The Toxic Substances Hydrology Program
Cape Cod Site

Biogeochemical Processes and the Importance of Geochemical Zones

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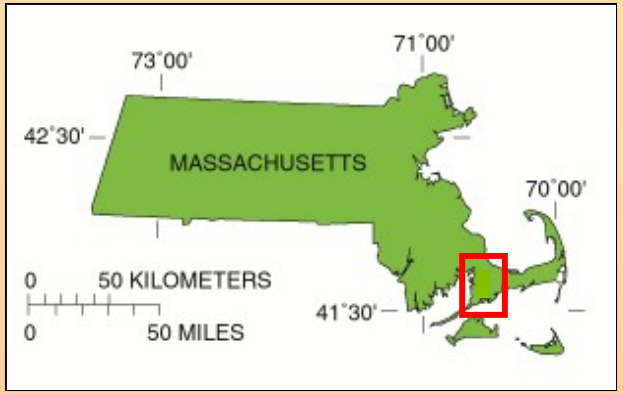
USGS
science for a changing world

Toxic Substances
Hydrology Program



Cape Cod Mantra

From there to here, and here to there,

gradients are everywhere*.

*Dr. Suess, sort of

Gradients that Affect Biogeochemical Processes

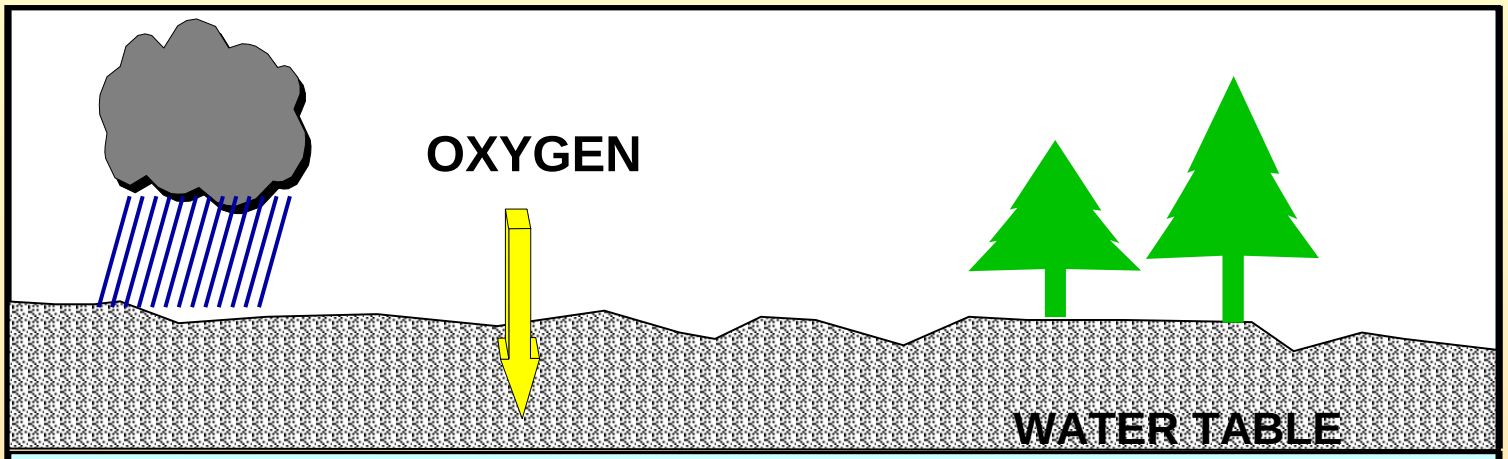
Physical Gradients
- Hydrology
- Geology
- Climate
- Seasonal

Gradients of Scale
- Spatial
- Temporal

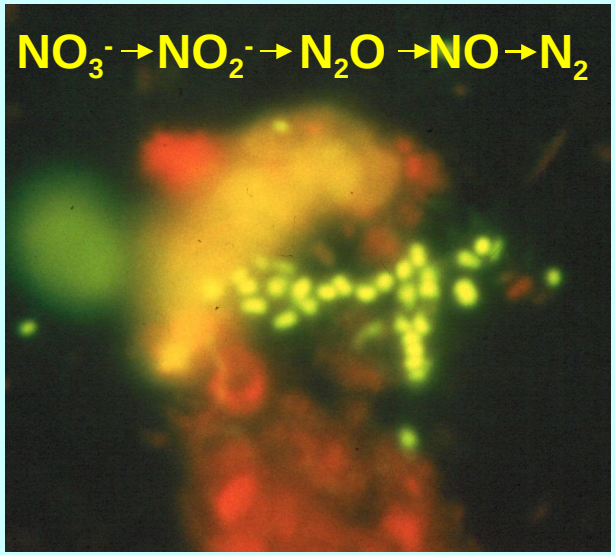
Geochemical Gradients
- Solute composition
- Solids composition
- Solids surface structure
- Electron supply
- Electron donors
- Nutrients

Biological Gradients
- Community structure
- Metabolism
- Competition
- Mobility
- Predation

