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Title: Perchlorate and Nitrate In Situ Bioremediation of Ground Water

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Perchlorate and Nitrate *In Situ* Bioremediation of Ground Water

**Presented to the International Sub-Surface Microbiology 2002
Conference**

**Session: Biodegradation of Aquifer Contaminants
Poster Number 126**

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Introduction

- Nitrate and perchlorate are growing worldwide problems as mobile anionic groundwater contaminants
- Biological reduction of nitrate and perchlorate in groundwater is under development as a technology to address these problems
- Maximum Contaminant Level (MCL) is 10 mg/L nitrate-N
- Proposed EPA groundwater limit is 1 $\mu\text{g/L}$ (ppb) perchlorate
- Two major sources of nitrate are over-fertilization and animal farms/dairies
- Perchlorate contamination is primarily from DoD propellant production and disposal (ammonium perchlorate)
- Use of nitric and perchloric acid at LANL without adequate removal upon waste water treatment resulted in groundwater contamination

Principles of Biological Denitrification

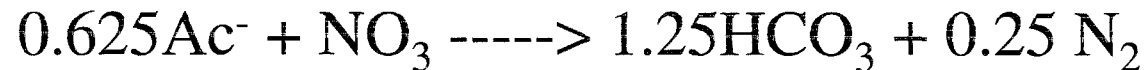
- “True” denitrification is a reductive process that yields energy for microbial cell growth
- Process sequentially reduces nitrate to nitrite, nitric oxide, nitrous oxide and nitrogen gas
- Organisms “respire” using nitrate as an electron acceptor in place of oxygen, organic carbon acts as electron donor
- Microorganisms are facultative anaerobes from many different genera
- Both carbon and phosphorus may be found limiting in natural ground waters

Principles of Microbial Perchlorate Reduction

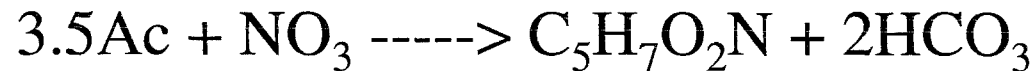
- Reduction of perchlorate is apparently ubiquitous in soil
- Process enzymatically reduces perchlorate to chlorate, then chlorite, with subsequent dismutation to chloride and oxygen
- Organisms “respire” using perchlorate as an electron acceptor in place of oxygen or nitrate, organic carbon acts as electron donor
- Microorganisms are facultative anaerobes from several different genera, primarily *Dechloromonas* and *Dechloromusa*
- Nitrate is an inhibitor of perchlorate reduction, mechanism of inhibition is unclear
- Anoxic conditions required for perchlorate reduction, redox potential required for reduction to proceed lower than that for nitrate reduction

Chemical Denitrification Reactions

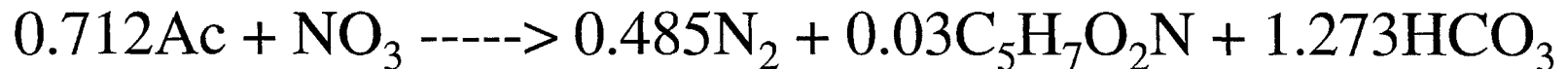
- Metabolic denitrification reaction:



- Cell component synthesis reaction:



- Combined reaction:



Ac = acetate; $\text{C}_5\text{H}_7\text{O}_2\text{N}$ = representative cellular material composition

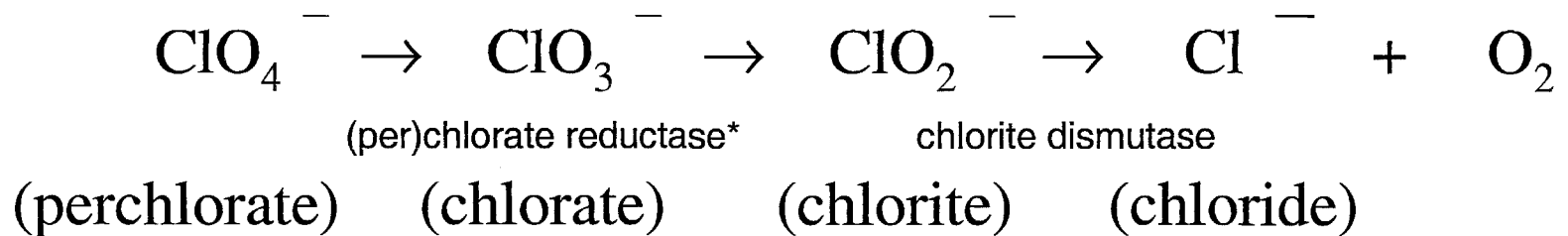
(Per)chlorate Reduction Reactions

- Overall metabolic reduction reaction:



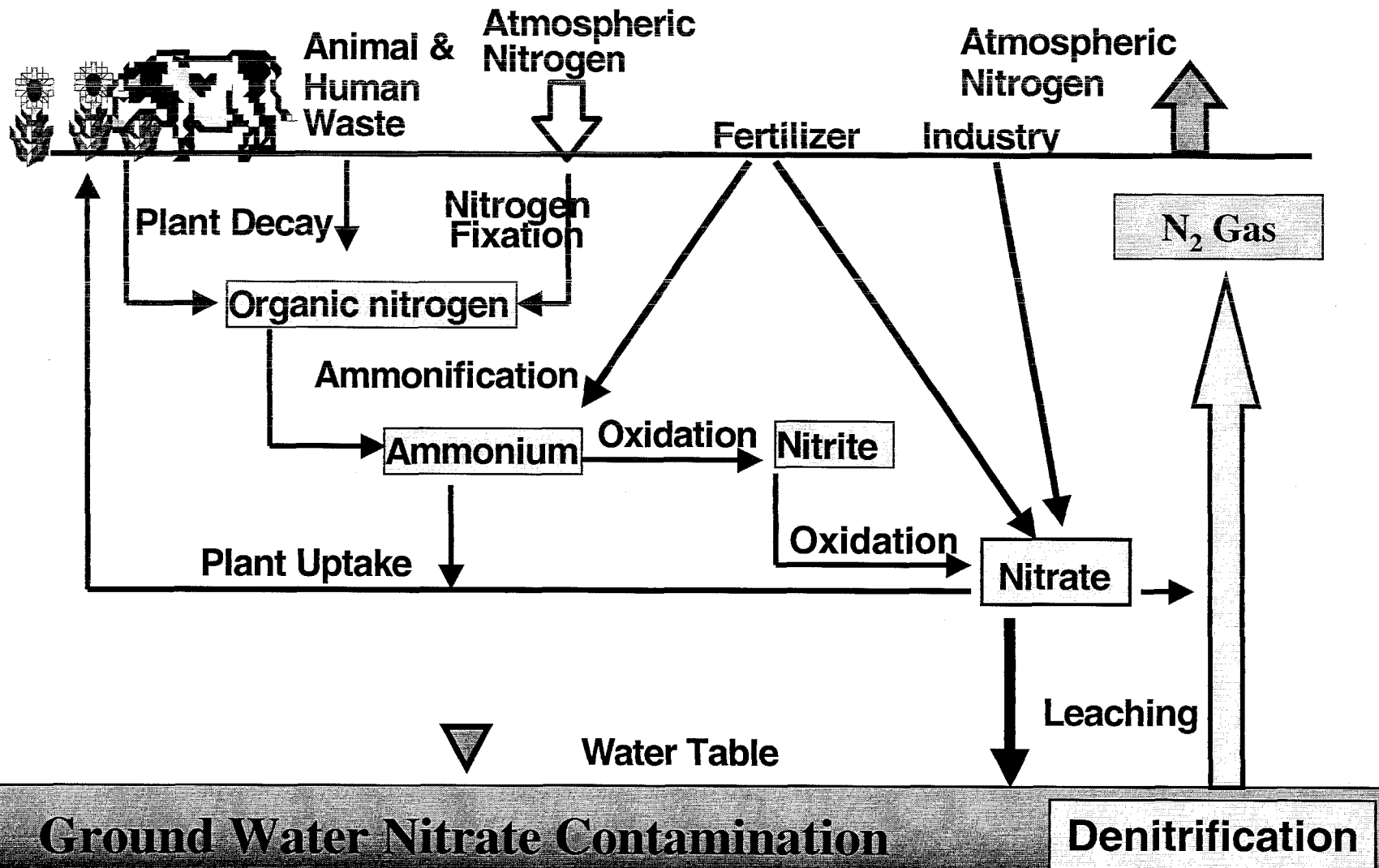
Ac = acetate

- Enzymatic reduction reactions:



*Both perchlorate and chlorate appear to be substrates of the same enzyme

The Environmental Nitrogen Cycle



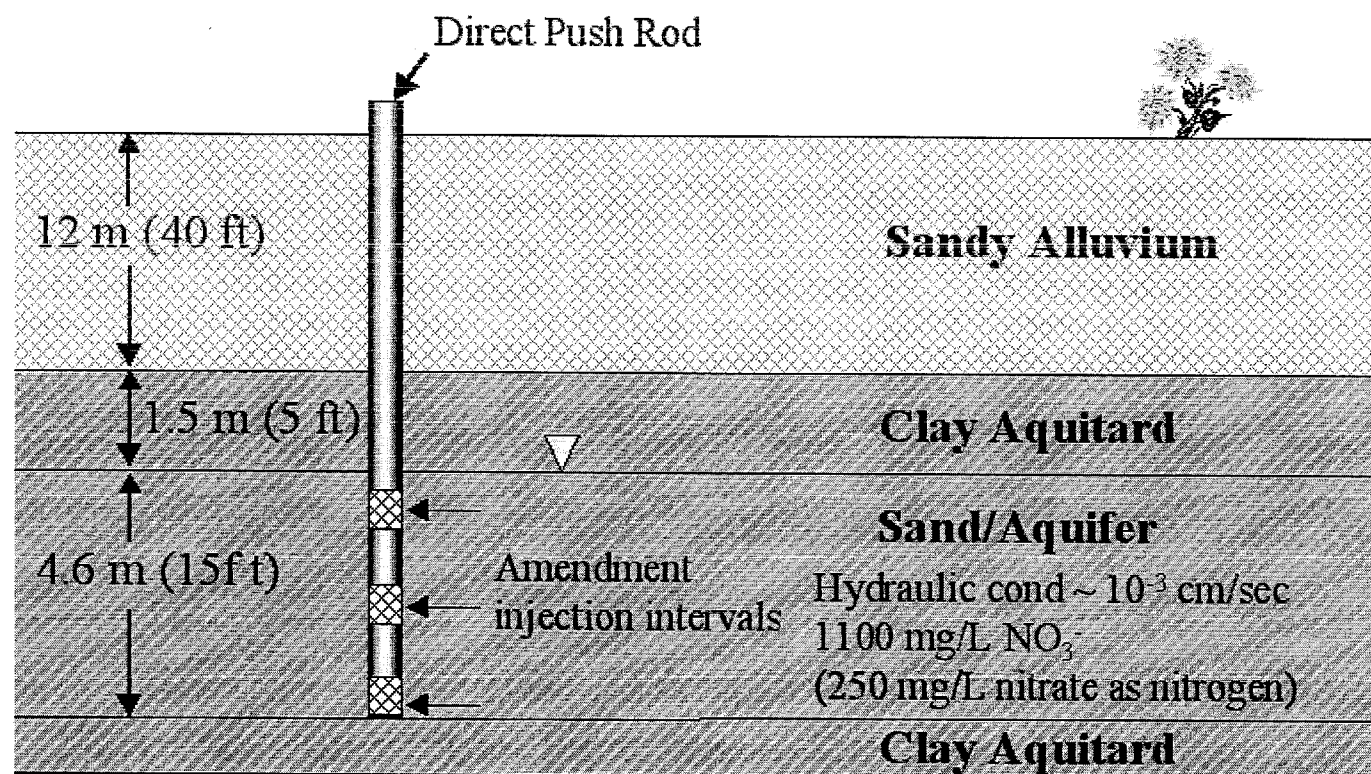
In Situ Bioremediation Demonstrations

- Passive Amendment Injection (Direct Push) for Denitrification
 - Albuquerque South Valley
- Active Amendment Injection (Inverted 5-Spot) for Denitrification
 - Albuquerque South Valley
- Permeable Reactive Barrier (PRB) for Multiple Contaminants
 - MultiBarrier in Mortandad Canyon
- Perchlorate Electron Donor Injection
 - Indian Head Division, Naval Surface Warfare Center (IHDIIV)
- Horizontal Flow Treatment Well (HFTW) for Perchlorate Reduction
 - Location TBD

Denitrification Demonstration Site

- Site is located in the South Valley of Albuquerque, NM
- Nitrate plume covers an area of about 0.85 square miles
- Caused by over-fertilization of a vegetable farm in the 1950s
- Nitrate-N levels at 215 - 250 mg/L in heart of plume
- Water table is 47 ft below ground surface
- At 42 ft is found a 5 ft thick clay aquitard, with a 15 ft thick sandy/loam soil aquifer below
- A second clay aquitard is found at 62 ft, confining the nitrate contamination
- Sand in aquifer is homogeneous with a saturated hydraulic conductivity of 10^{-3} cm/s and a flow gradient of 0.005 ft/ft
- Groundwater flows in an East-Southeast direction

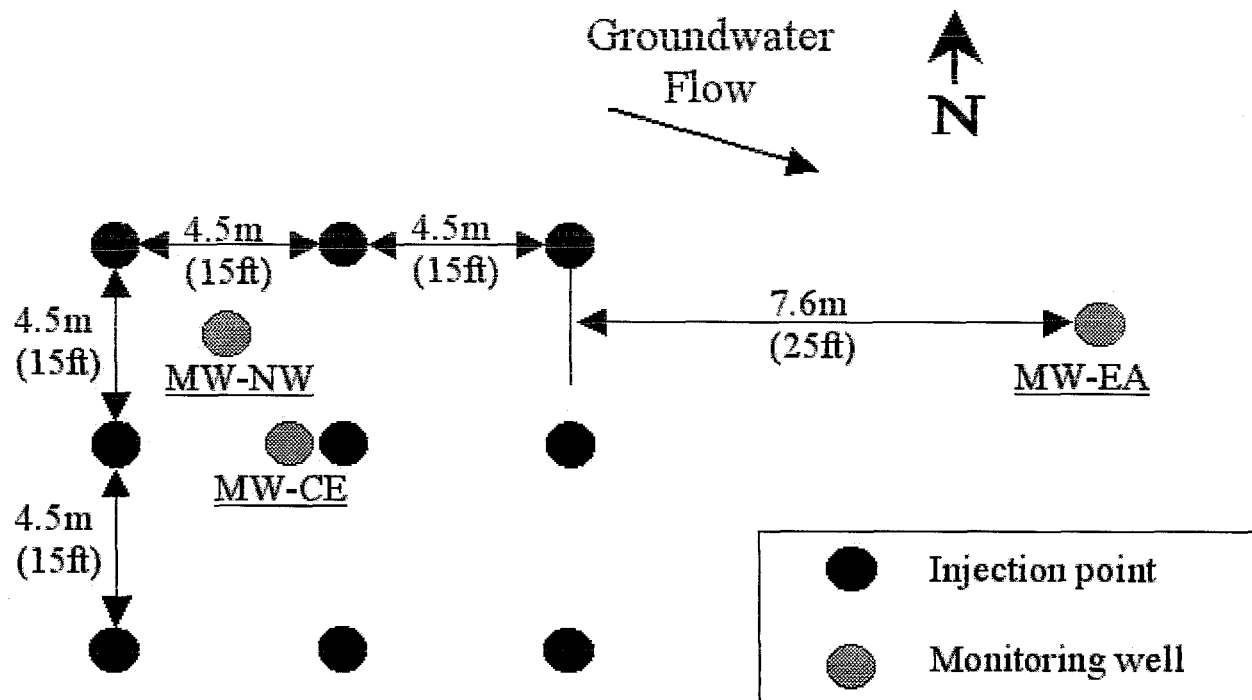
Denitrification Demonstration Site Aquifer Description



