Reductive Bio-Modification of Sediment Contaminants: An *In Situ*, Molecular Hydrogen Formation Approach.

NATO/CCMS Pilot Study
Prevention and Remediation In Selected Industrial Sectors: Sediments. Ljubljana, Slovenia. June 17-22, 2007

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East Central University

East Central University
Ada, Oklahoma
~4000 Students

Ada is Home to the US-EPAs Ground Water Research Center

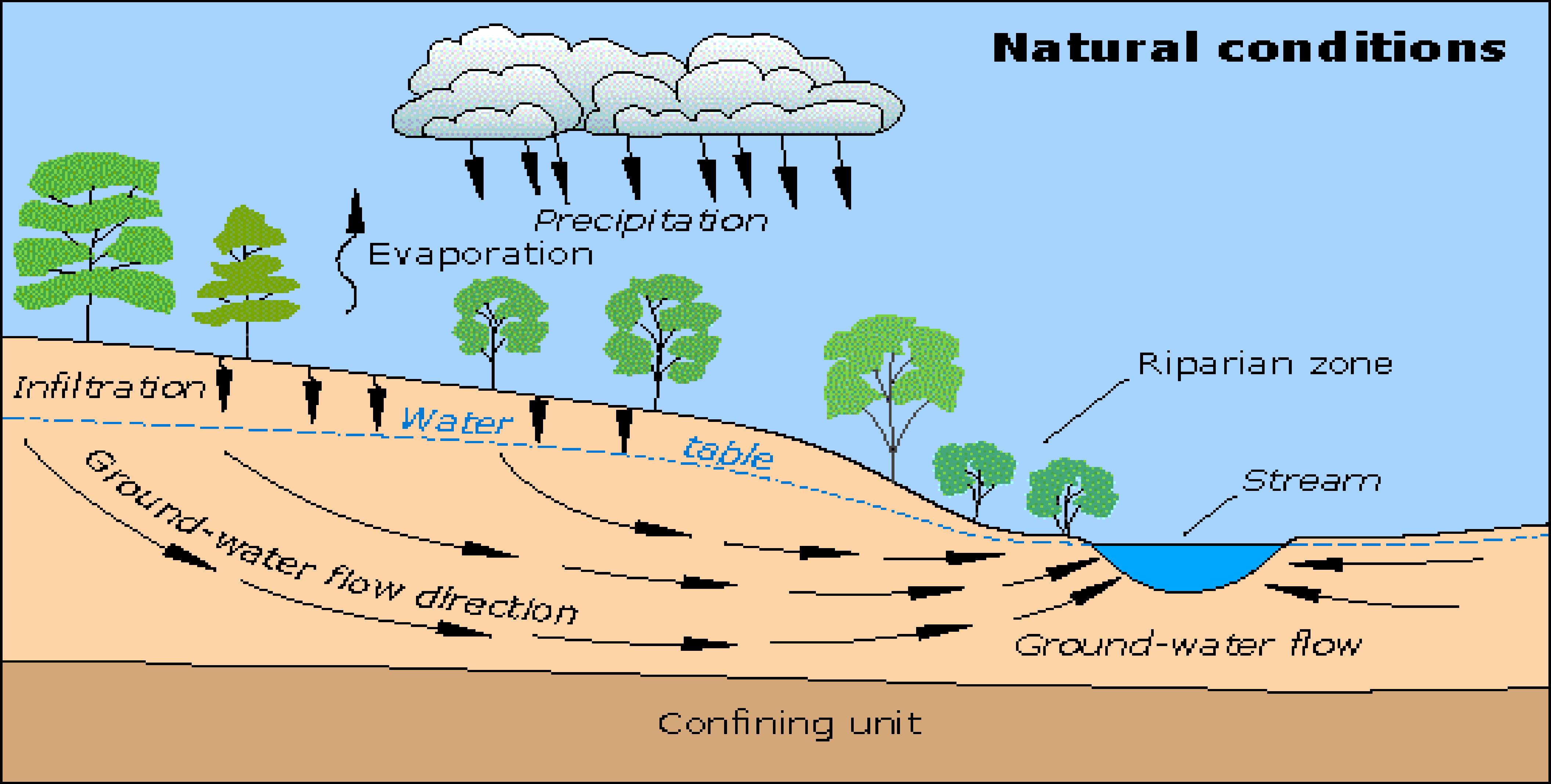
Assumption: *Dredging may be necessary but it is not desirable.*

- **Efficacy Questions**
- **Ecological Impacts**
- **Sustainability Questions**

Can we treat *in situ* effectively?

Sediments: System Management Factors

- **Dynamic System**
  - **Δ Solution Transport Rate**
  - **Δ Particulate Transport Rate**
    - ***Contaminant Transport Rate is a Function of Both***
  - ***Prediction of Contaminant Distribution Difficult***
  - ***Control of Treatment/Residence Time Difficult***
- **Mixture of Contaminants**
  - **Sink for Multiple Sources**
  - **Point and Non-Point → linear source**
- **Concentration vs Mass Loading (mass flux)**
  - ***Descrete Receptor-More likely than most media***
  - **Do we manage for the media or the receptor?**



Redox gradients, flood plain, reversing hydraulic gradient, velocity profiles, baseflow, storm flow

Is *in situ* Biotreatment an Option?

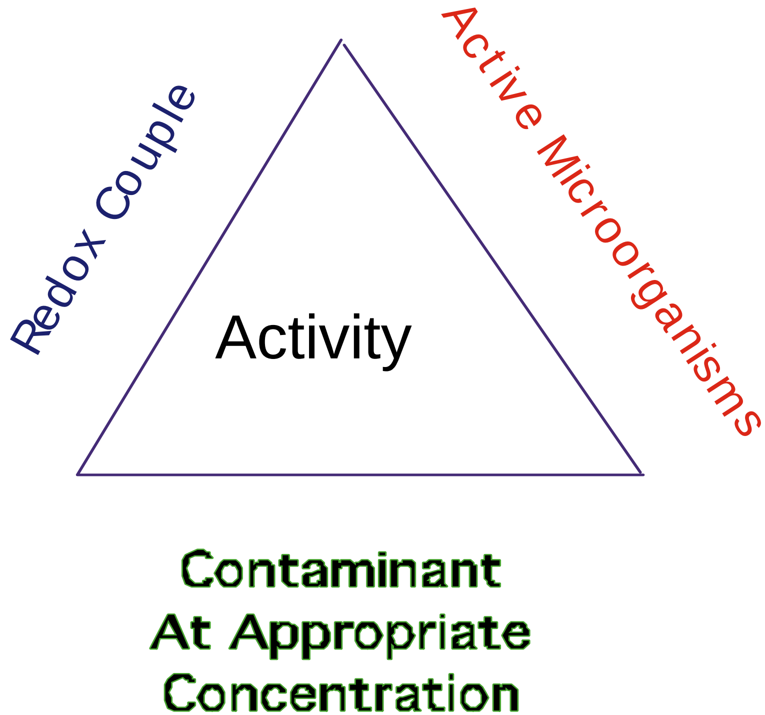
Bioaugmentation: *Addition of microbes*

- Sediments contain significant native populations
- Challenges: GW-transport, Sediment-dispersal