Denitrification in Ground Water



$NO_3^- \rightarrow NO_2^- \rightarrow N_2O \rightarrow NO \rightarrow N_2$



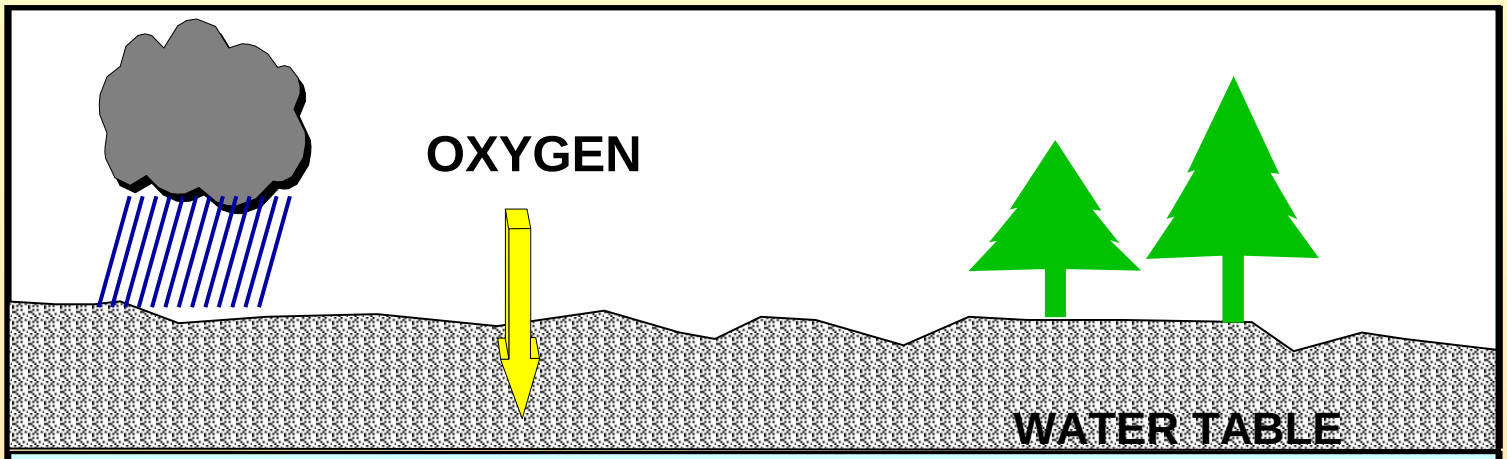
Micro-colony on sand grain

Photo by R. Harvey

Controlling Factors
Physical

GROUND WATER FLOW

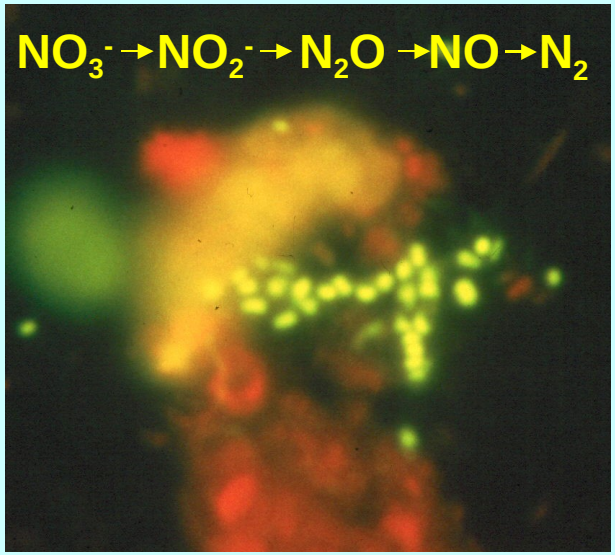
Denitrification in Ground Water



NITRATE

e^- DONOR

GROUND WATER FLOW



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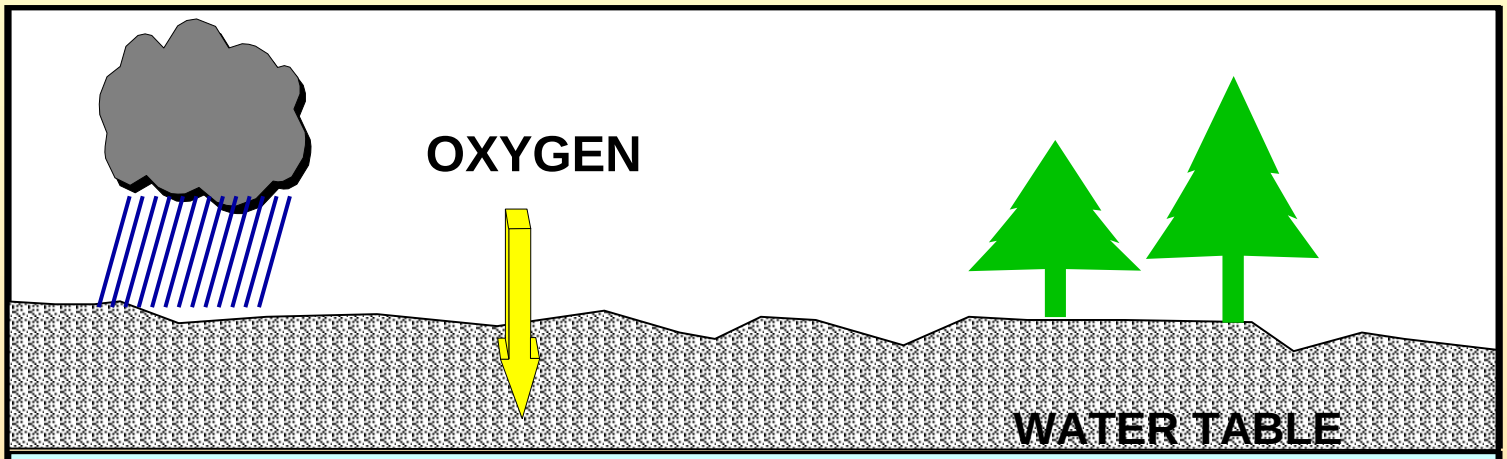
Controlling Factors

Physical

Geochemical

Denitrification in Ground Water



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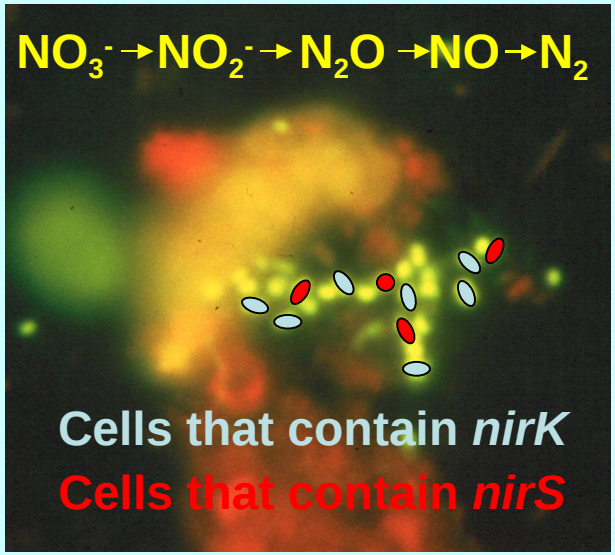

Micro-colony on sand grain

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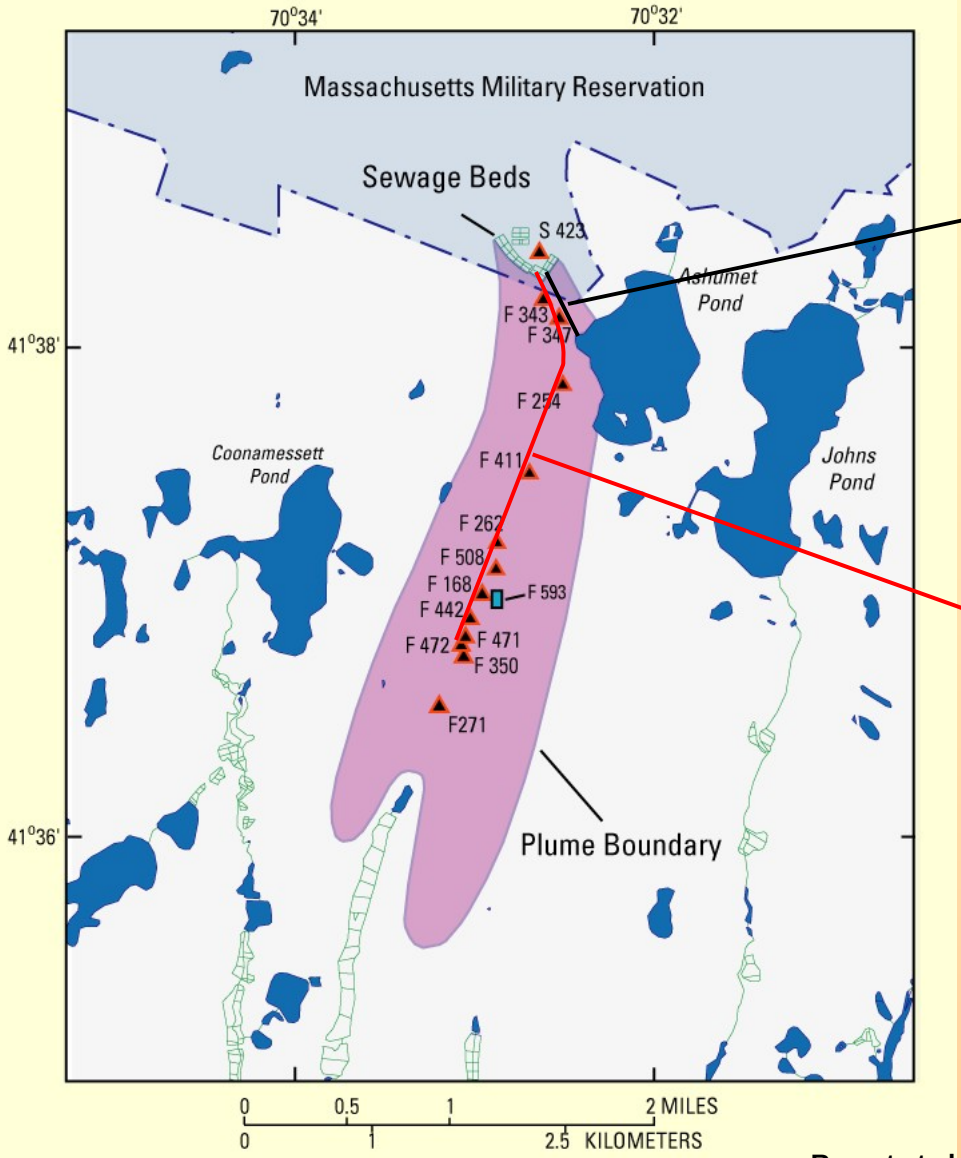
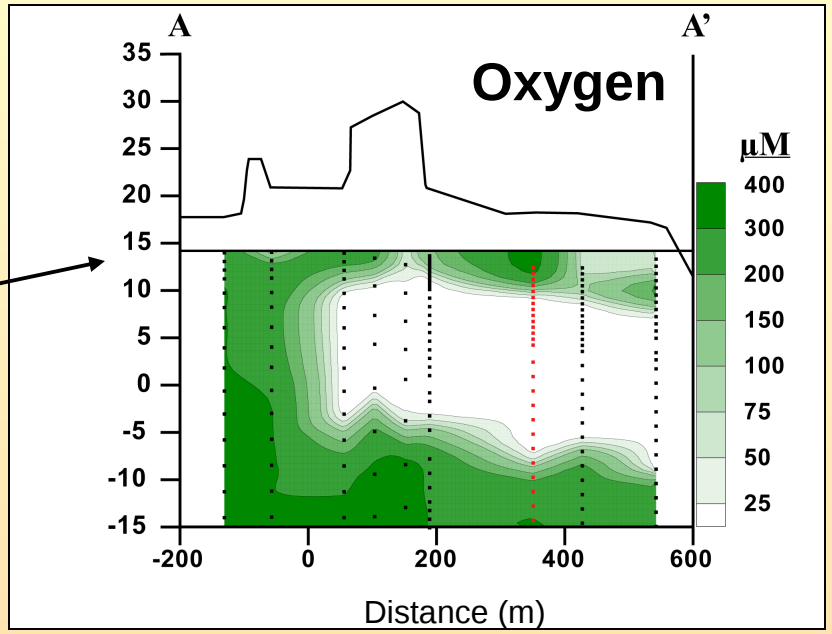
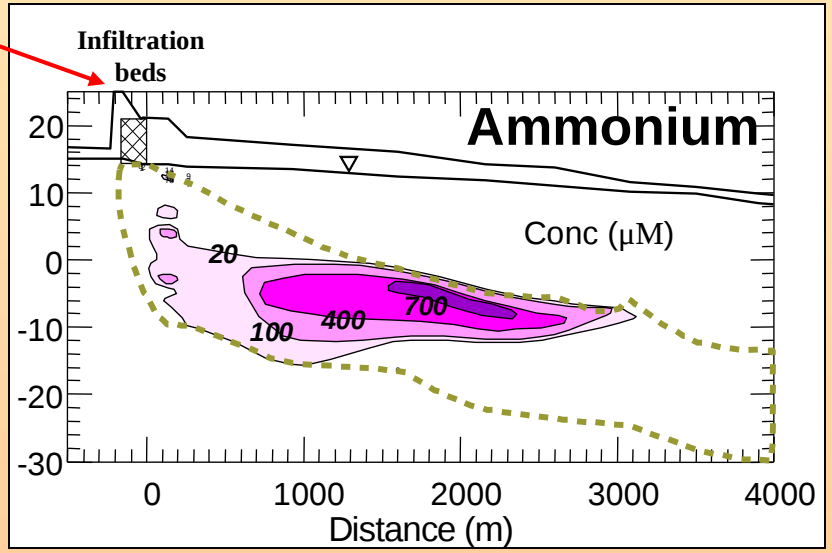
Controlling Factors