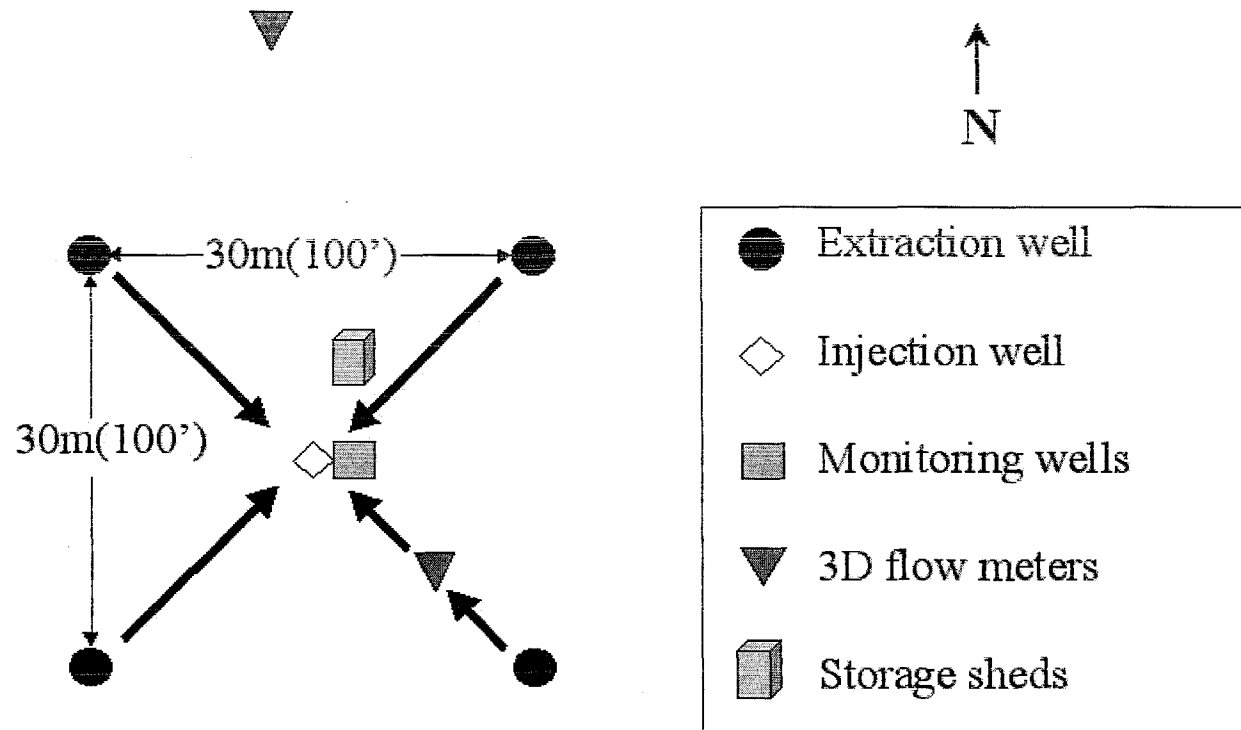
Amendment Injection Methods

- Two amendment injection systems were compared:
 - Passive “direct push” application of amendment - 9 points
 - Active “inverted five-spot” injection and recirculation
- Amended with sodium acetate, sodium trimetaphosphate and sodium bromide (as tracer)
- Amounts of amendment used were based on stoichiometry, area and estimated water volume
 - Direct push treated 30 x 30 x 15 ft or 13,500 cubic feet (30,200 gallons of water)
 - Active system treated 100 x 100 ft² area with circular treatment zone of ~300,000 gallons of water

