kg soy oil
  - No buffer required (assuming 0.5 g/Kg Fe(III) reduced)

- High TCE (1000 mg/Kg)
  - H_2 demand = 51,300 moles H_2 → 280 Kg soy oil
  - Buffer required (assuming 0.5 g/Kg Fe(III) reduced)
    → 41,600 moles OH^-
    → 9,000 Kg $NaHCO_3$
    → 2,100 mg/L Na in groundwater

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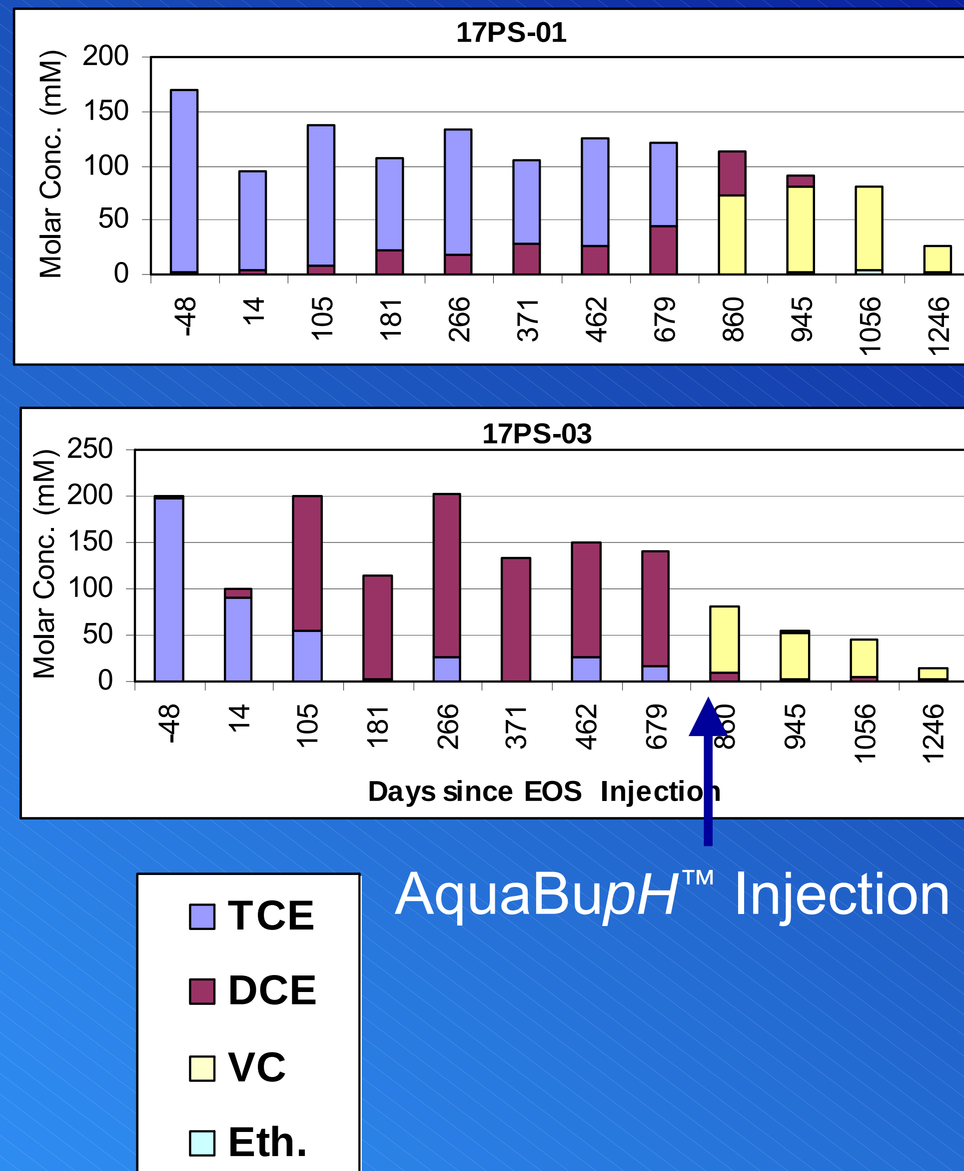
Charleston NWS Pilot Test Effect of Buffering on VOCs

- pH increase stimulated biodegradation
- Rapid conversion of
  - TCE → *cis*-DCE
  - *cis*-DCE → VC → ethene
- TCE is BDL
- 50 – 200 µg/L ethene produced
- DHC increases from BDL to 10^6 cells/mL



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Lessons Learned

- H_2CO_3 and HCl will be produced during anaerobic bioremediation
- $Fe(OH)_3$ reduction (when significant) can consume significant amounts of H^+, limiting pH decline
- For low – moderate CVOC levels
  → buffer addition may not be required
- For high CVOC levels
  → large amounts of buffer may be required
- To increase ambient pH of aquifer,
  → large amounts of buffer may be required
- If ambient pH < 6.5, measure
  - Base required to increase soil pH
  - Groundwater acidity

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North Carolina State University
Water Resources & Environmental Engineering
Graduate Research Symposium

March 5, 2010 (12:00 to 5:30)

Sustainability

Solid Waste Management

Air Pollution & Risk Analysis

Water & Wastewater Engineering

Groundwater Remediation

Water Resources

Coastal Engineering

Hydrologic Modeling

Environmental Management & Systems Analysis

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