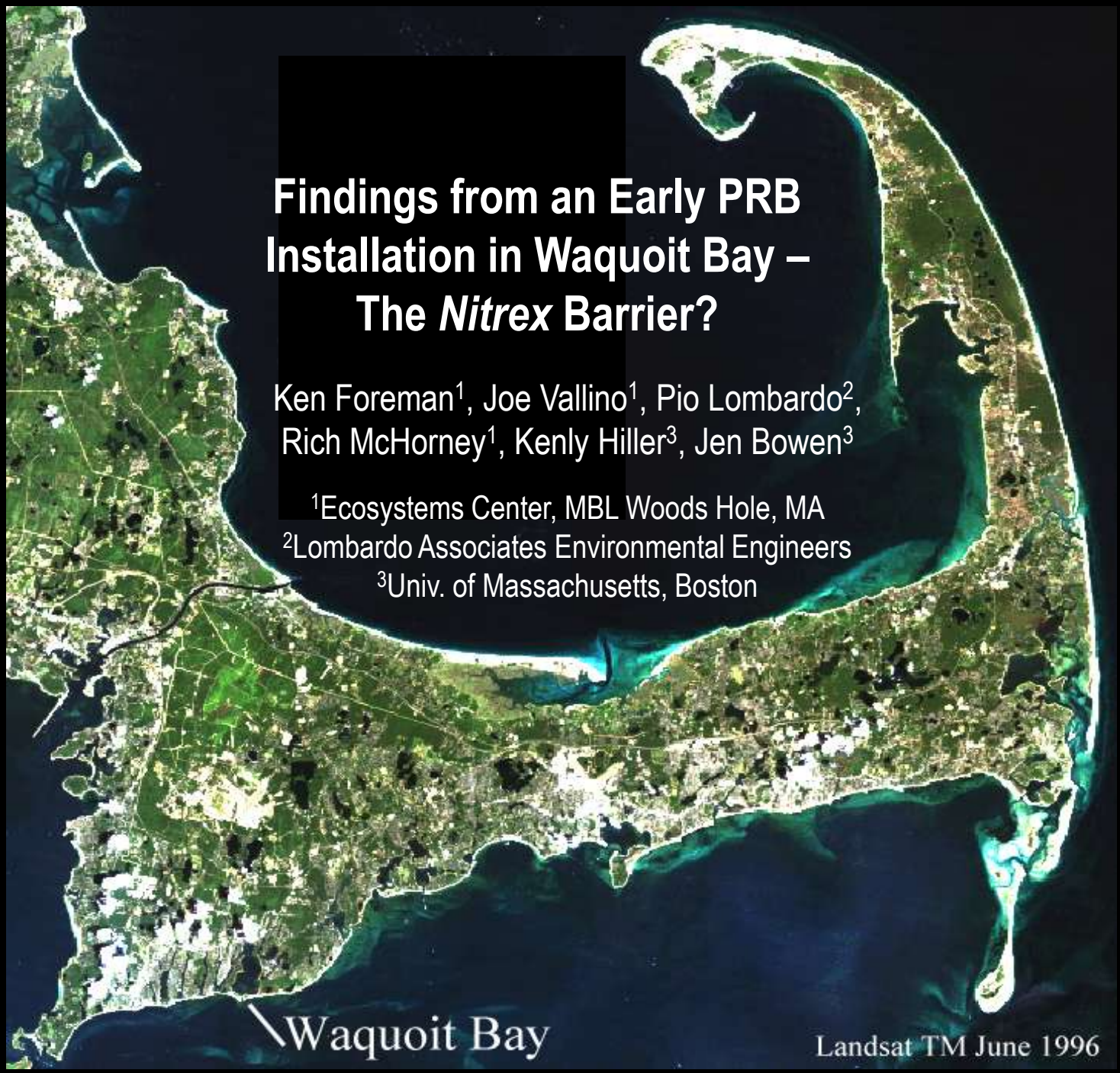