Direct Push Demonstration System



Inverted 5-Spot Demonstration System



Monitoring and Analytical Methods

- Direct Push System

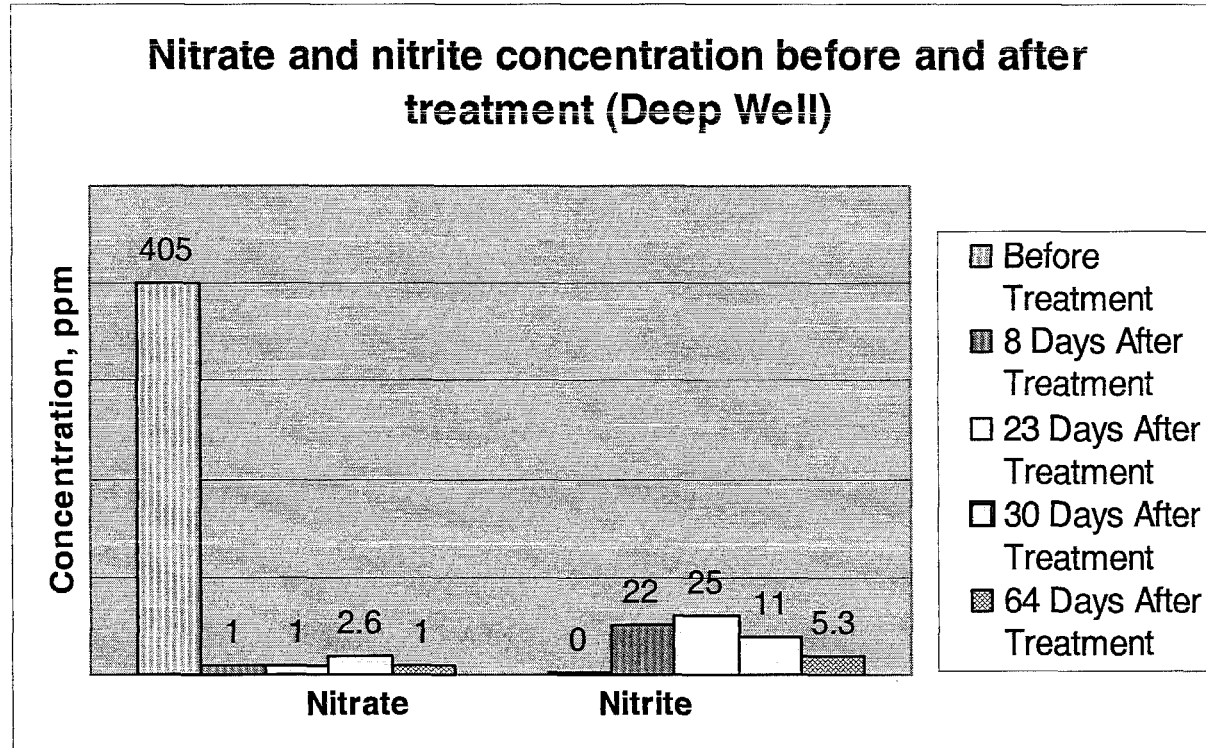
- Water from three monitoring wells (MW-EA, MW-NW, MW-CE) analyzed weekly
- Samples drawn by hand using a bailer, 1.2 well volumes discarded before taking sample
- Bromide determined with Orion Ion Selective Electrode
- Nitrate and nitrite determined with Dionex DX-500 Ion Chromatograph

- Inverted 5-Spot System

- Water from two nested monitoring wells, one shallow (~50 ft.) and one deep (~65 ft.), analyzed at 8, 23, 29 and 64 days post-treatment
- Sampling and analysis performed as in other system

Results - Inverted 5-Spot System

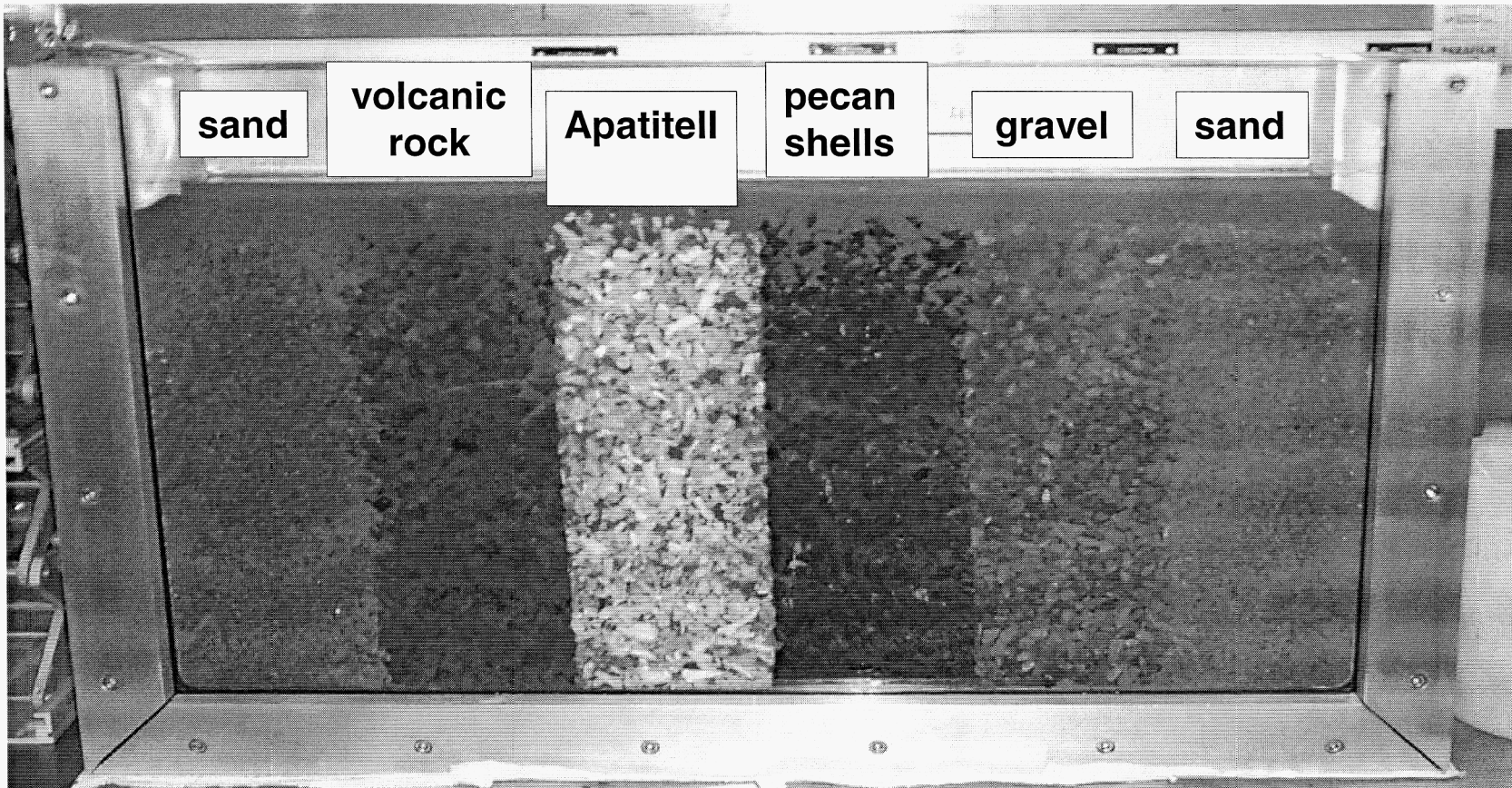
- Nitrate and nitrite concentrations in deep monitoring well