Biostimulation: *Addition of nutrients, electron donor/acceptors*

- Relatively organic rich
- Often oxygen limited
- Dispersal issue

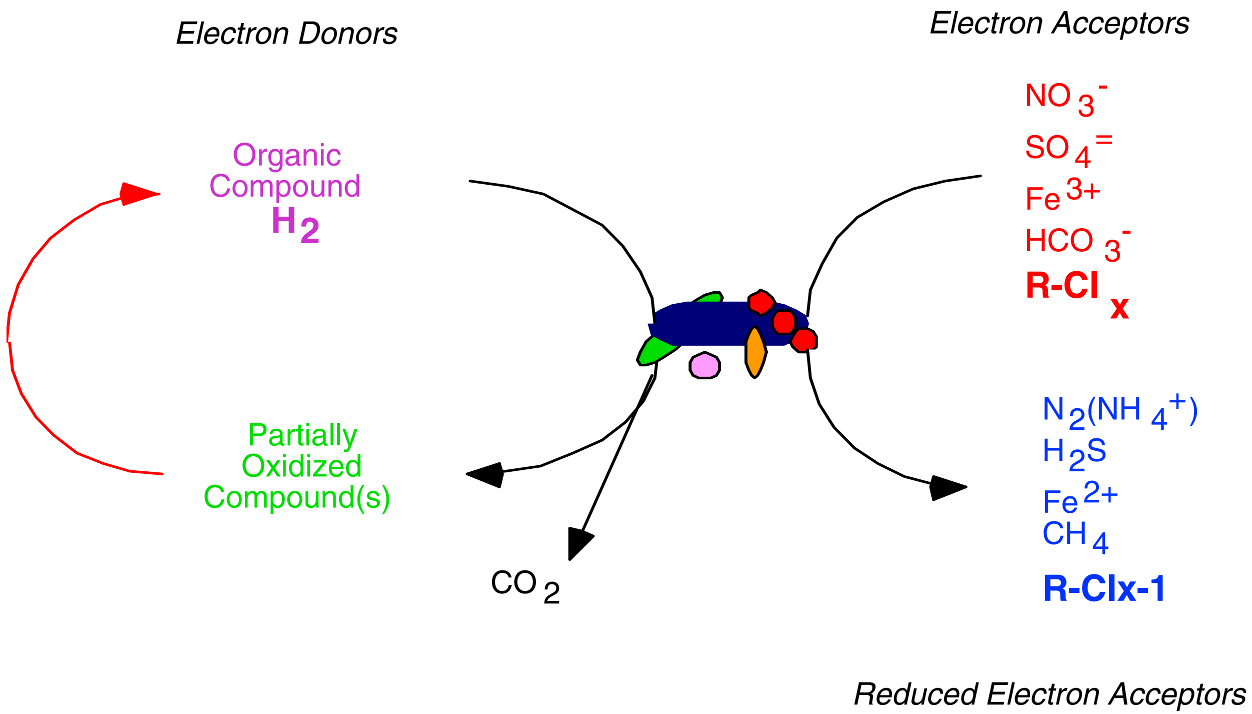
Biodegradation Triangle



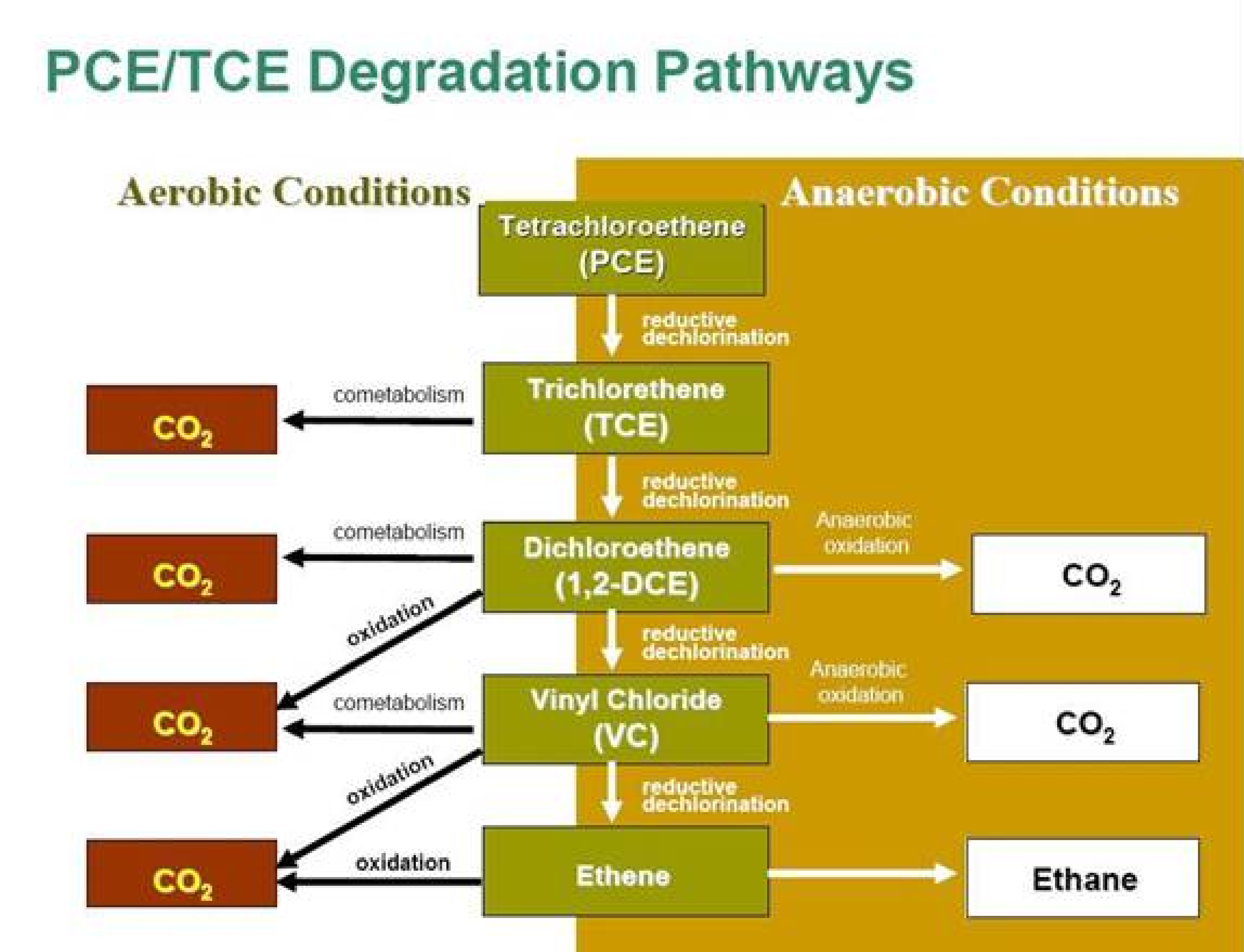
Reductive Bio-transformations

- Oxygen Limited Conditions
- Fermentation
  - substrate is both oxidized and reduced, (Ethanol, CO_2)
- Anaerobic Oxidation
  - Discrete electron donor and acceptor (not O_2)
- Hydrogen is the Energy Currency in Anaerobic Consortial Systems
- Applicable to a Wide Variety of Chlorinated Organics (PCBs, PCE, PCP, HCB, CT) , inorganics (Nitrate) and metals (Cr^{VI}).