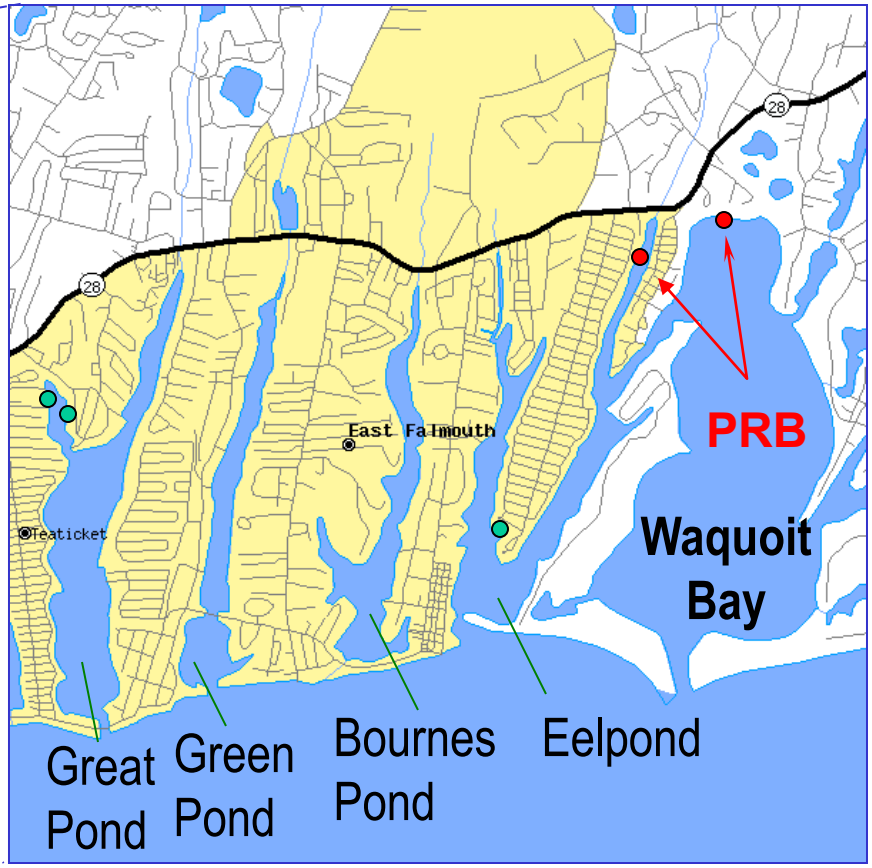