MultiBarrier *In Situ* PRB for Groundwater Remediation

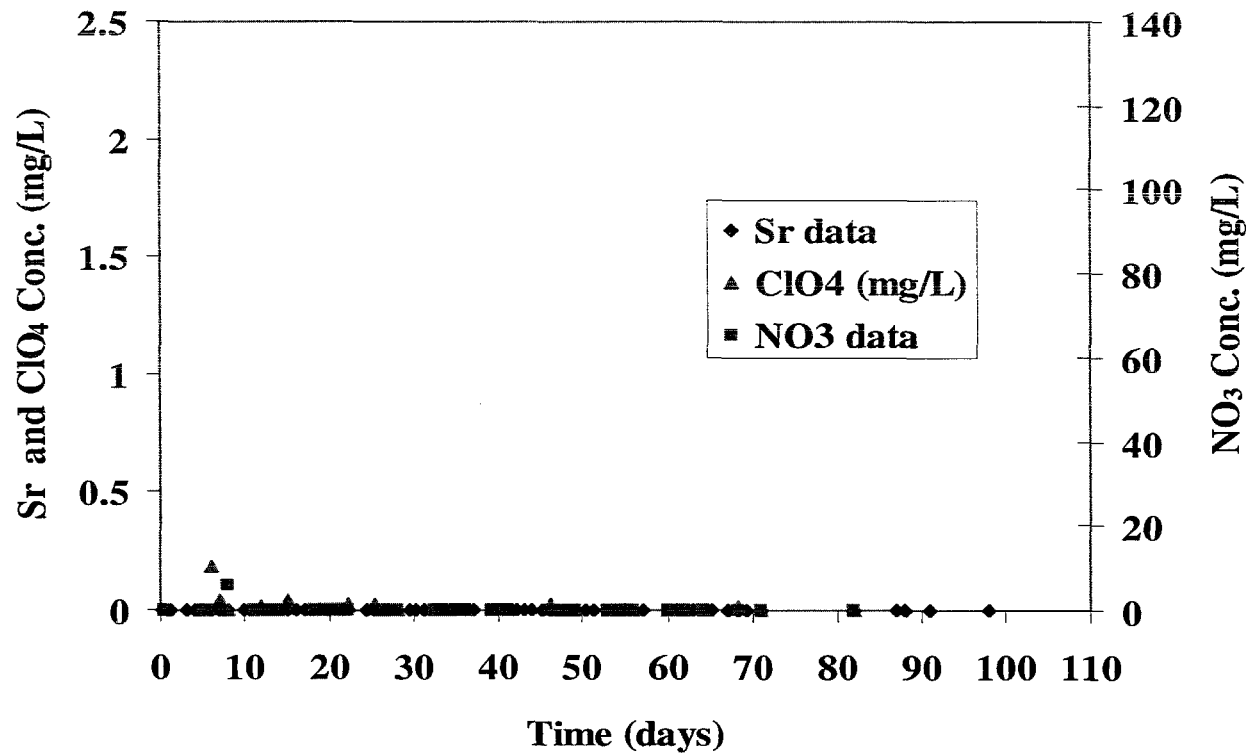
- Designed to remove radionuclides (e.g. Sr, Am, Pu, U), metals (e.g. Pb, Co, Cr), nitrate and perchlorate
- Four sections with unique purpose: colloid barrier, apatite, biobarrier, gravel polishing section
- Bench-scale batch studies, column studies in 1- and 2- dimensions to demonstrate effectiveness of each section
- Bench-scale mock-up of full-scale system in final design sequence, actual groundwater used over ~one year period