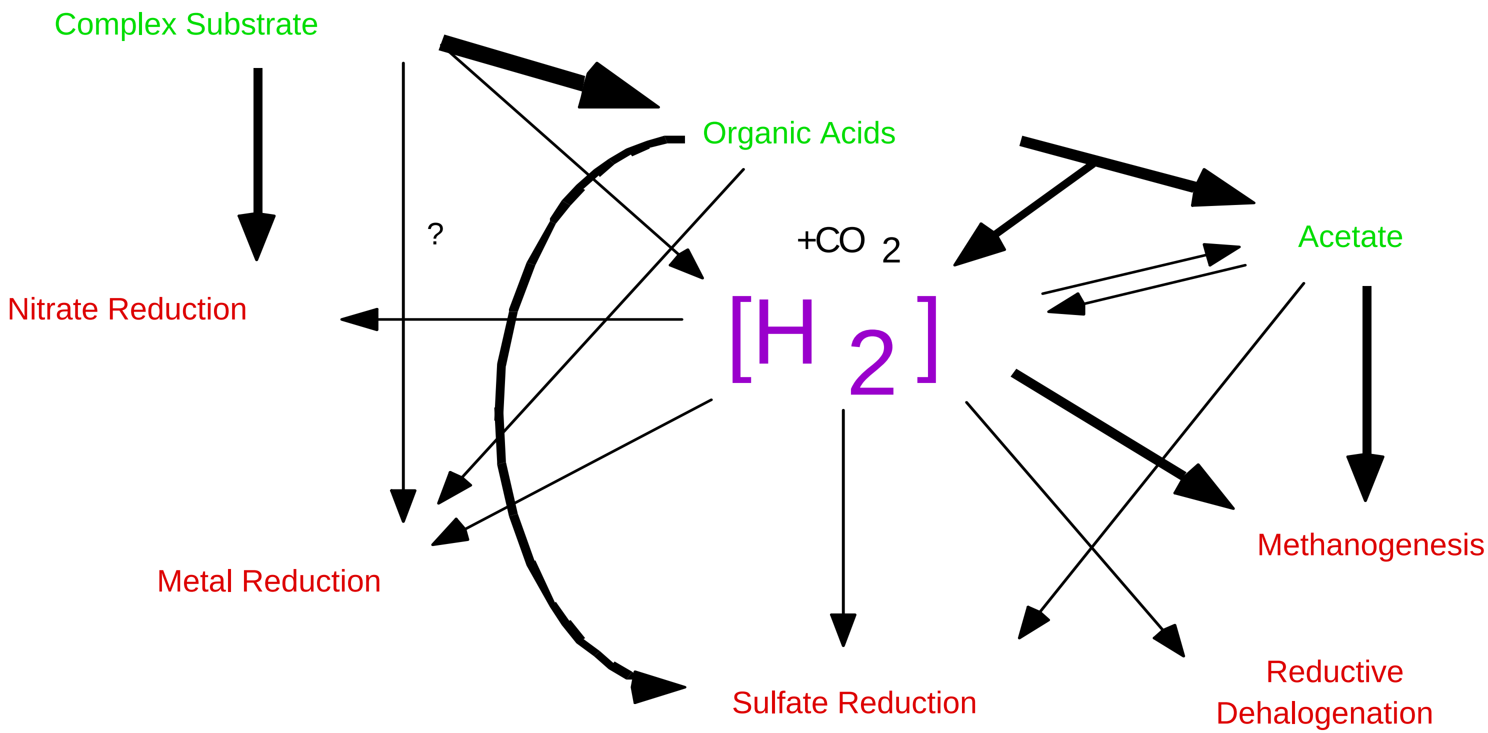
ANAEROBIC OXIDATION-REDUCTION



SEWELL, '95


PCE/TCE Degradation Pathways
Aerobic Conditions
Anaerobic Conditions
Tetrachloroethene (PCE)
reductive dechlorination
Trichlorethene (TCE)
cometabolism
CO_2
reductive dechlorination
Dichloroethene (1,2-DCE)
cometabolism
CO_2
Anaerobic oxidation
CO_2
oxidation
reductive dechlorination
Vinyl Chloride (VC)
cometabolism
CO_2
Anaerobic oxidation
CO_2
oxidation
reductive dechlorination
Ethene
oxidation
CO_2
Ethane

Reducing Equivalent Flow in Anaerobic Biotransformations



How do We Stimulate Reductive Biotransformations?

- Hydrogen limiting bio-reactant
- Metabolic Formation
  - Complex substrate addition (bio-stimulation)
  - HRC
- Direct Injection
  - Low solubility
  - Hazardous

The story of Postgate's nail

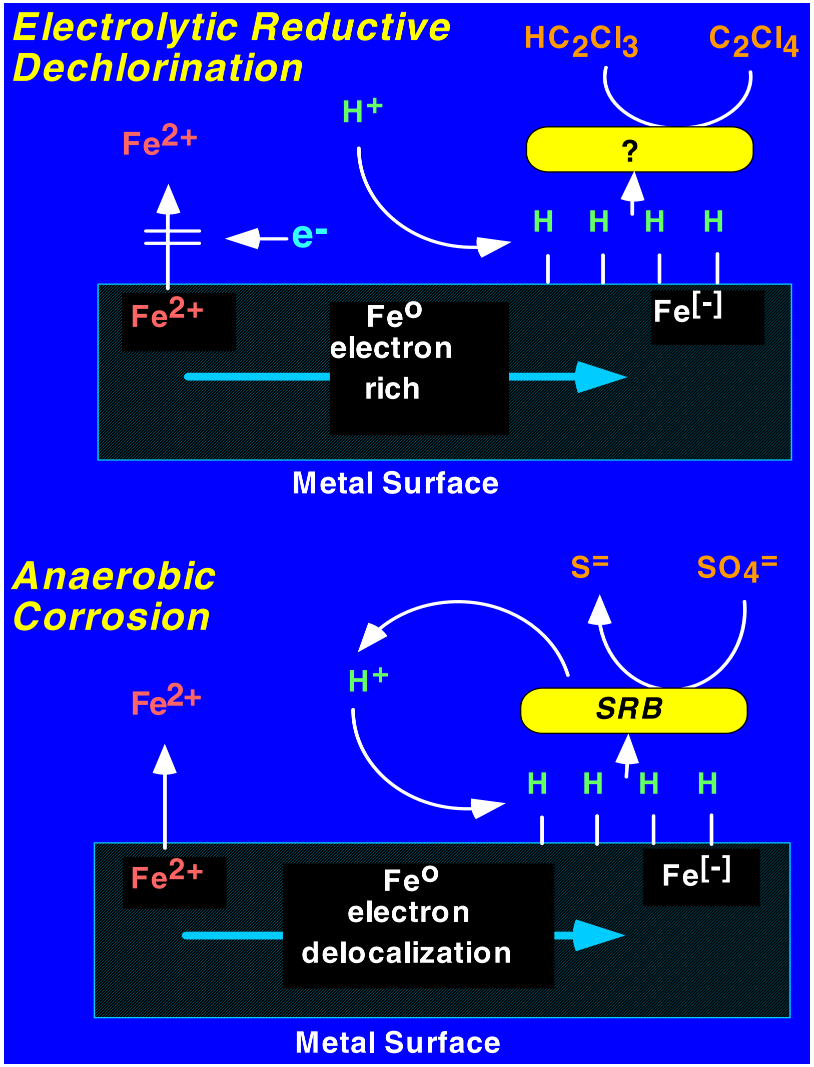


Figure 2. Bottom: Microbial consortia operating at the surface of corroding iron, transferring electrons from removed hydrogen, and reducing sulfate. Top: Microbial consortia operating at the surface of metal that is electrolytically generating hydrogen and transferring electrons to chlorinated hydrocarbons.

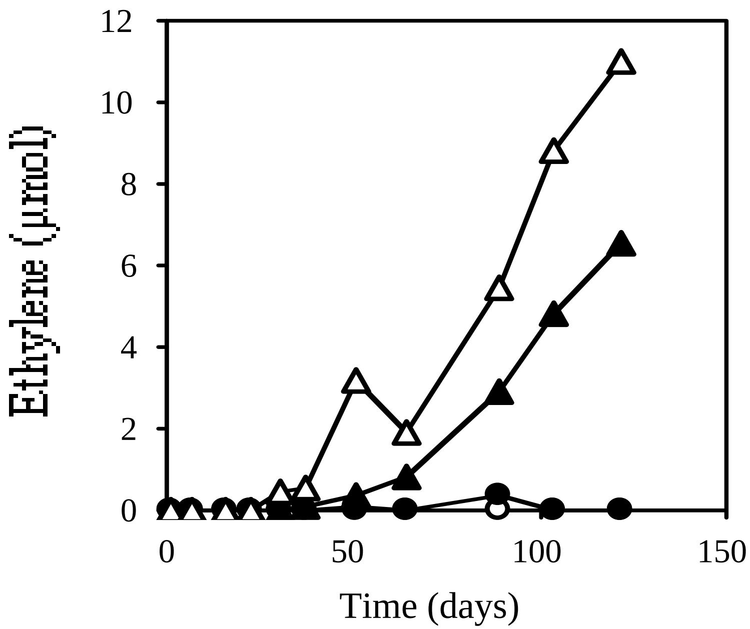
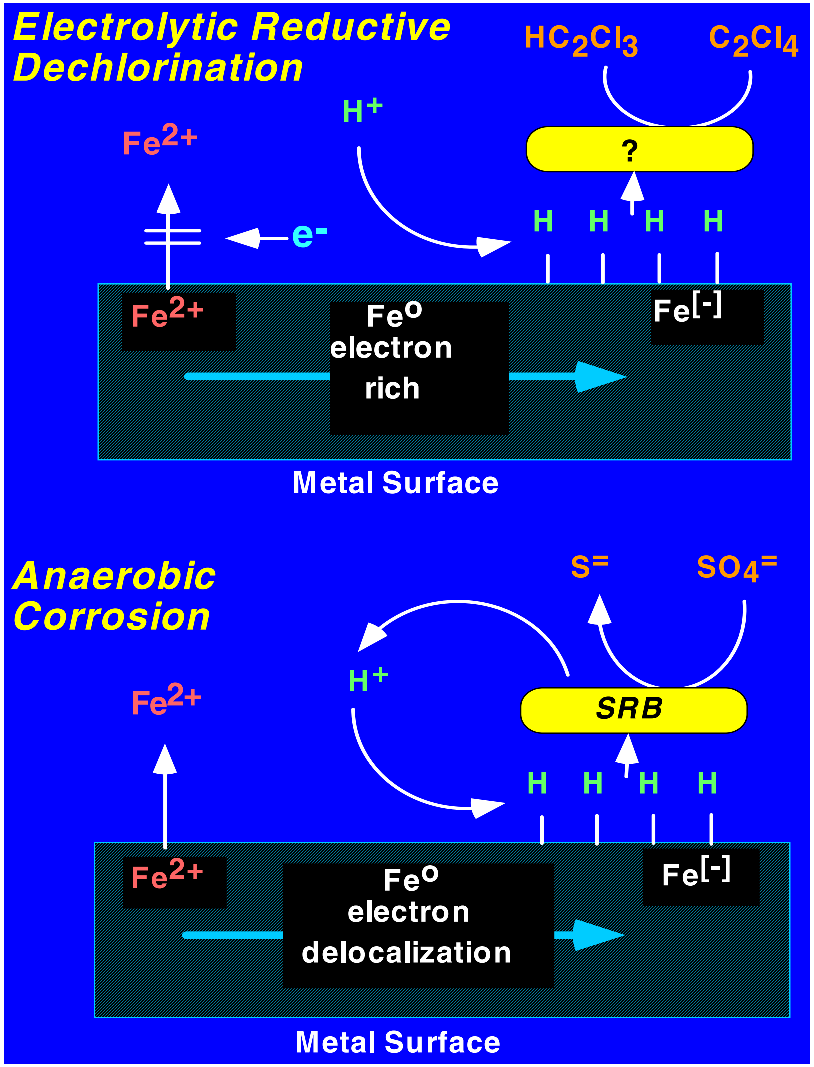