Physical
Biological
Geochemical

Gradients in Cape Cod Contaminant Plume

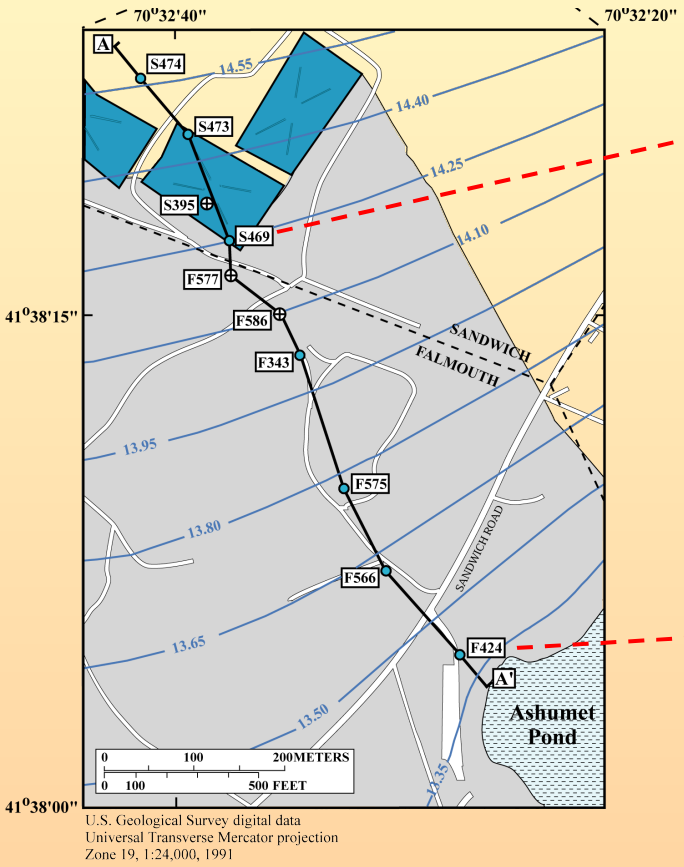


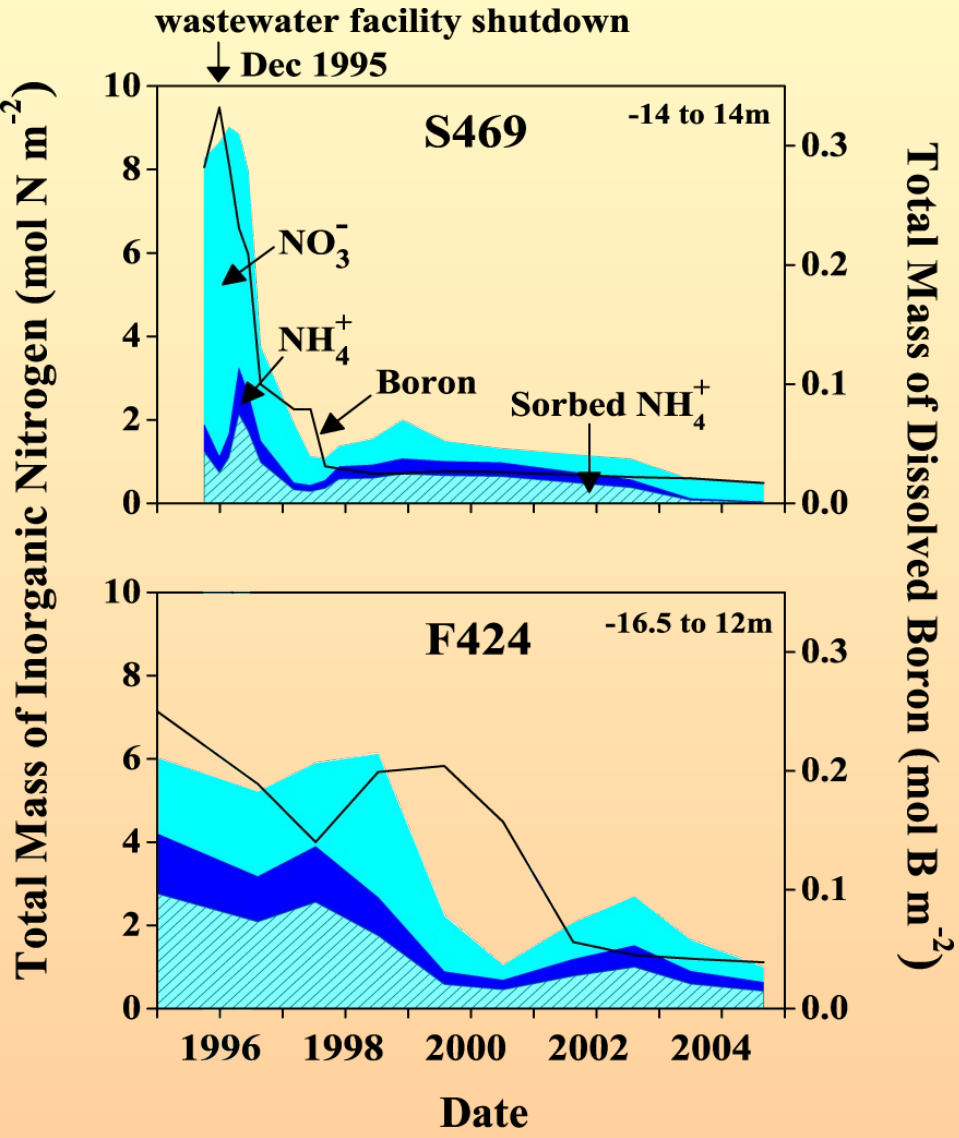




Repert et al, 2004, ES&T 40:1154; Bohlke et al, 2006, Wat Resour Res 42:W05411

Gradients in Cape Cod Contaminant Plume





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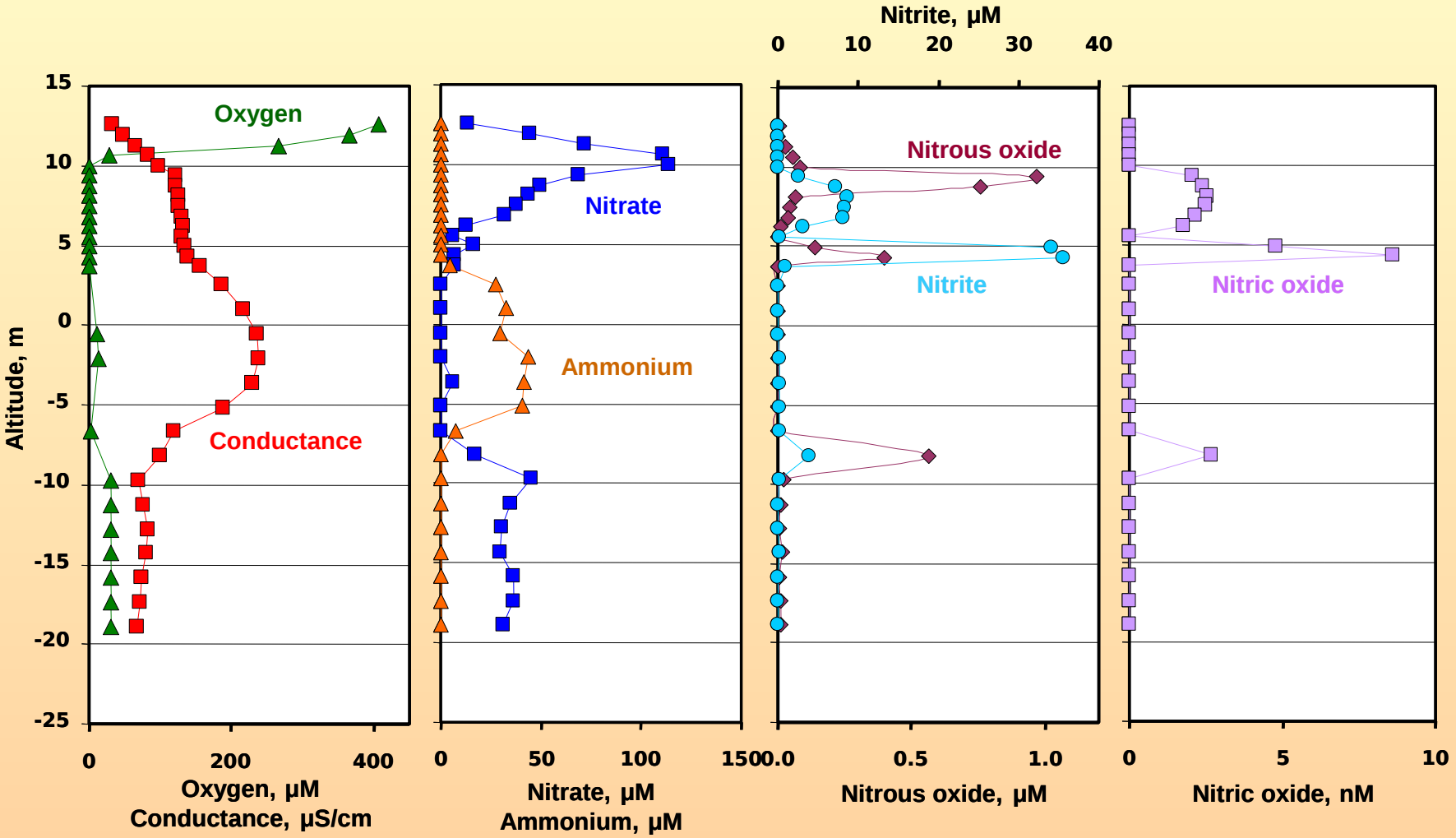
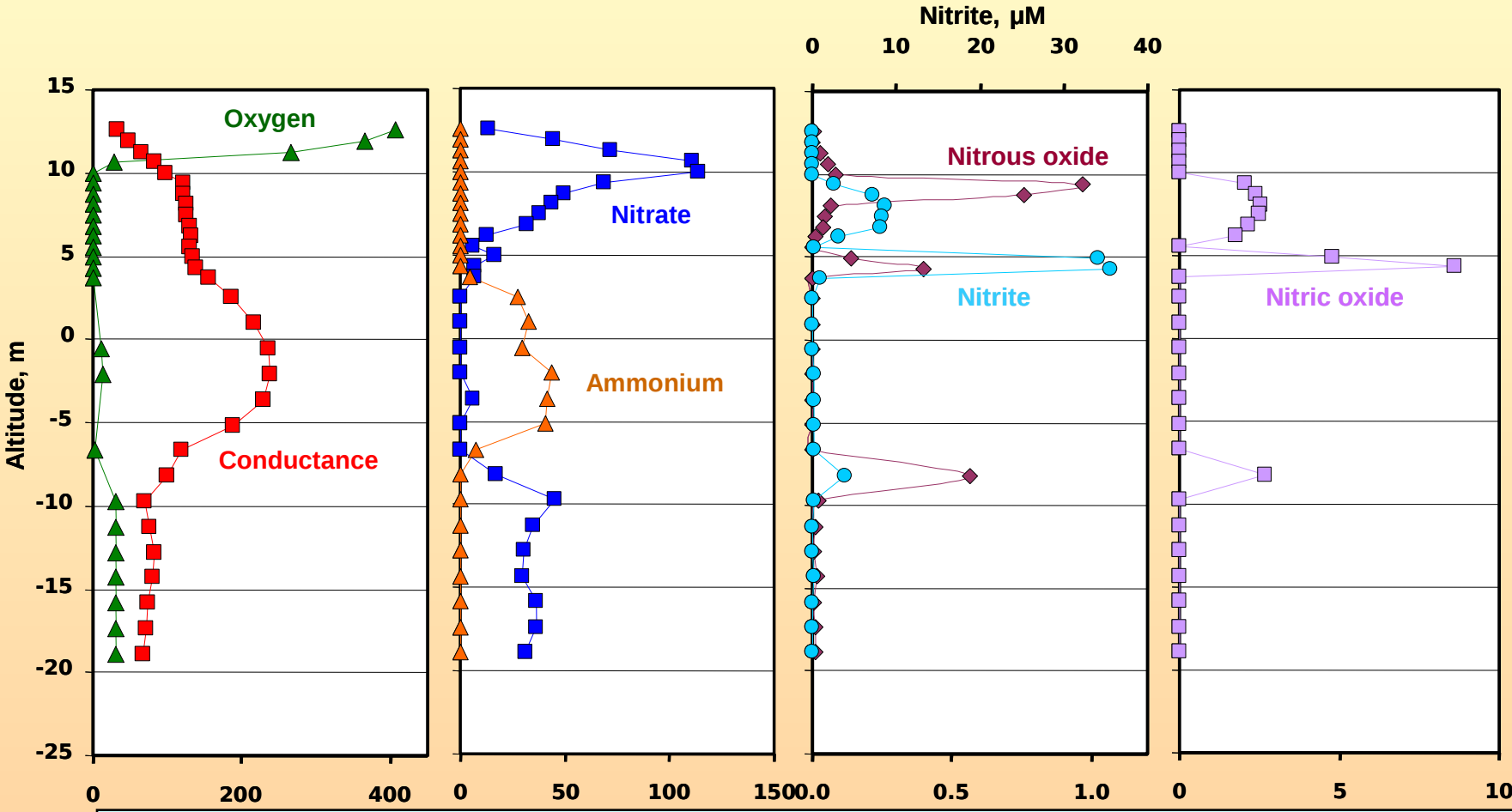
DIN Species in Cape Cod Contaminant Plume



Well site is ~2 yr ground water travel time from contaminant source

Smith et al, 2008, ES&T 42:8245

DIN Species in Cape Cod Contaminant Plume



Trace N species indicate zones of active N cycling

Active zones are narrow and restricted by gradients

Biogeochemical Processes Studied at Cape Cod Site

General processes

- Growth—Bacteria and protists
- Movement—transport and chemotaxis
- Predation
- DOC degradation

Specific processes

- Oxygen respiration
- Denitrification
- Nitrification
- Hydrogen consumption
- Methane oxidation
- LAS degradation
- Iron oxidation
- Arsenic reduction
- Acetate uptake
- Glucose uptake
- Anammox

Related studies

- Redox zone modeling
- Bioremediation—*in situ* and *ex situ*
- Antibiotic transport