PRB Demonstration Design



2D Mock-up of PRB Design

PRB Laboratory Results

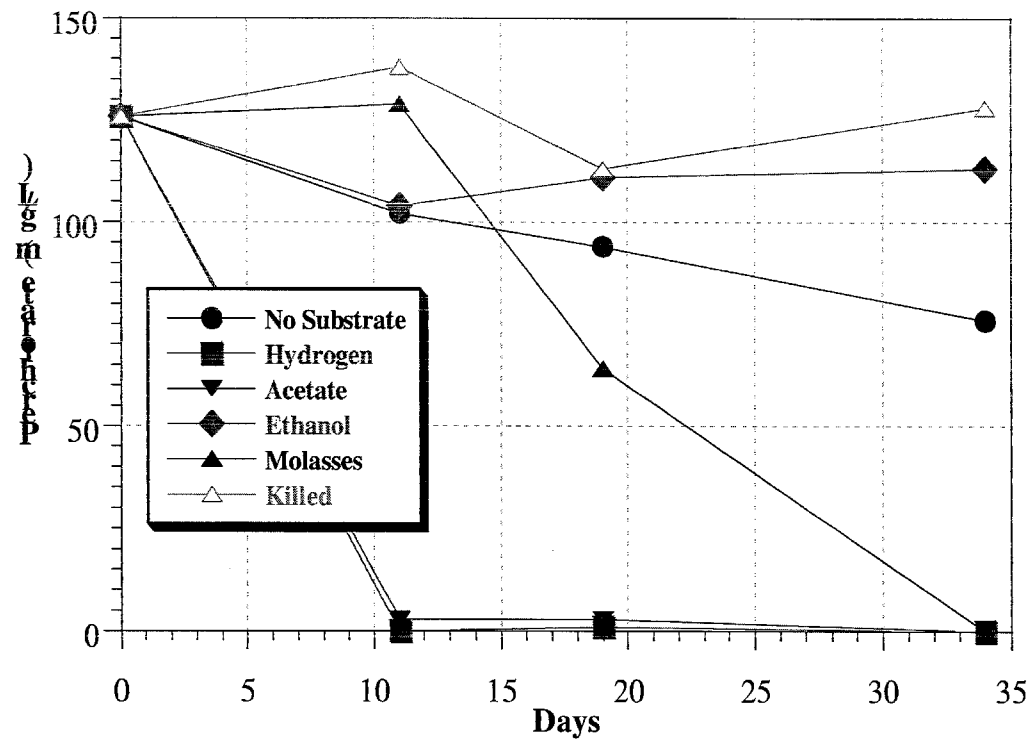


Effluent concentrations of strontium, nitrate and perchlorate from 2D box

IHDIV *In Situ* Perchlorate Reduction Demonstration

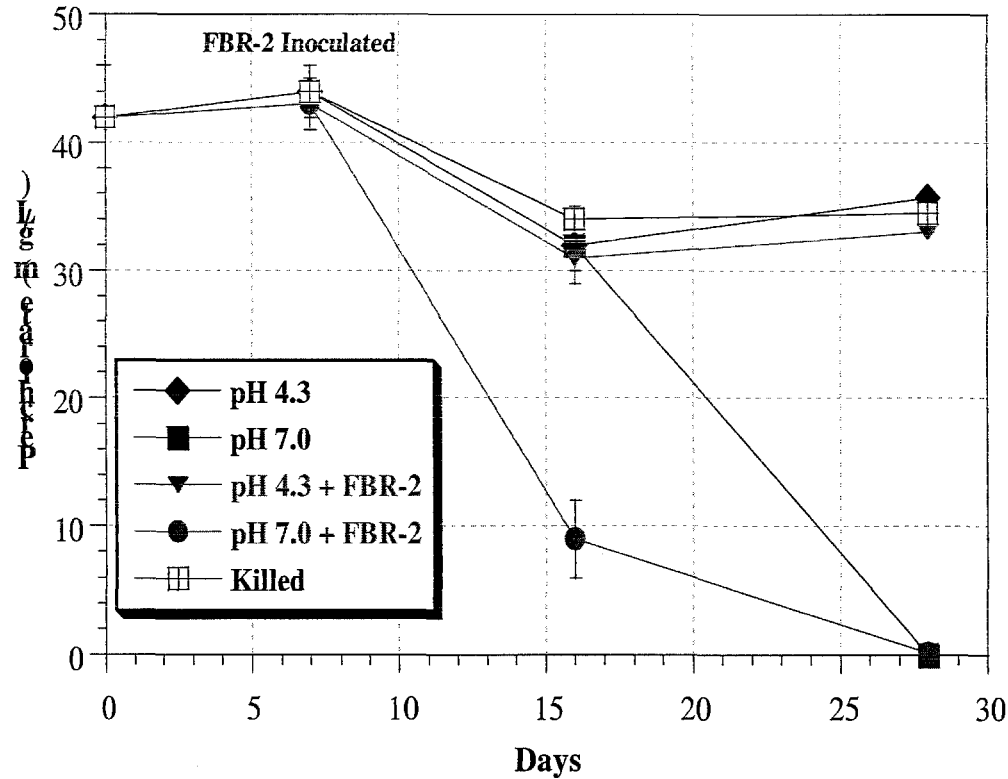
- Site located behind “Hog Out” facility (Building 1190) at Indian Head
- Laboratory studies show that naturally-occurring perchlorate-reducing bacteria are present in groundwater aquifer at site
- Bacteria can be stimulated with electron donor (acetate or lactate), will result in perchlorate reduction from >50 mg/L to below detection, however, natural pH (~4.3) is too low
- Buffering of aquifer to near-neutral pH will be necessary to achieve reduction
- Experimented with bioaugmentation using FBR-2 strain isolated from *ex situ* fixed-bed bioreactor reducing perchlorate