FIGURE 1. Environmentally benign products production from PCE degradation and concurrent methane formation with cathodic hydrogen as electron donor (O control; ● enrichment only; s iron B (5 g/L) only; ∆ enrichment + iron B (5 g/L))

The story of Postgate's nail



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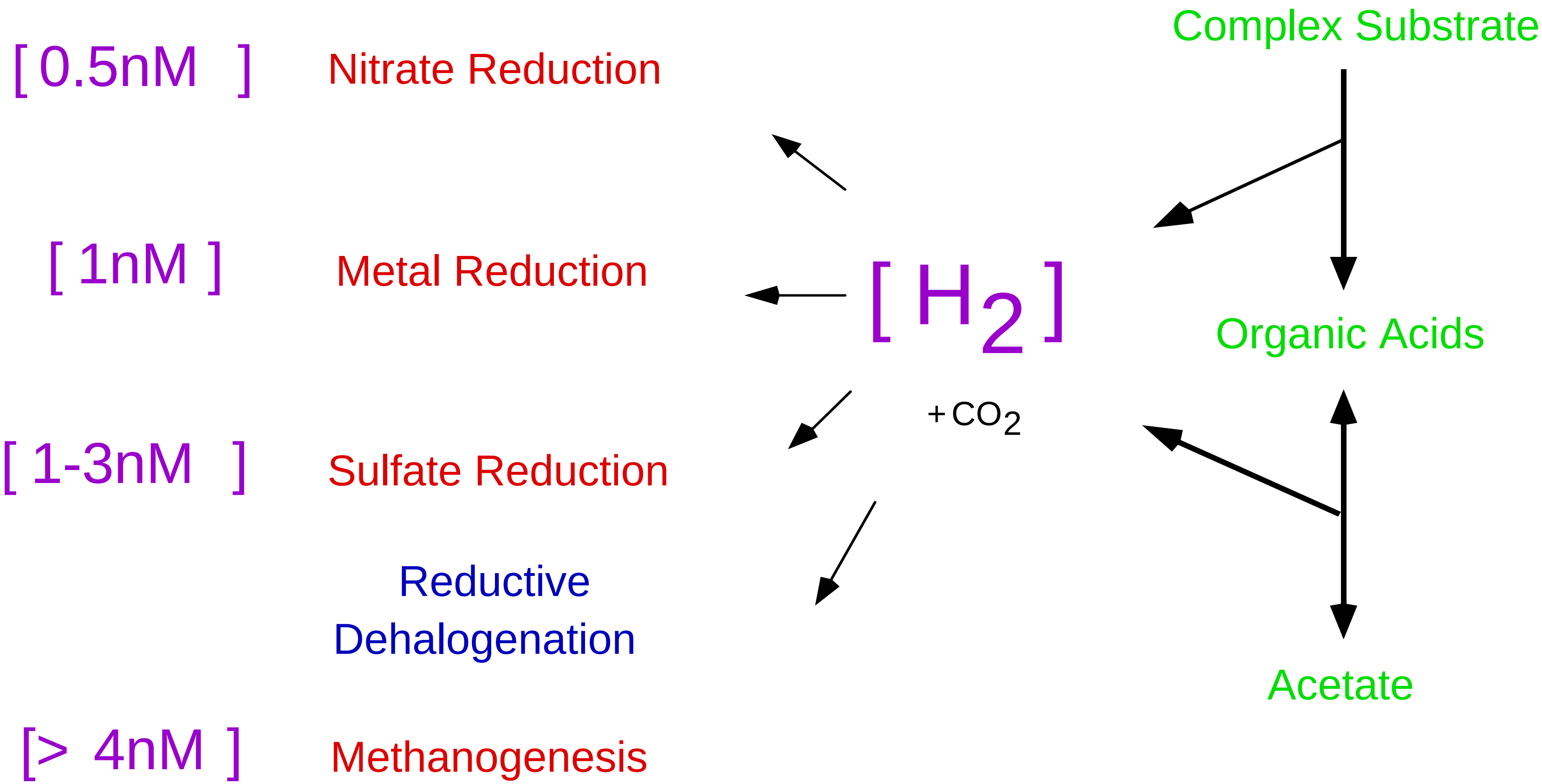
Reducing Equivalent Flow in Anaerobic Biotransformations