- Community level characterization
- Survival of introduced microbes

http://ma.water.usgs.gov/capecodtoxics/

Global Nitrogen Budget

- **N is an essential element for all forms of life**

- **Nitrogen gas is predominant form of global N. It is converted to reactive or fixed N by microorganisms and by humans.**

  N availability controls productivity of many natural environments

  Humans have doubled the input of fixed N to global land surface

- **The function of N cycle processes will be key to understanding the net result of altering the global fixed N budget and the impact on groundwater.**

Approaches for Assessing N-Cycling Processes

Physical/Geochemical Influences

Fine-scale temporal and spatial characterization:
geochemistry, hydrologic gradients, aquifer solids,

In situ Assessment with Tracer Tests

1) Rate quantification: acetylene, $^{15}NO_3^-$, $^{15}NO_2^-$, ^{15}NO, $^{15}NH_4^+$

2) Response to added substrates: NO_3^-, NH_4^+, DOC, formate, H_2, $^{13}CH_4$, Fe(II), O_2

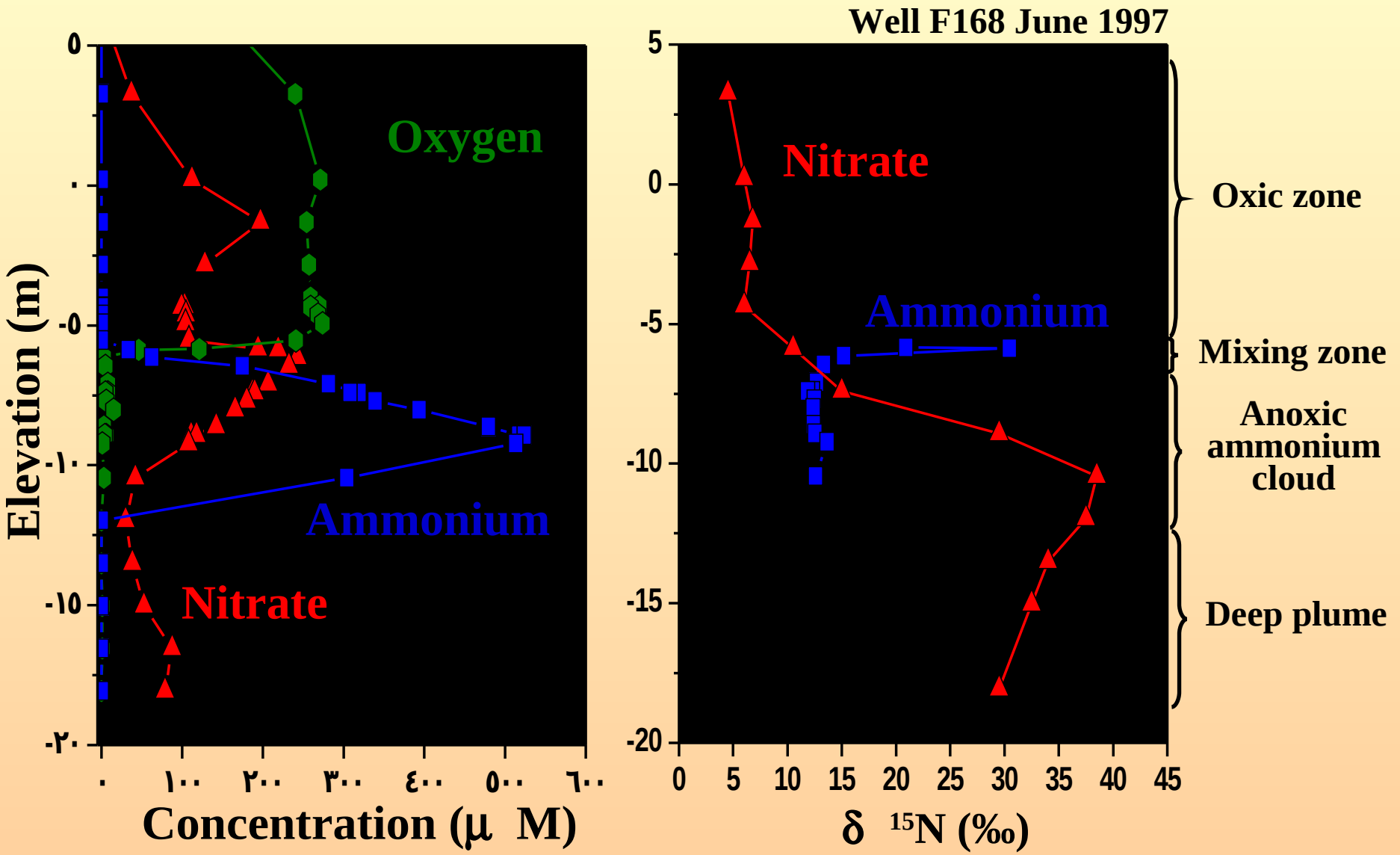
Laboratory Assessment

1) Core incubations: short-term bulk activity assays

2) Enrichment & pure cultures: characterize physiological capacity of selected microorganisms