Findings from an Early PRB Installation in Waquoit Bay – The *Nitrex* Barrier?

Ken Foreman[1], Joe Vallino[1], Pio Lombardo[2], Rich McHorney[1], Kenly Hiller[3], Jen Bowen[3]

[1]Ecosystems Center, MBL Woods Hole, MA
[2]Lombardo Associates Environmental Engineers
[3]Univ. of Massachusetts, Boston

In 2005, two test barriers installed in Waquoit Bay & Childs River



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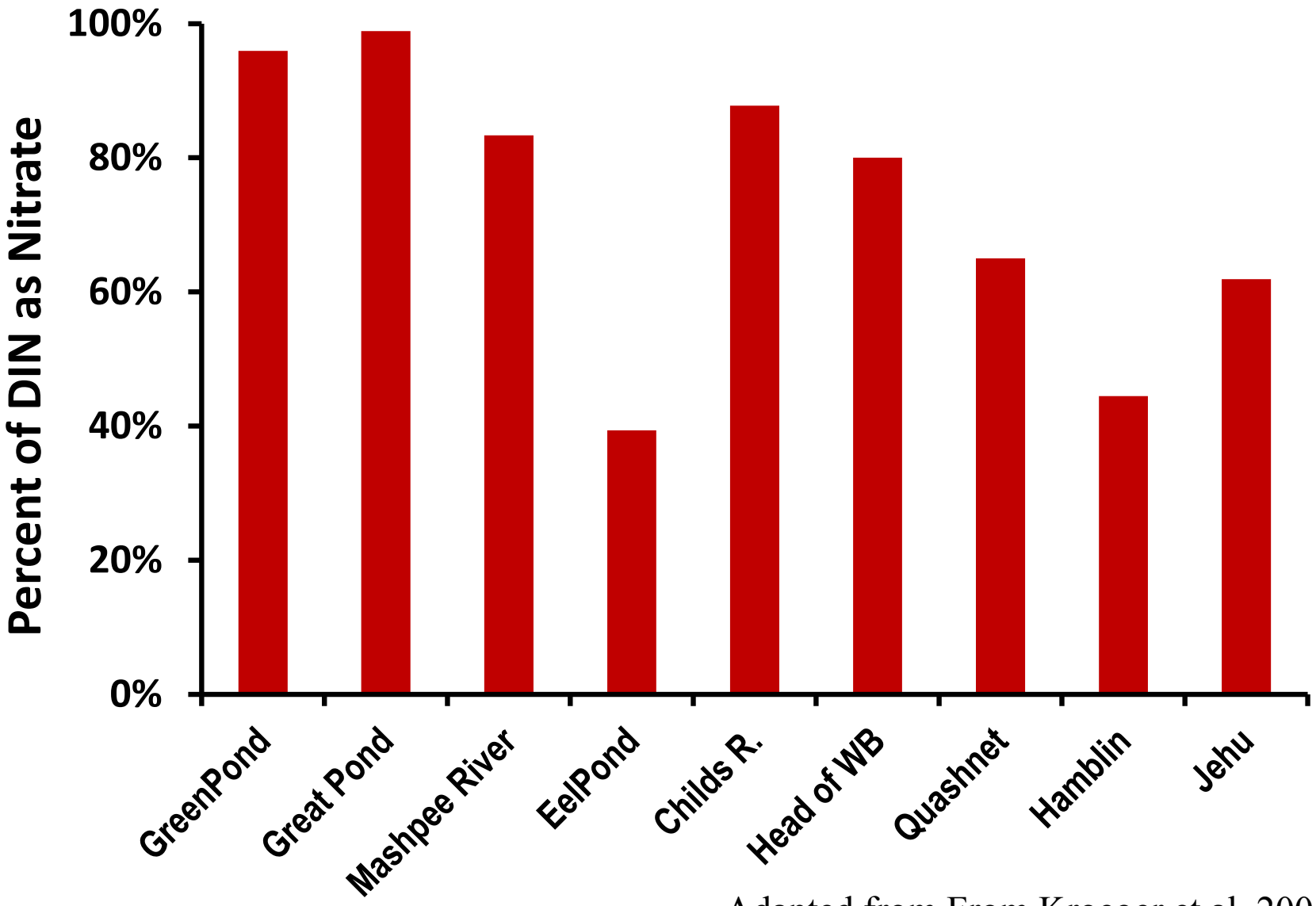
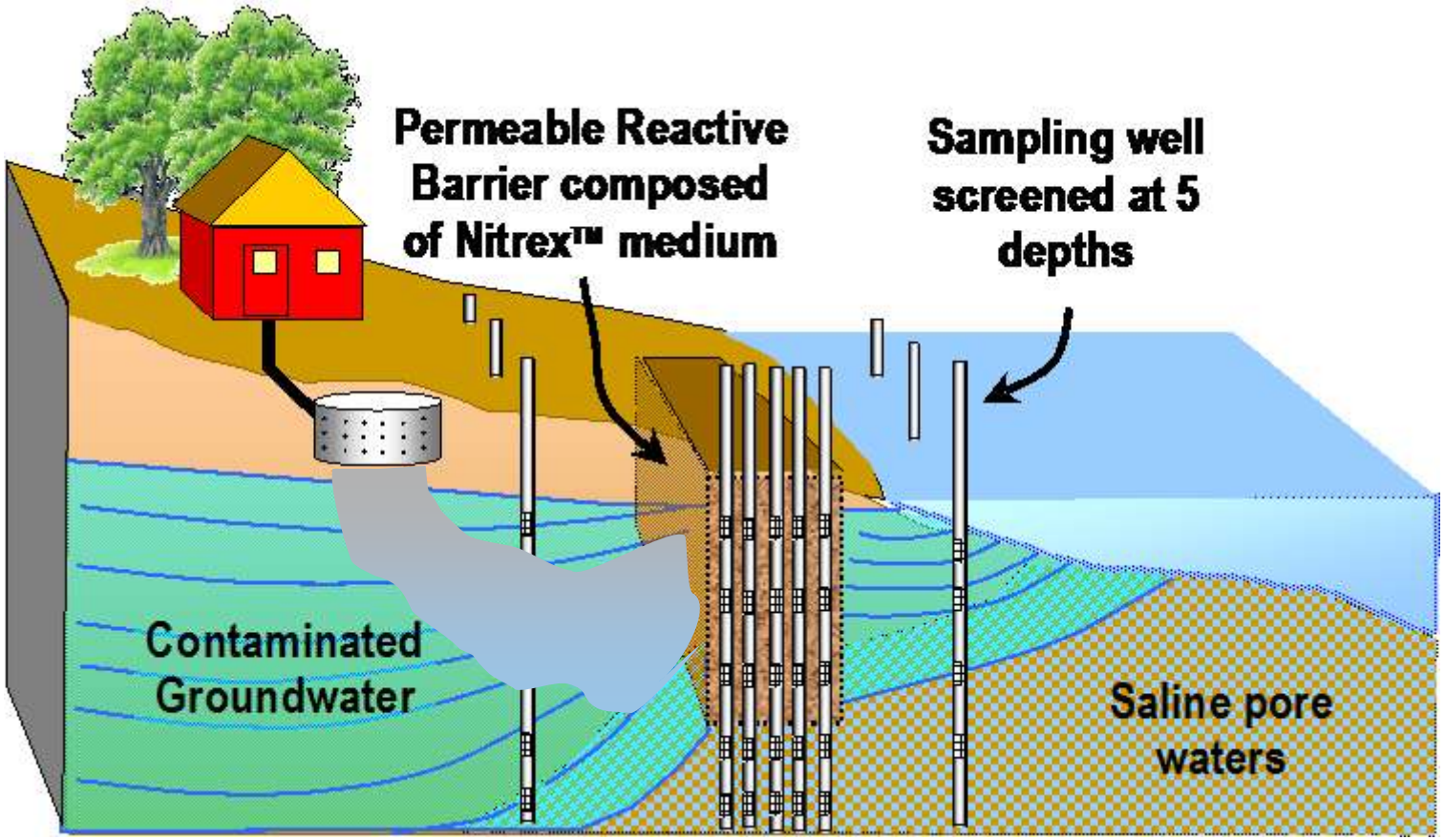
Dissolved Nitrogen in Groundwater on Cape Cod