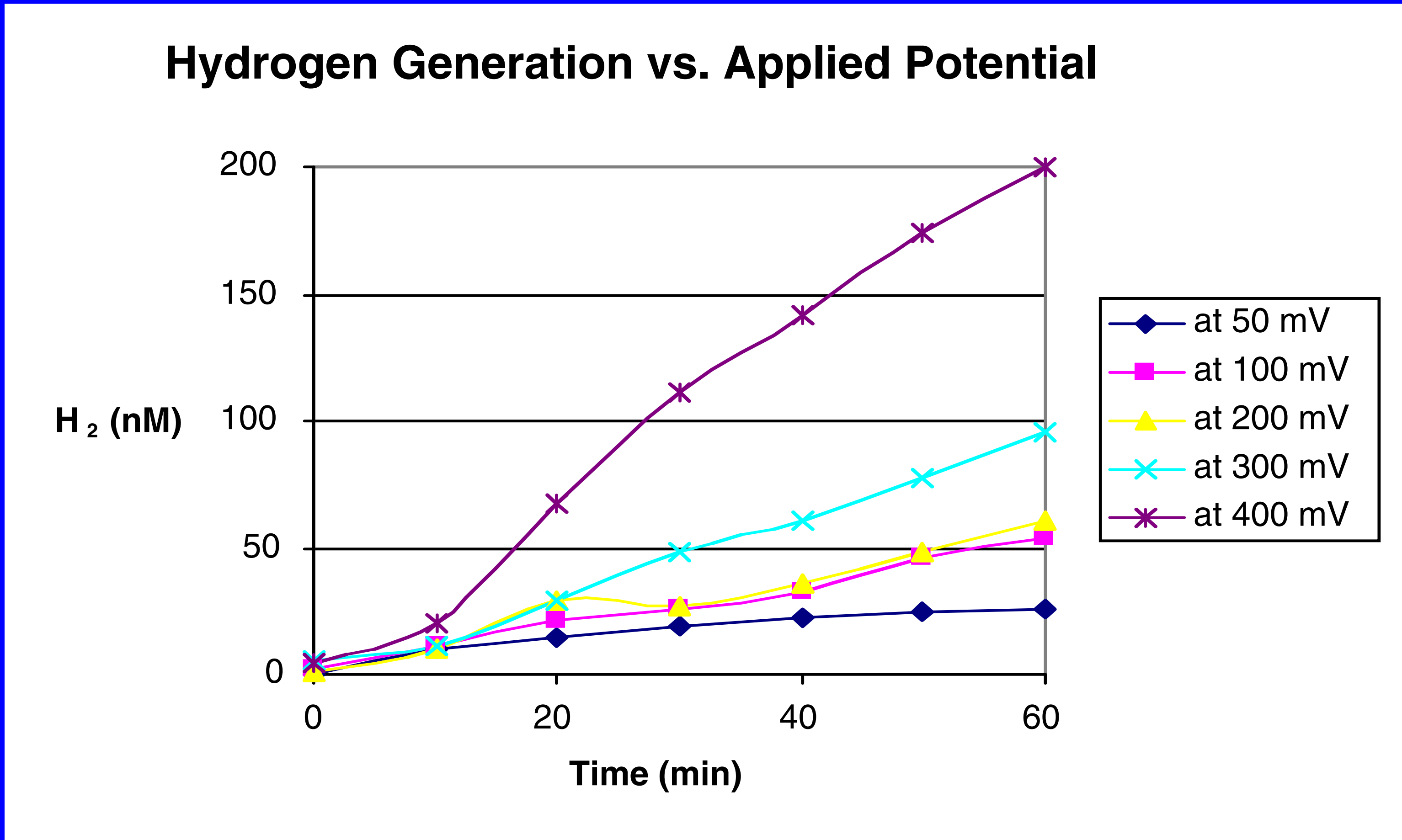
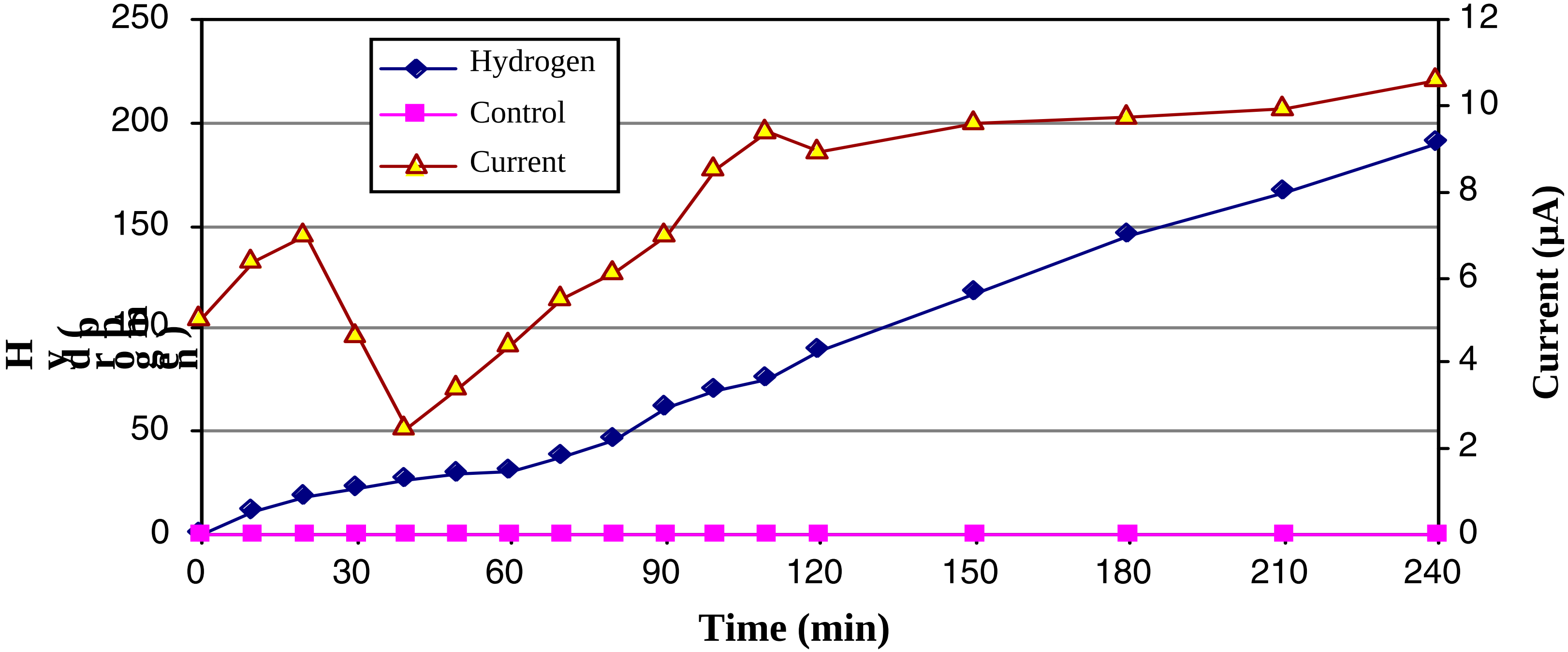


Figure 7. Hydrogen production versus applied potential.

$2H^+$ (aq) + $2e^-$ (induced potential) -> $2H^\cdot$ (surface) <-> H_2 (aq)

(Not electrolysis, proton reduction)



Hydrogen Evolution

Experimental conditions: 150 mL water, Na_2SO_4 3500mg/L, headspace 150mL, mild steel electrode, 0.18 g each, diameter 0.83mm, 40mm long, distance between cathode and anode 40mm, voltage 0.03 V

Figure 6. Quantification of evolved hydrogen at a constant applied potential of 0.03V