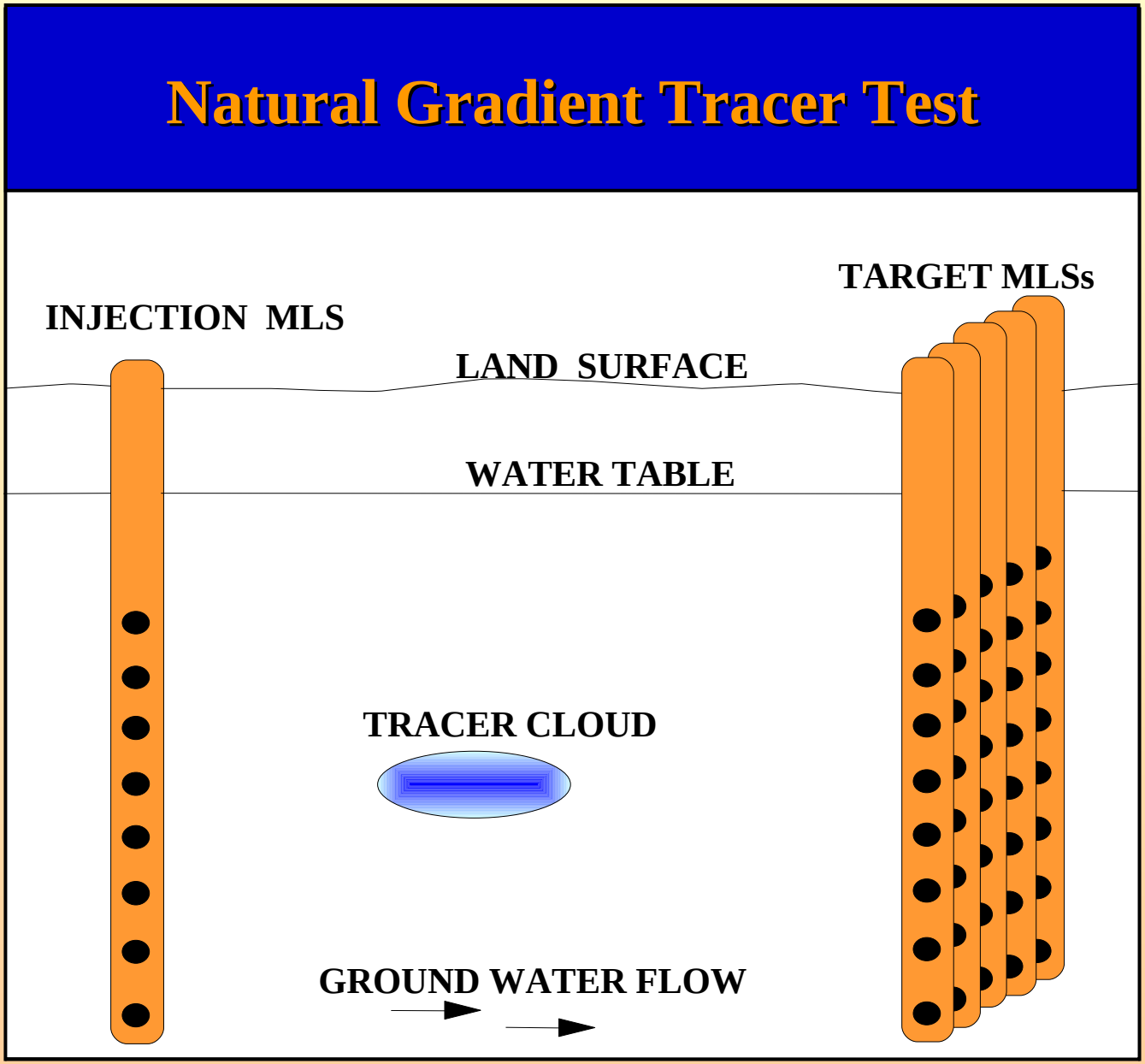
3) DNA extraction and probing

Depth Profile Near Ammonium Toe



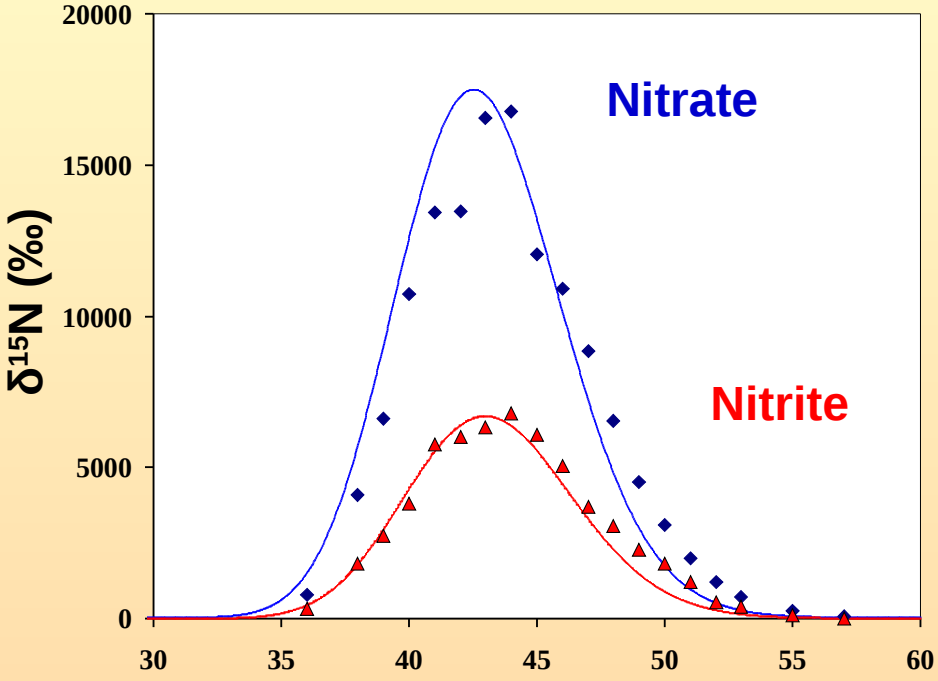
Bohlke et al, 2006, Wat Resour Res 42:W05411

