Indigenous Microbial Transformation of Chromium VI in Soil Under Varying Redox Conditions

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OUTLINE

- Background
- Literature Review
- Objectives
- Materials & Methods
- Results
- Conclusions
- Implications

Background

- Cr in natural water: < 200 µg/L
- Cr in natural soils (solids): <200 mg/kg
- Cr from anthropogenic sources:
  - chrome plating, tanneries, wet scrubber wastewater from metal smelting, etc.
  - CrVI ranked 16 by ATSDR for SF sites
- Drinking water standards:
  - total Cr US 100 µg/L, E.U. 50 µg/L
  - CrVI Switzerland 20 µg/L

Chemistry of Chromium

- **CrIII**
  - Exists in reducing environments
  - Ppt as oxides & hydroxides, pH>5.5
  - Strong adsorption onto solids
  - Soluble when pH<3.6
  - Less toxic
- **CrVI**
  - Exists in oxidizing environments
  - Soluble as chromate from pH, 2-14
  - Weak adsorption in acidic conditions
  - Mobile in soil
  - Toxic; carcinogen, mutagen

Biotransformation of CrVI to CrIII

- Direct biological reduction of Cr
  - Reductase under aerobic or anaer. conditions
  - Anaerobic, chromate is used as electron acceptor
- Bio-induced chemical reduction
  - Sulfate reducing
    - SO_4^{-2} to H_2S
    - Sulfide ppts
    - H2S oxidized
  - Iron reducing
    - Fe^{+3} to Fe^{+2}

Reported Bench Studies for CrVI treatment

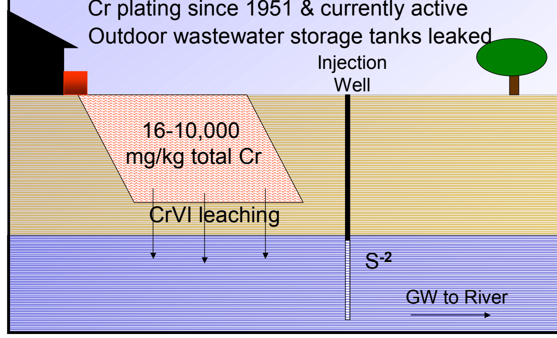
- Batch tests with enrichment cultures in liquid
  - Enzymatic Activity
    - Yeast, E. coli, Bacillus, Pseudomonas
    - 150 to 2 mg/L to 5 to <0.05 mg/L, 18-72 hrs
  - Sulfate Reducing Activity
    - 100-1000 mg/L to 0.8-100 mg/L, 24-96 hrs
  - Biosorption, Yeast, 2mg/L to 1mg/L, 24hrs
- Indigenous Microbes in soil
  - Aerobic, 400 to 1840mg/L 33%-100%red., 15-21 days
  - Anaerobic, carbon added; 200 mg/L 60% red. 128days

Experimental Objectives

- Find optimal conditions for bioremediation of CrVI in site soil at **10°C**
  - Use microbes indigenous to site soil
  - Effect of carbon addition
  - Effect of redox conditions
  - Toxicity effects of high levels of chromium

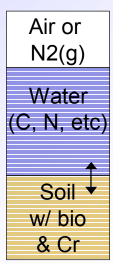
Site Description

Denver, CO
Cr plating since 1951 & currently active
Outdoor wastewater storage tanks leaked



Experimental Methods

- **Top Soil Samples**
  - Low Cr Soil: ~1000 mg/kg
  - High Cr Soil: >10,000 mg/kg
- **Conditions in Batch Tests**
  - 40-mL vials, 10 g soil, 20 mL groundwater
  - Duplicate vials
  - **10°C**
- **Controls – autoclaved soil**



Biotransformation Tests

- Low & High Contaminated Soil
- With & Without Carbon (500 mg/L)
- Non -Spiked & Spiked w/ 30 mg/L CrVI
- Six Redox Conditions
- CONTROLS for all conditions

Redox Conditions

Condition	Headspace	E-acceptors	Nutrients
Aerobic	Air		
Aerobic + N	Air		NH_4^+
Nitrate Reducing	N_2	NO_3^-	
Sulfate Reducing	N_2	SO_4^{-2}	
Iron Reducing	N_2	Fe^{+3}	
Anaerobic	N_2		

Toxicity Experiments

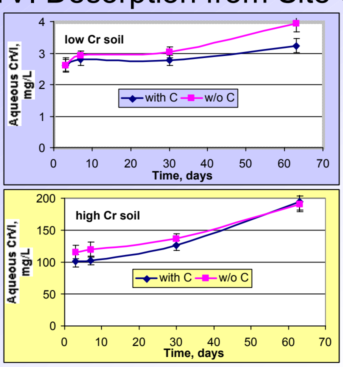
- Low Chromium Soil
- Carbon Added (500 mg/L)
- 3 Redox Conditions
  - Aerobic + N
  - Nitrate reducing
  - Sulfate reducing
- CrVI Spiked: 0, 12, 30, 50, 100, 200 mg/L
- CONTROLS for all conditions