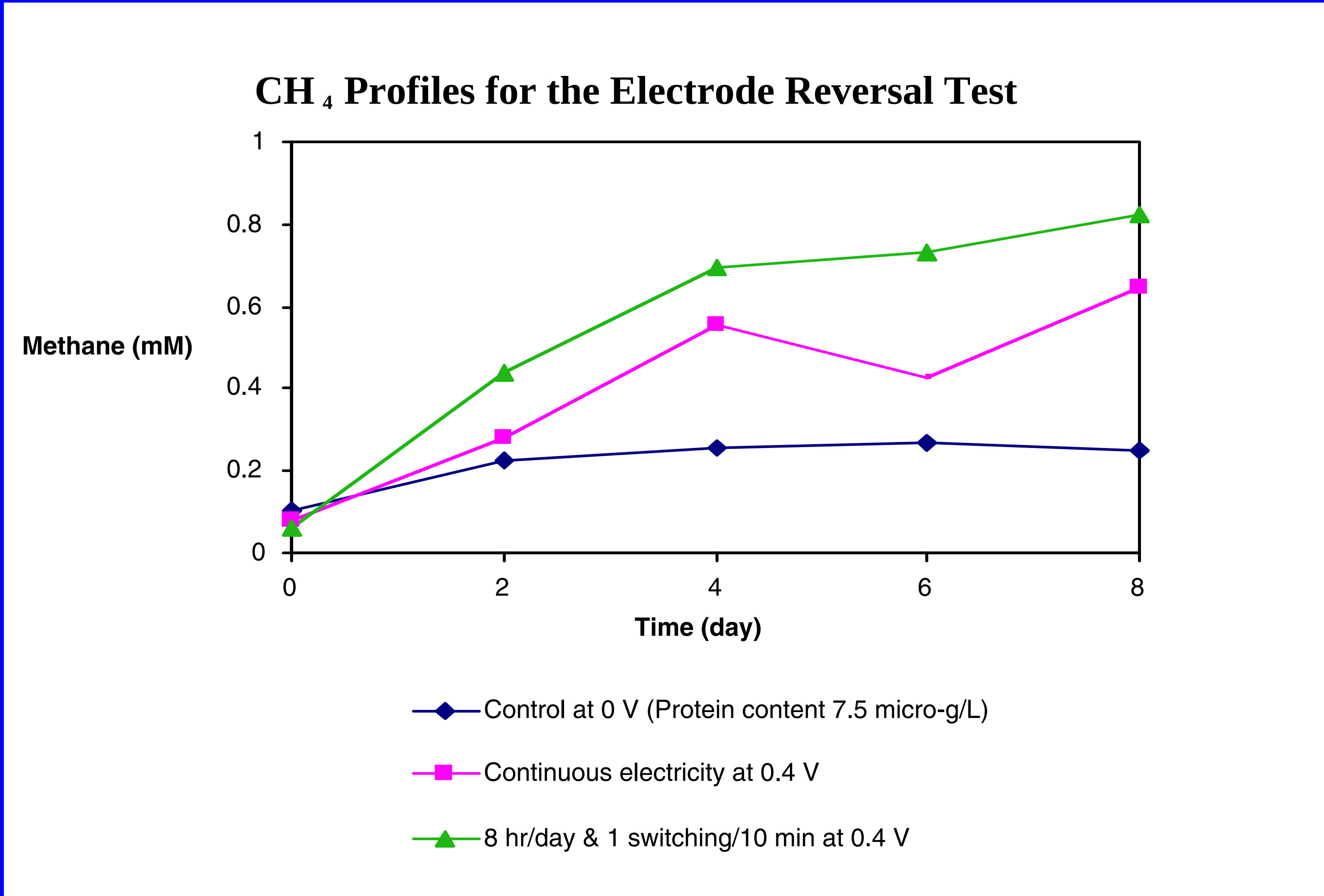
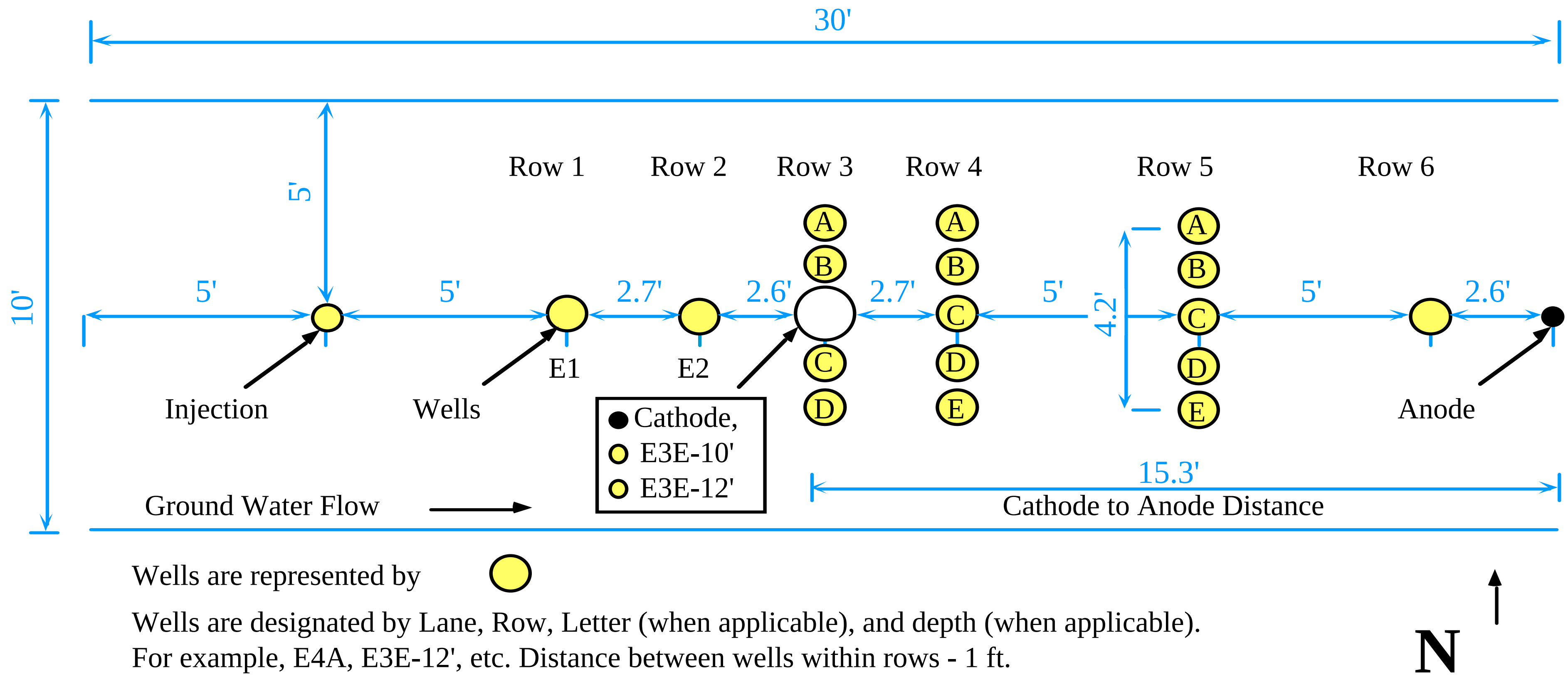


Figure 14. Methane concentration profiles for the systems tested at 0 V, 0.4 V continuous, and 0.4 V with reversal.



Wells are designated by Lane, Row, Letter (when applicable), and depth (when applicable).
For example, E4A, E3E-12', etc. Distance between wells within rows - 1 ft.
Note: Row 3 wells C, D, and E are out of sequence with Row 4 and 5 wells.

Figure 16. Lane E map showing the anode, cathode, installed monitoring wells and physical dimensions.

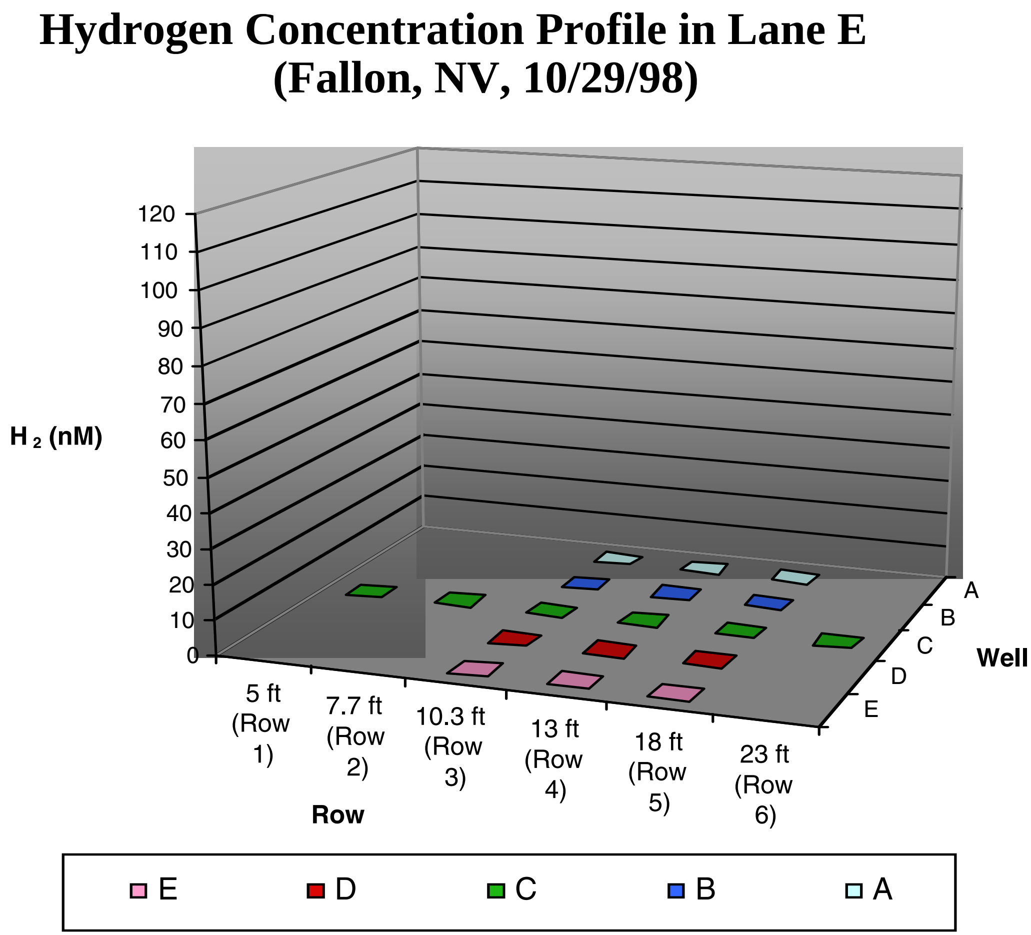


Figure 17. Fallon, NV, pilot test Lane E hydrogen profile on October 29, 1998.