Natural Gradient Tracer Test

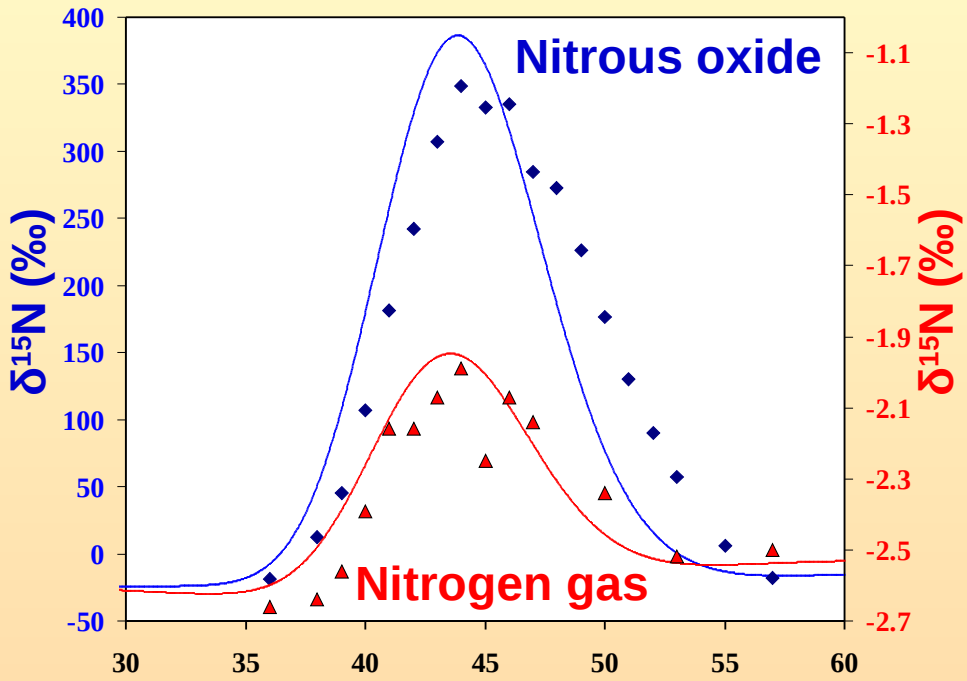


Natural Gradient ^{15}N Tracer Test for Denitrification

Tracers: $^{15}NO_3^-$, Br^-



Breakthrough curves after 10 m transport



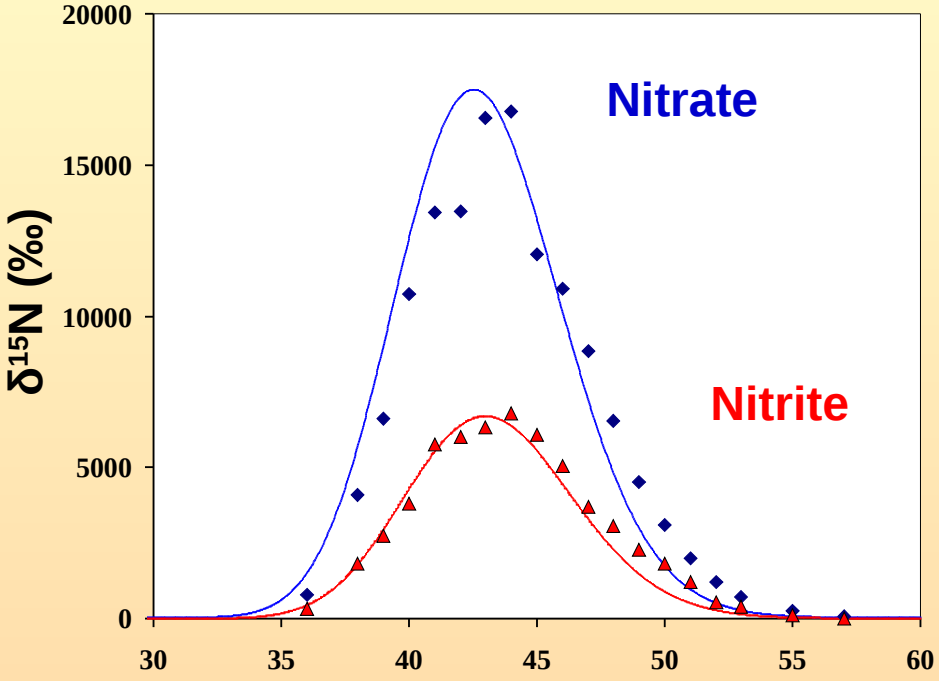
Lines are best-fit simulations

- **Advection & dispersion matched using bromide**
- **^{14}N & ^{15}N simulated independently**

Smith et al, 2004, Wat Resour Res 40:W07101

Natural Gradient ^{15}N Tracer Test for Denitrification

Tracers: $^{15}NO_3^-$, Br^-



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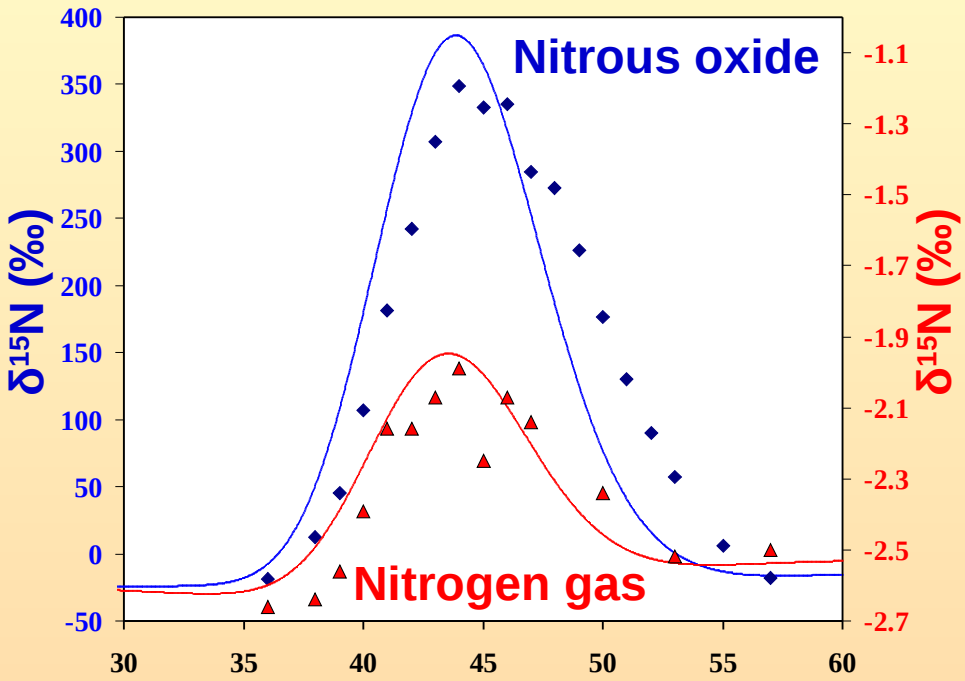
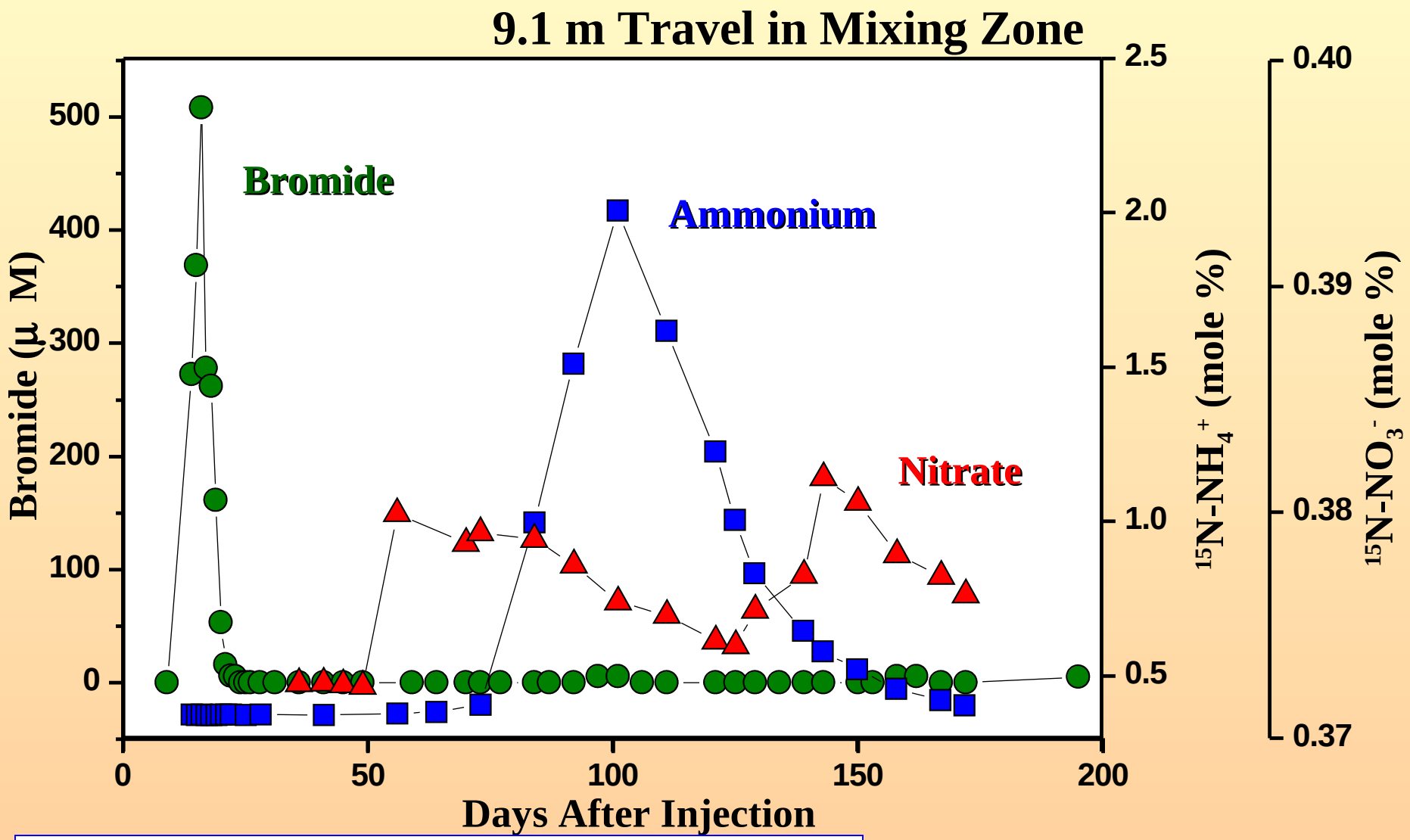


Reduction Rate: NO_3^- —(36)→ NO_2^- —(13)→ N_2O —(20)→ N_2 nmol N L^{-1} day^{-1}