Adapted from From Kroeger et al. 2006

Schematic diagram showing how **Permeable Reactive Barrier** could be installed at the groundwater / saltwater interface to stimulate denitrification which is limited by Carbon supply

$$5CH_2O + 4NO_3^- \rightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^-$$



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PRB Installations (NITREX™)

Childs River

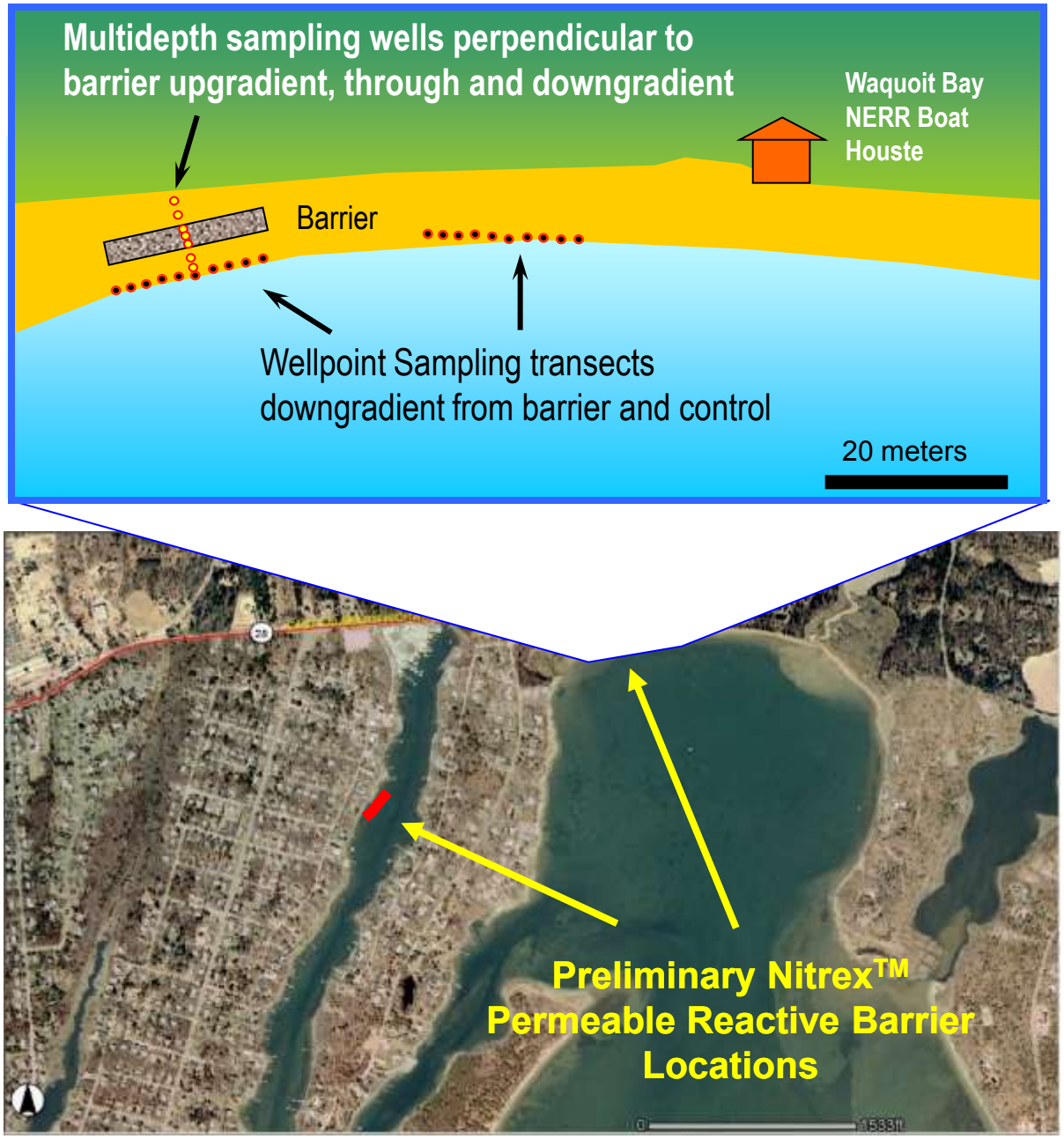
Installed:	Jul 2005
Length:	12 m
Width:	1.8 m
Depth:	1.5 m