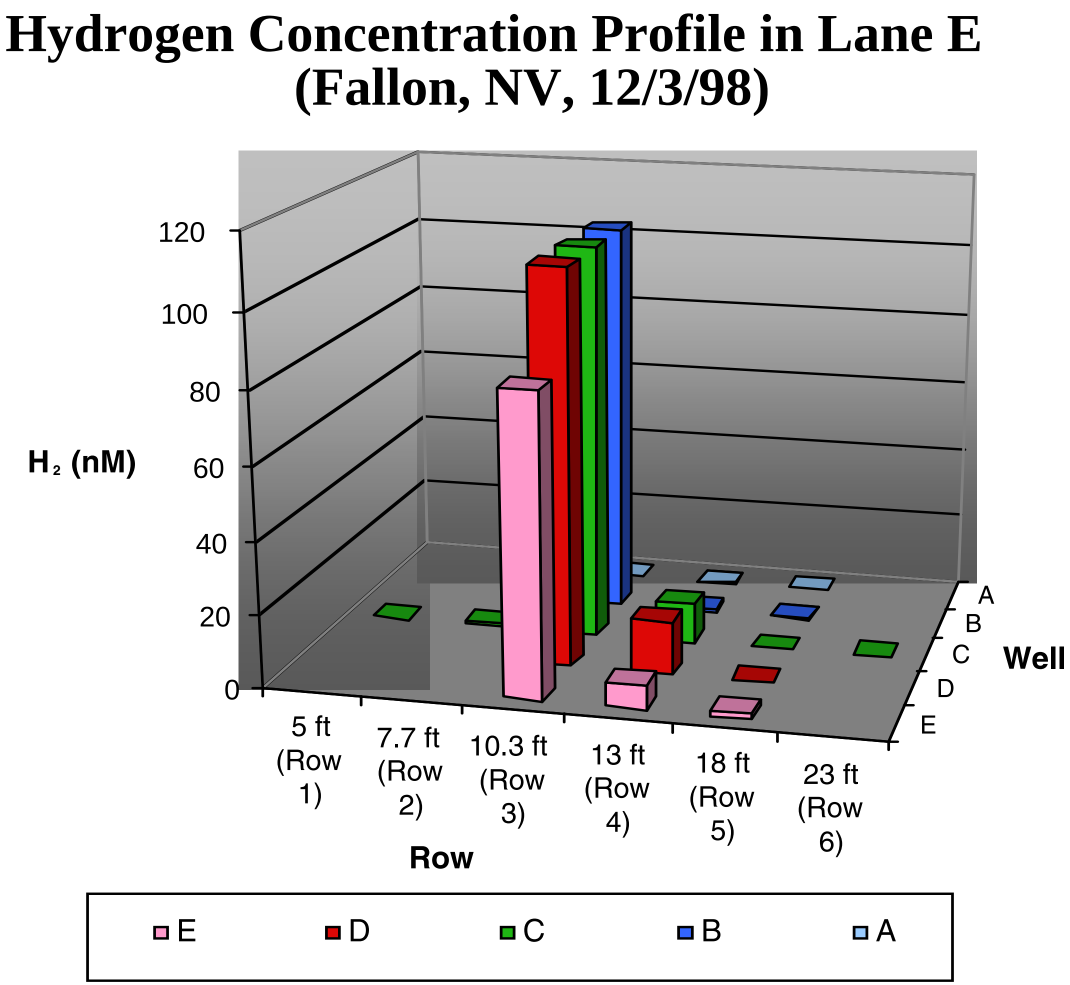
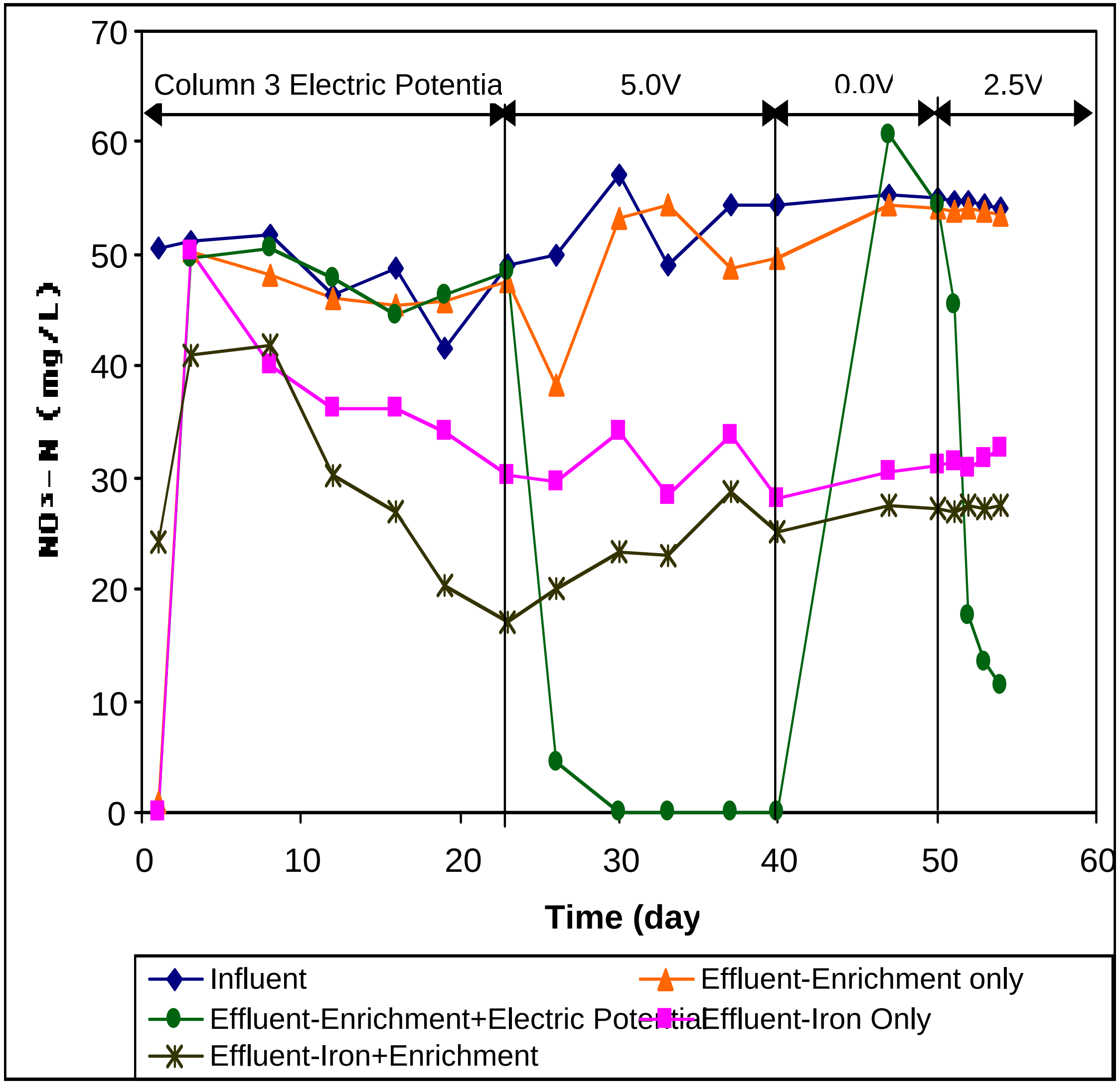
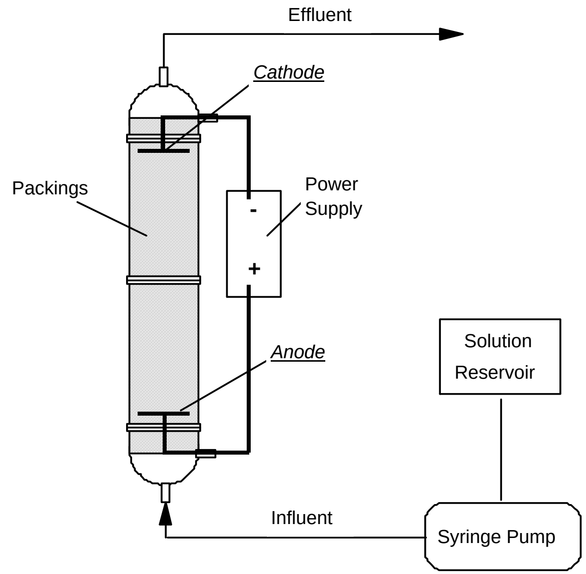


Figure 19. Fallon, NV, pilot test Lane E hydrogen profile on December 3, 1998.