Total Denitrification Rate: 24 nmol N L^{-1} day^{-1}

Smith et al, 2004, Wat Resour Res 40:W07101

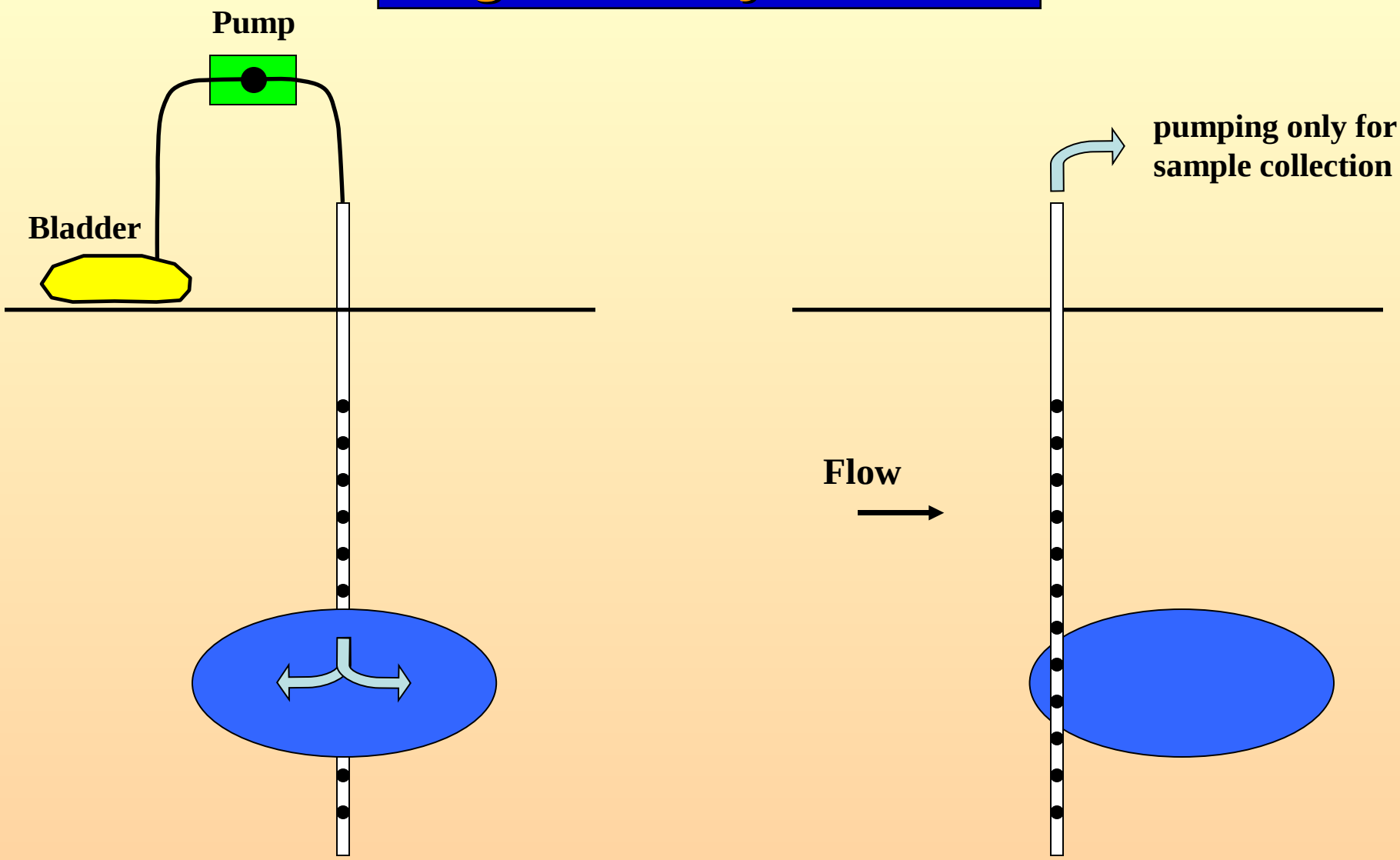
Natural Gradient Tracer Test with $^{15}NH_4^+$