Analytic Methods

- CrVI in aqueous samples
  - diphenylcarbazide (Standard Methods)
- Headspace Gas Composition
  - GC/TCD for oxygen, nitrogen
- Ammonia
  - Nessler method
- Nitrate
  - Spectrophotometric abs (Standard Mths)
- Aq. Fe+2, sulfide - not detected

RESULTS

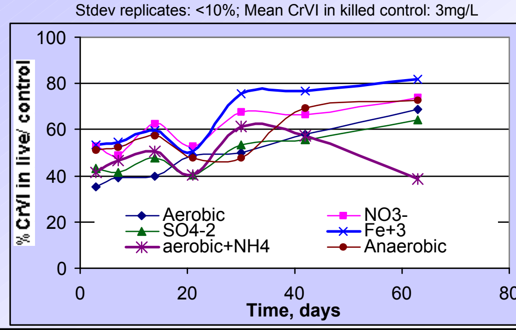
CrVI Desorption from Site Soil



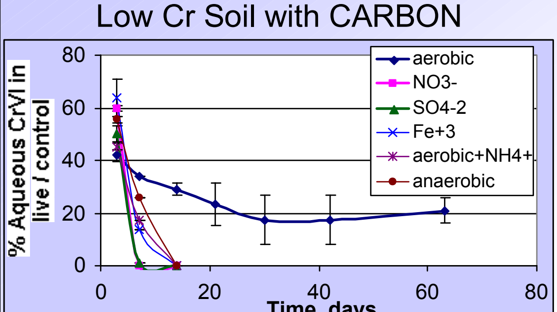
CrVI Biotransformation in Low Cr Soil

(w/o Carbon)

Stdev replicates: <10%; Mean CrVI in killed control: 3mg/L



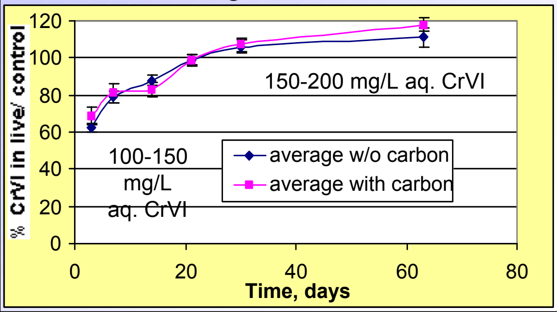
CrVI Biotransformation in Low Cr Soil with CARBON



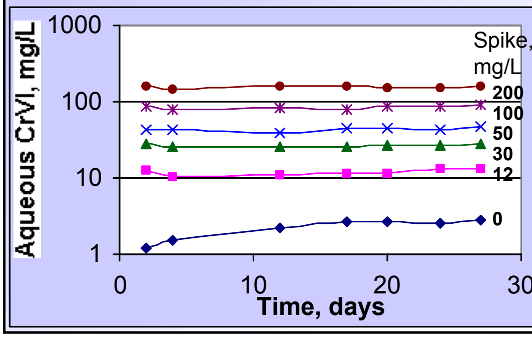
Biotransformation of CrVI in Spiked Low Cr Soil

- Without Carbon
  - Aq. CrVI steady at 70-100% of controls
  - No signif. diff. betw. redox conditions
- With Carbon
  - Aerobic + NH4+
    Complete CrVI removal in 9 weeks
  - Other redox
    15-40% removal in 1-9 wks

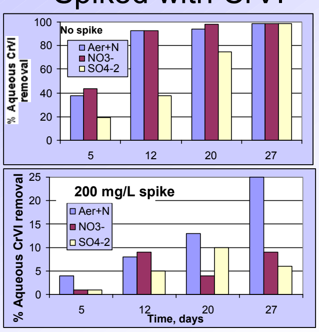
CrVI Biotransformation in High Cr Soil



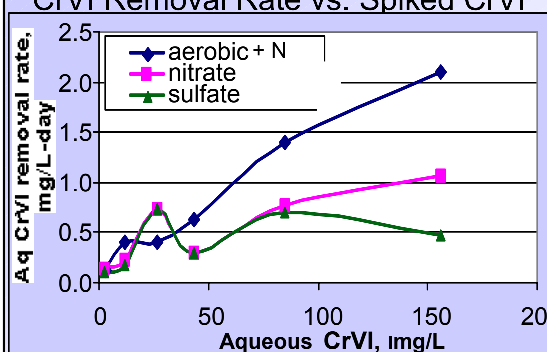
Toxicity Study: CrVI in Controls



CrVI Removal in Low Cr Soil Spiked with CrVI



CrVI Removal Rate vs. Spiked CrVI



Conclusions

- Indigenous Microbes can be promoted to Transform CrVI in Soil
- Supplemental Carbon promotes CrVI reduction
- Supplemental Nitrogen helps aerobic microbes
- CrVI can be transformed under all conditions tested
- Aerobic + NH4 was the least impacted by CrVI toxicity at high concentrations

Implications

- No need to isolate specific bacteria and seeding is not needed for in situ treatment.
- Optimal redox could be site specific
- Toxicity effects may relate to total Cr

Acknowledgment

- **Power Engineering, Denver, CO**