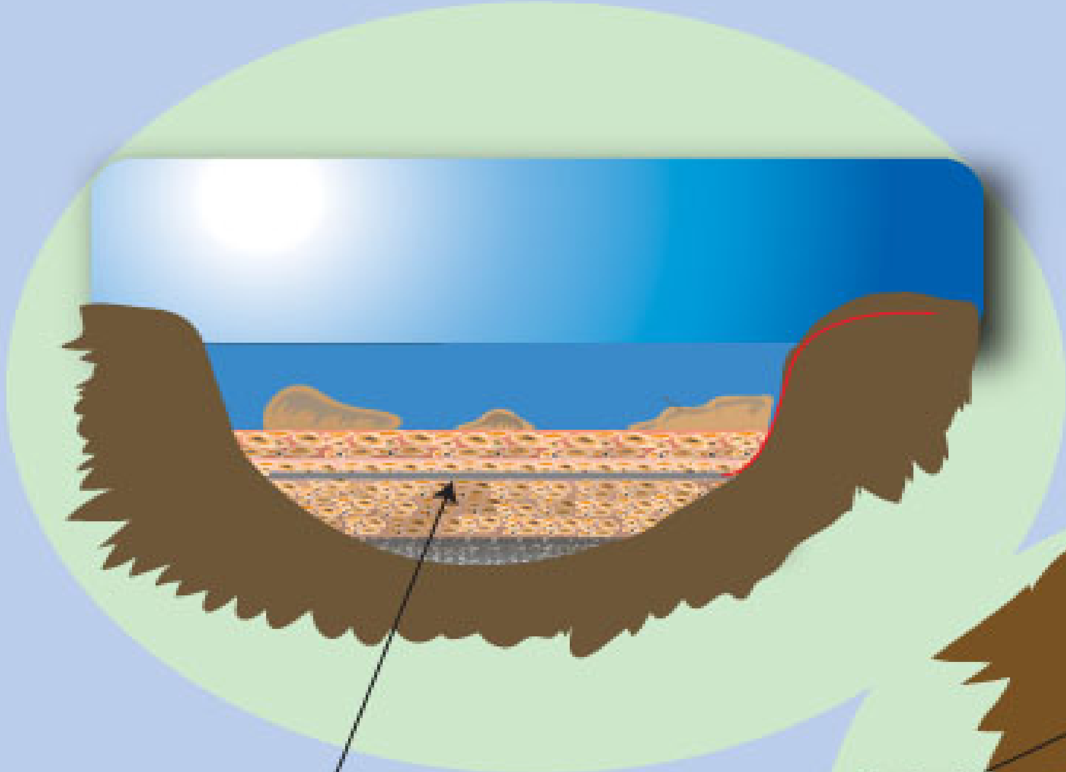




$$NO_3^- \rightarrow NO_2^- \rightarrow N_2$$

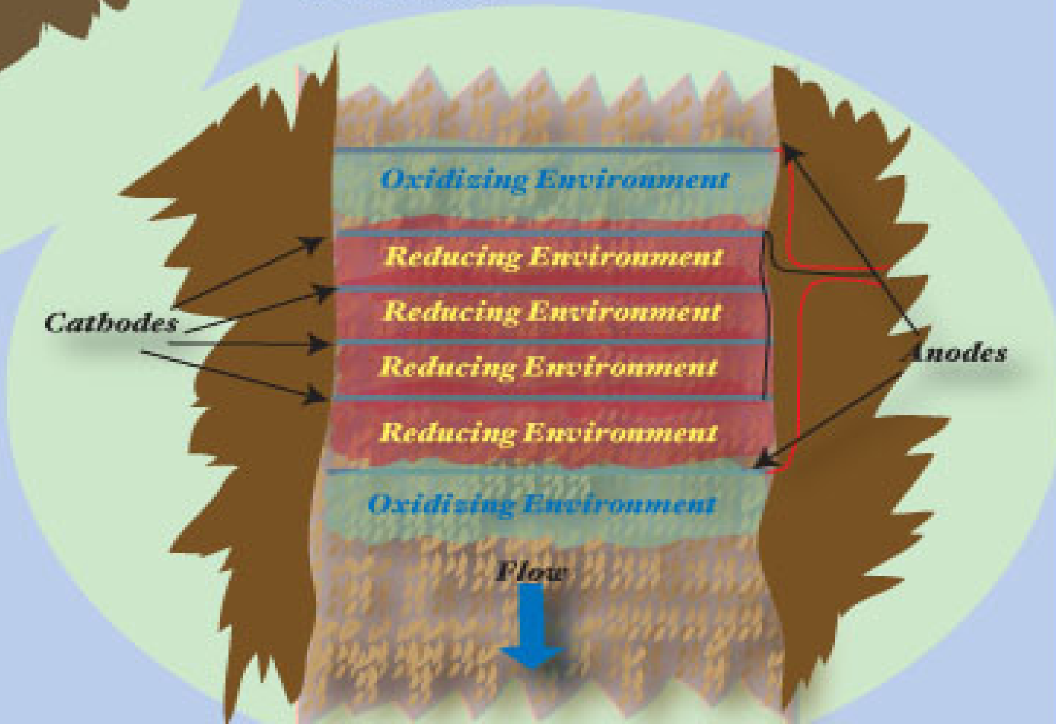
$$2NO_3^- + 5H_2 \rightarrow N_2 + 4H_2O + 2OH$$

Biolance



Depth of Rods and Number Dependent on Contamination

Ability to change anode/cathode arrangement to switch from reducing environment to oxidizing in contaminated sediments.

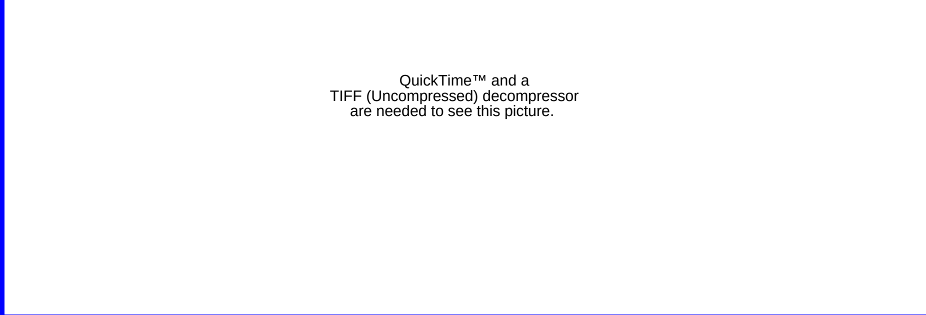


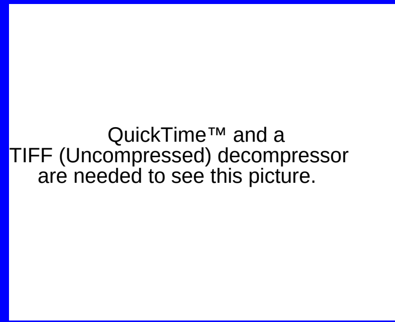
The ability to switch "environments" increases the range of contaminants which can be treated. In addition will decrease time frame for remediation.

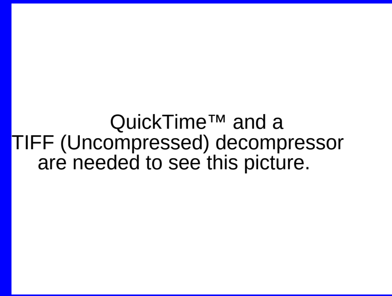
Sediment Treatment using Biolance

Guy W. Sewell

Great Eastern 1860's







Cable laying is a proven technology

Line-Electrode Characteristics:

- Ferrous based
- Maximize surface area
- Nutrient-biomass delivery
- Sample collection

Power Characteristics:

- Low power requirements
  - Solar panel
  - Battery
- Low Hazard

BioLance Application to Sediments

BioLance Advantages

- *In situ* application
- Ease of installation
- Low cost installation and operation
- Can be easily applied where needed to intercept the plume or source

BioLance Disadvantages

- Requires electricity source
- Hydrogen is potentially hazardous
- Electrodes may need replacement
- There is a lack of performance data due: ROI, rates
- Attenuation rates may be very slow

Summary

- BioLance may be applicable to sediments
- Low cost *in situ* technology
- Appropriate for *ex situ* applications also
- Ecologically Benign
- Enhances Native Processes
- Applicable to a variety of bio-reducible contaminants

Next Step: Field Trials