IHDIV Perchlorate Reduction Laboratory Results



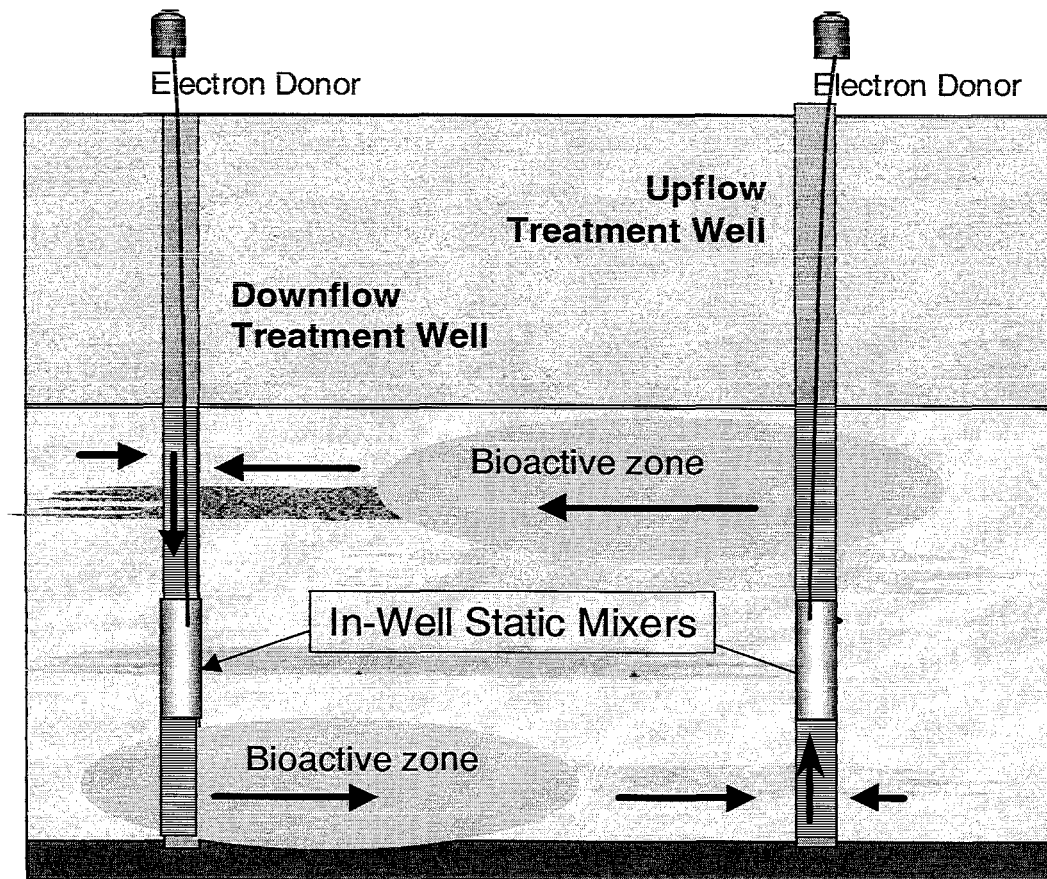
**Influence of Different Electron Donors on Perchlorate Reduction
in Aquifer Microcosms from the IHDIV Hog Out Site**

IHDIV Perchlorate Reduction Laboratory Results



**Influence of pH on Perchlorate Reduction in Aquifer Microcosms
from the IHDIV Hog Out Site (With and Without FBR-2 Inoculum)**

HFTW Demonstration Design



Conclusions

- Albuquerque South Valley passive denitrification system was not successful due to retention of nutrients in soil near injection well and poor mixing with groundwater
- Active denitrification system worked extremely well for 10 days, biofouling then became severe and the system was shut down
- Nitrate and nitrite concentrations in the deep monitoring well were below the ground water limits of 10 mg/L at 64 days in the active denitrification system
- Lab-scale demonstration of PRB system for nitrate and perchlorate removed contaminants to below detection for ~one year prior to breakthrough, a modified design is due for installation in fall 2002 in Mortandad Canyon, Los Alamos, NM

Conclusions, Cont'd.

- Lab-scale studies of perchlorate reduction determined feasibility of electron donor addition at multiple sites (Jet Propulsion Lab., IHDIV, Rocky Mountain Commercial Facility, Longhorn Army Ammunition Plant, Boeing Corp.)
- Demonstration is in progress of electron donor injection for *in situ* bioremediation of perchlorate at IHDIV “Hog Out” Site
- A second demonstration using HFTW Bioremediation System is planned for an as yet to be determined site with nitrate and perchlorate contamination
- Both nitrate and perchlorate are amenable to *in situ* bioremediation using many variable engineered systems, both at land surfaces and in deep-well injection systems

Acknowledgements

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