WBNERR

Installed:	Aug 2005
Length:	20 m
Width:	3.7 m
Depth:	2.0 m

Sampling Layout

Permanent Wells and Wellpoints



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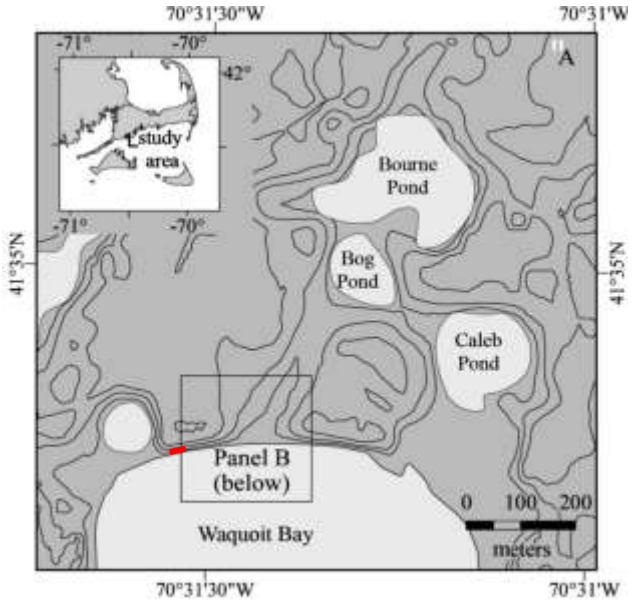
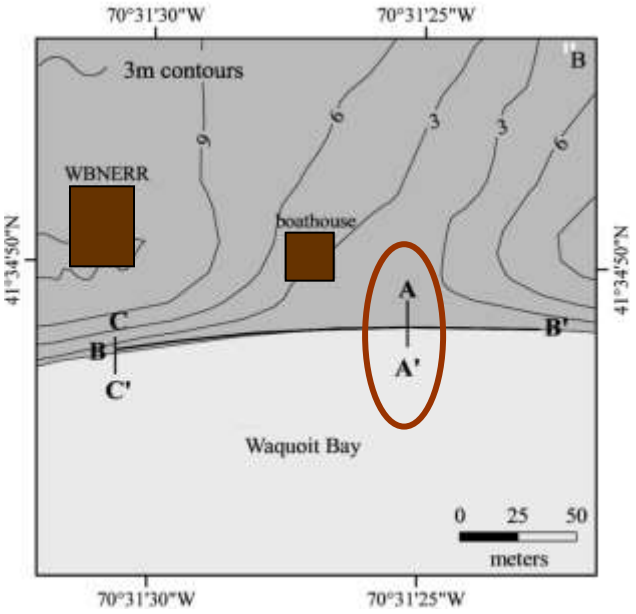
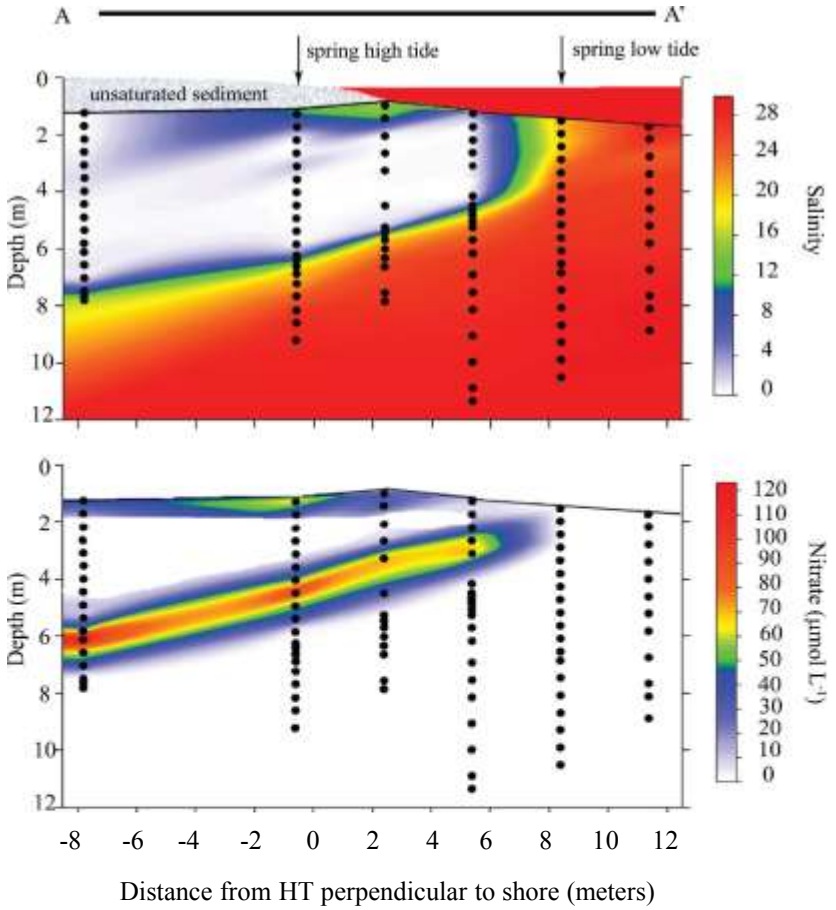
Conditions in Waquoit Bay ideal for testing PRB concept:

- Shallow GW flow through sandy aquifer
- Discrete NO_3 plume
- Underlying sewater forces GW flow upward through seepage face







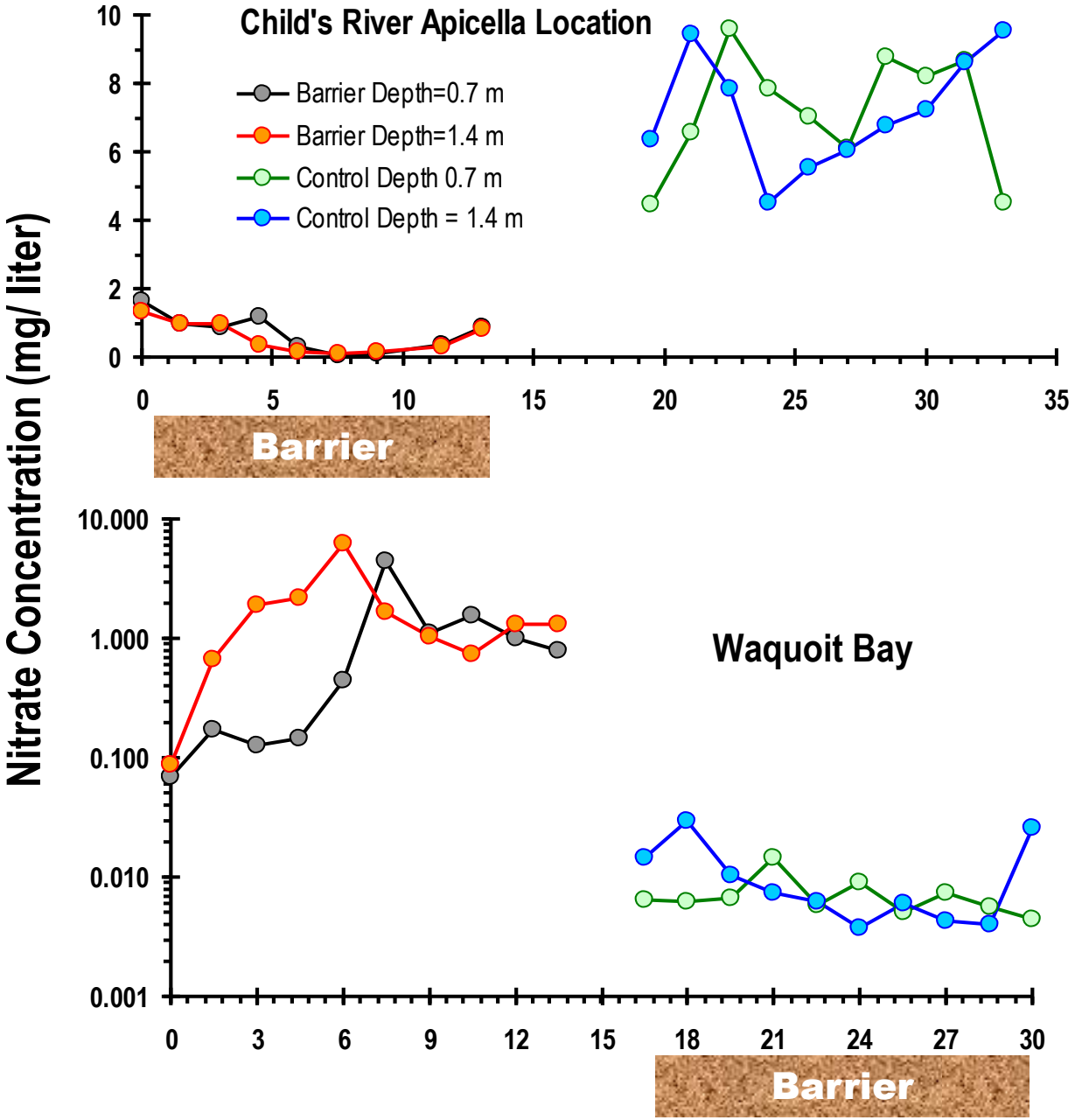
Data from: Kroeger & Charette 2008

Limnol. & Oceanogr. 53:1025-39

Summer 2007