Nitrification rate: 90 nmol N L^{-1} day^{-1}

Bohlke et al, 2006, Wat Resour Res 42:W05411

Single Well Injection Test

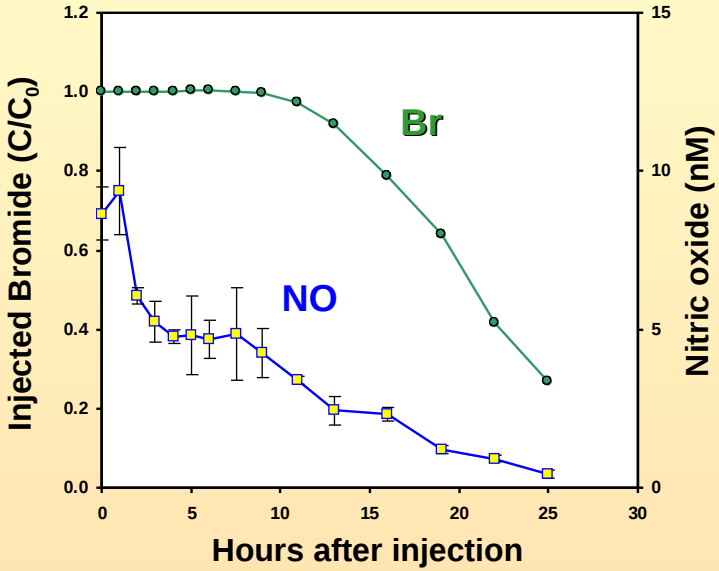


Injection

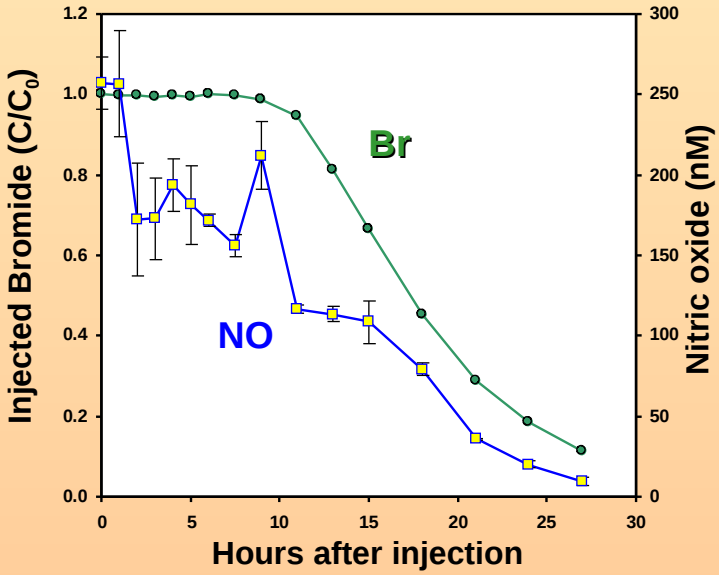
Sample Collection

Net NO Consumption

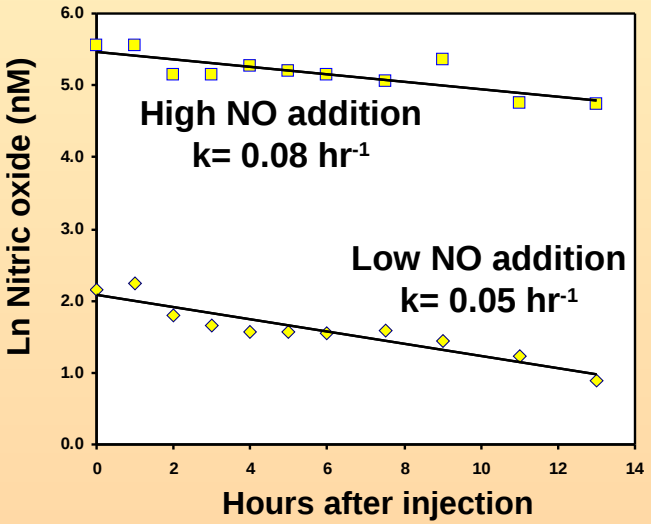
Added NO--10 nM



Added NO--250 nM

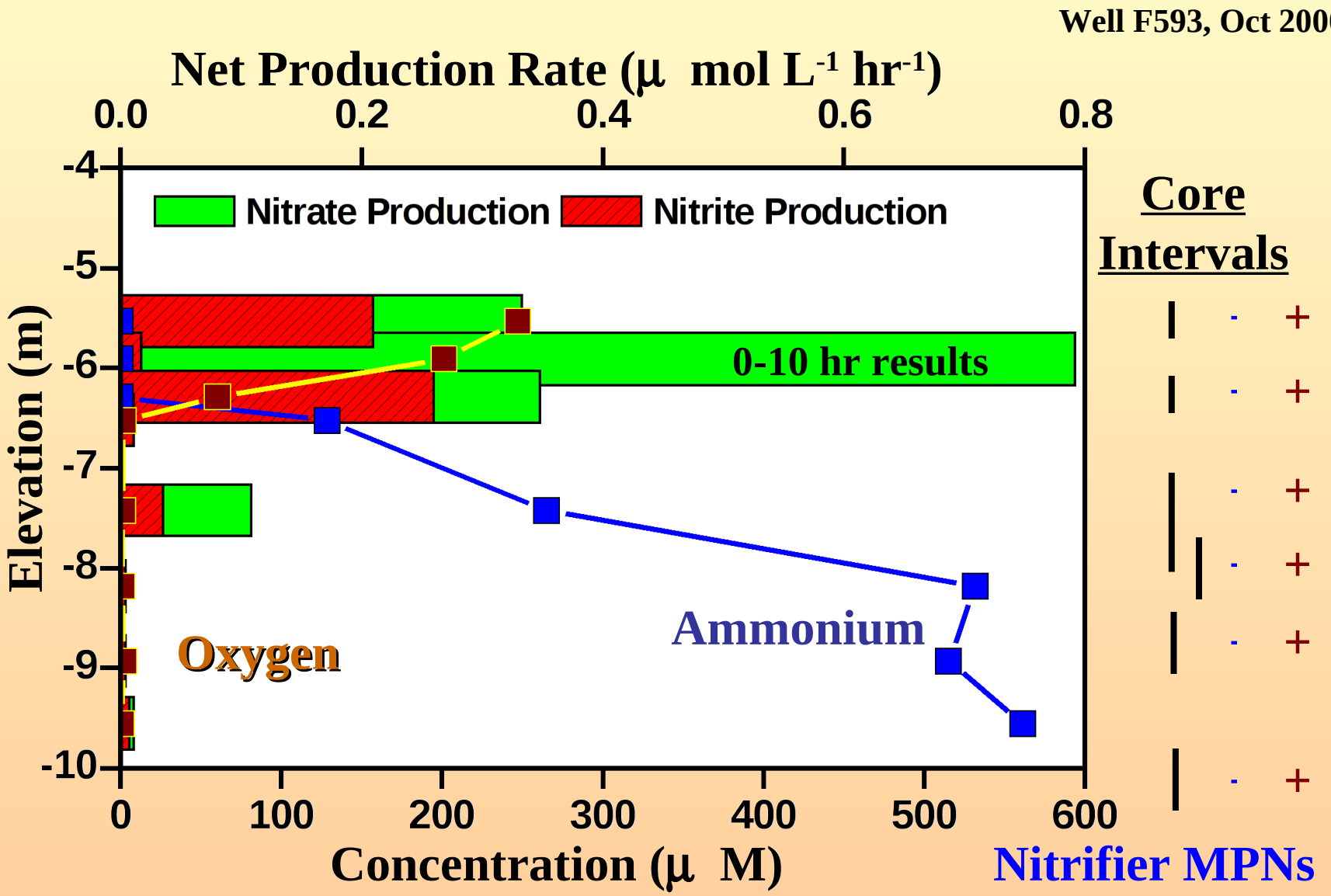


NO Consumption Rate Constants



Smith et al, 2008, ES&T 42:8245

In Situ Nitrification Potential



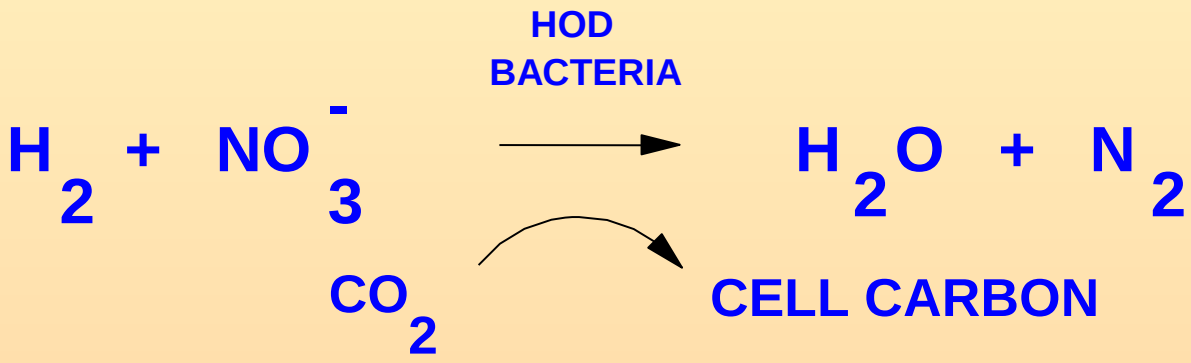
Smith et al, 2006, Microb Ecol 51:22; Miller et al, 2009, J Cont Hydrol (in press)

Electron Donors for Denitrification

Organic carbon	Heterotrophic denitrification
Hydrogen	Lithotrophic denitrification
Sulfide	
Methane	
Ammonium	
Iron	

Hydrogen Coupled Denitrification for Nitrate Remediation

•Hydrogen-oxidizing denitrifying (HOD) bacteria were isolated from Cape Cod aquifer and tested in bioreactors to remediate nitrate contamination.

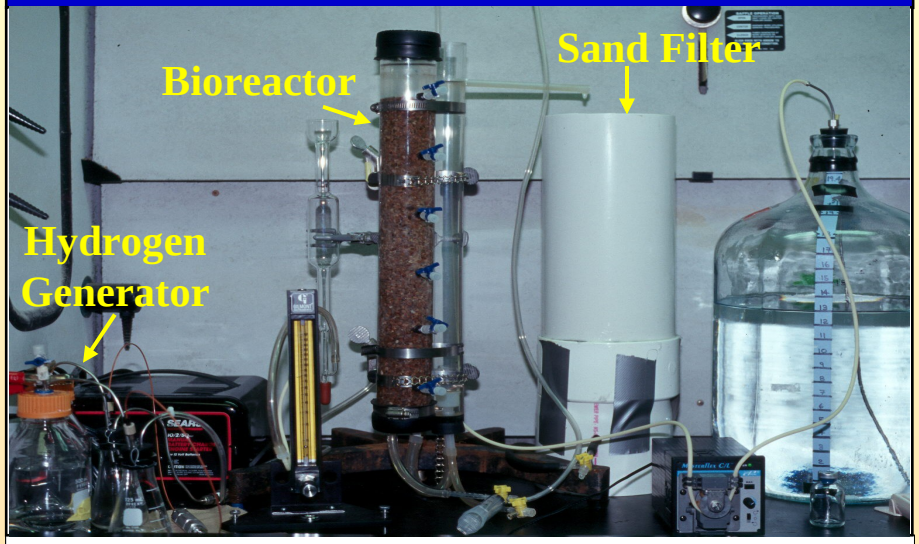


Advantages of HOD Process

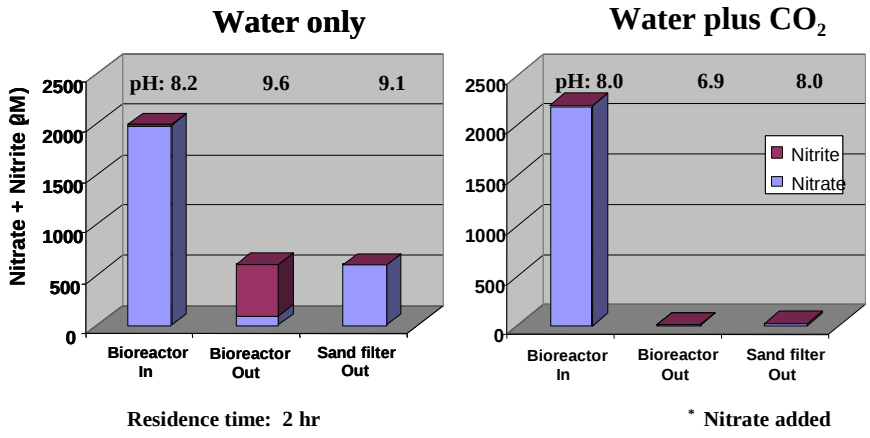
- Autotrophic—requires only CO_2
- Innocuous end-products
- HOD bacteria widely found in groundwater

US Patent 6863815

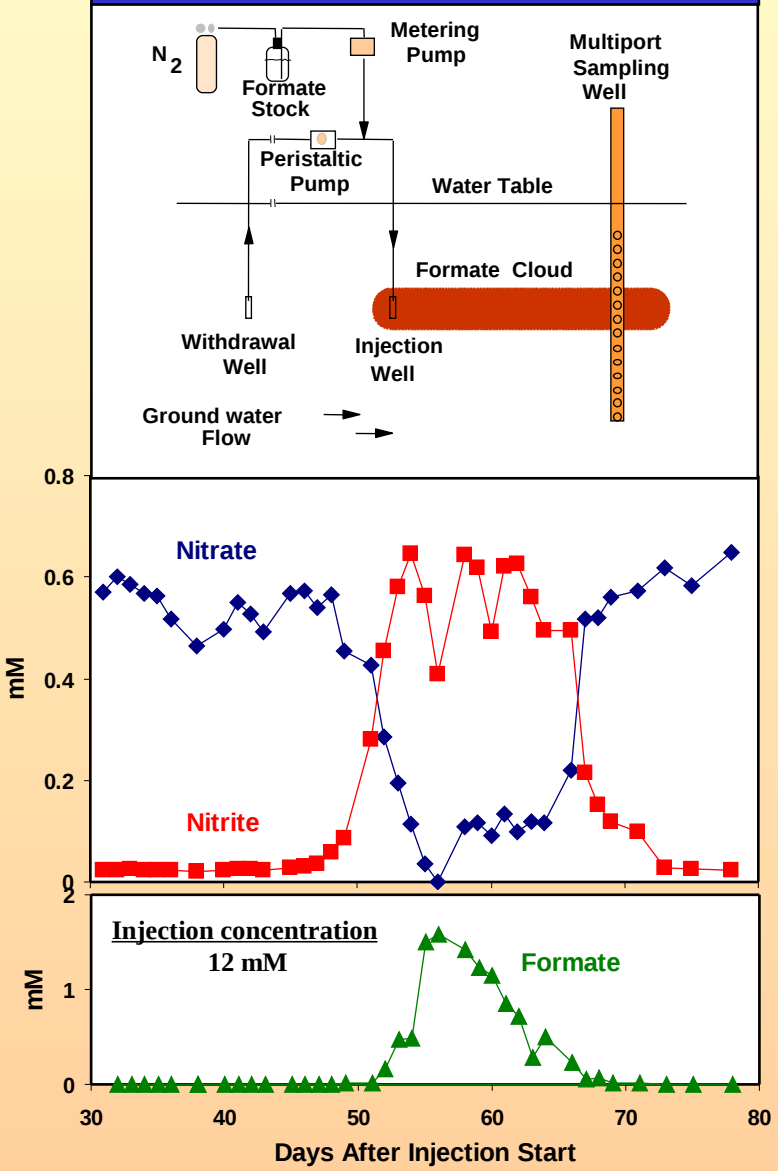
Hydrogen-Oxidizing Denitrifying Bioreactor



Ground Water From Granite Aquifer*



Formate Injection Test



US Patent 6863815; Smith et al, 2005 Wat Res 39:2014; Smith et al, 2001, ES&T 35:196

Future Research Topics

Functional gene assessment and activity assays within an *in situ* context

Nitrogen-cycling processes

- **Anammox**
- **Long term role of nitrification & denitrification in plume**
- **Lithotrophic denitrification**

Natural restoration

Impact of remediation technologies on biogeochemical processes

Degradation at low concentrations of specific wastewater-derived organic compounds

Cape Cod Gravel Pit Sampling Array

Cape Cod Gravel Pit Sampling Array