Two years after installation

Wellpoint sampling shows >90% Nitrate removal at beach seepage zone



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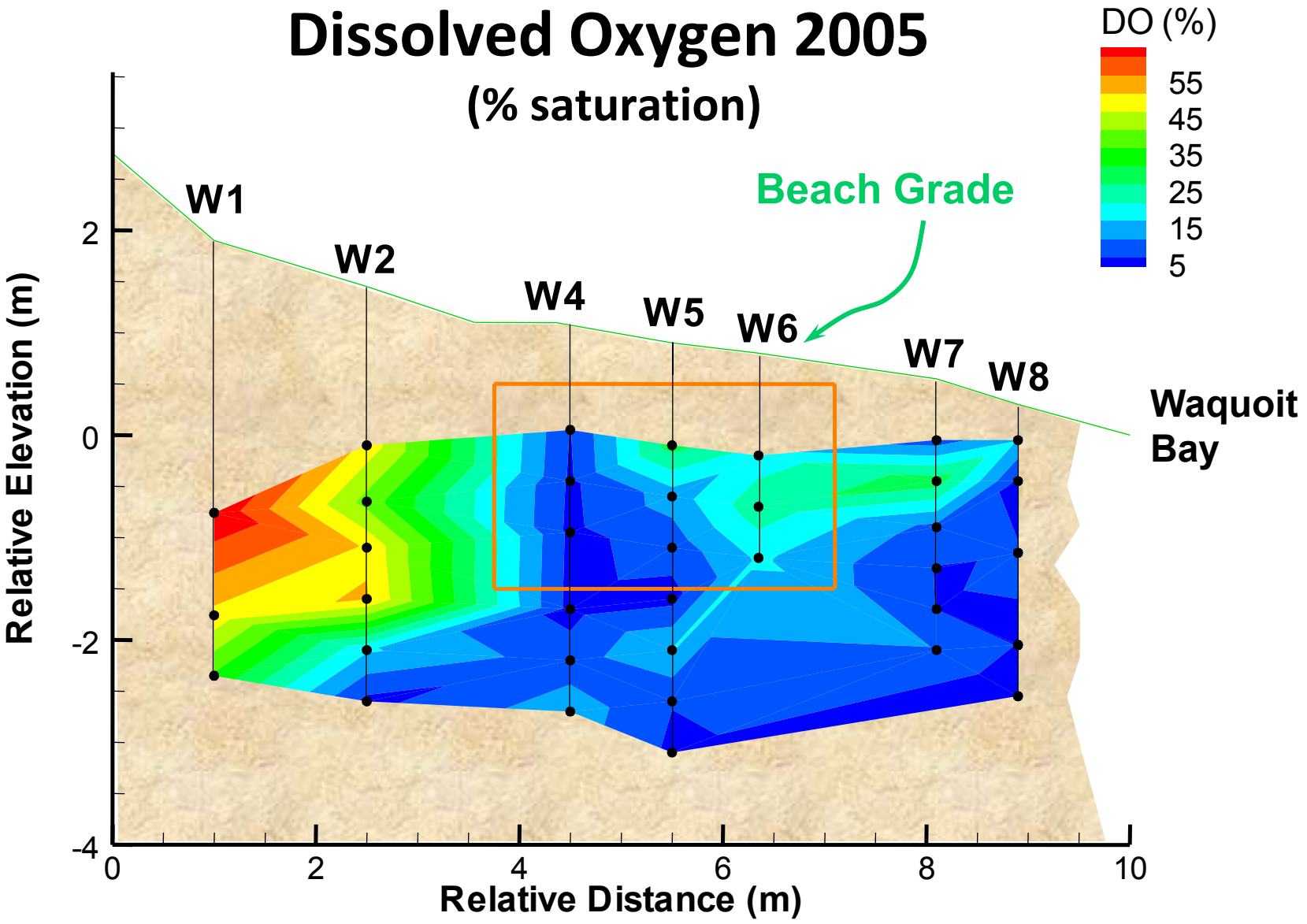

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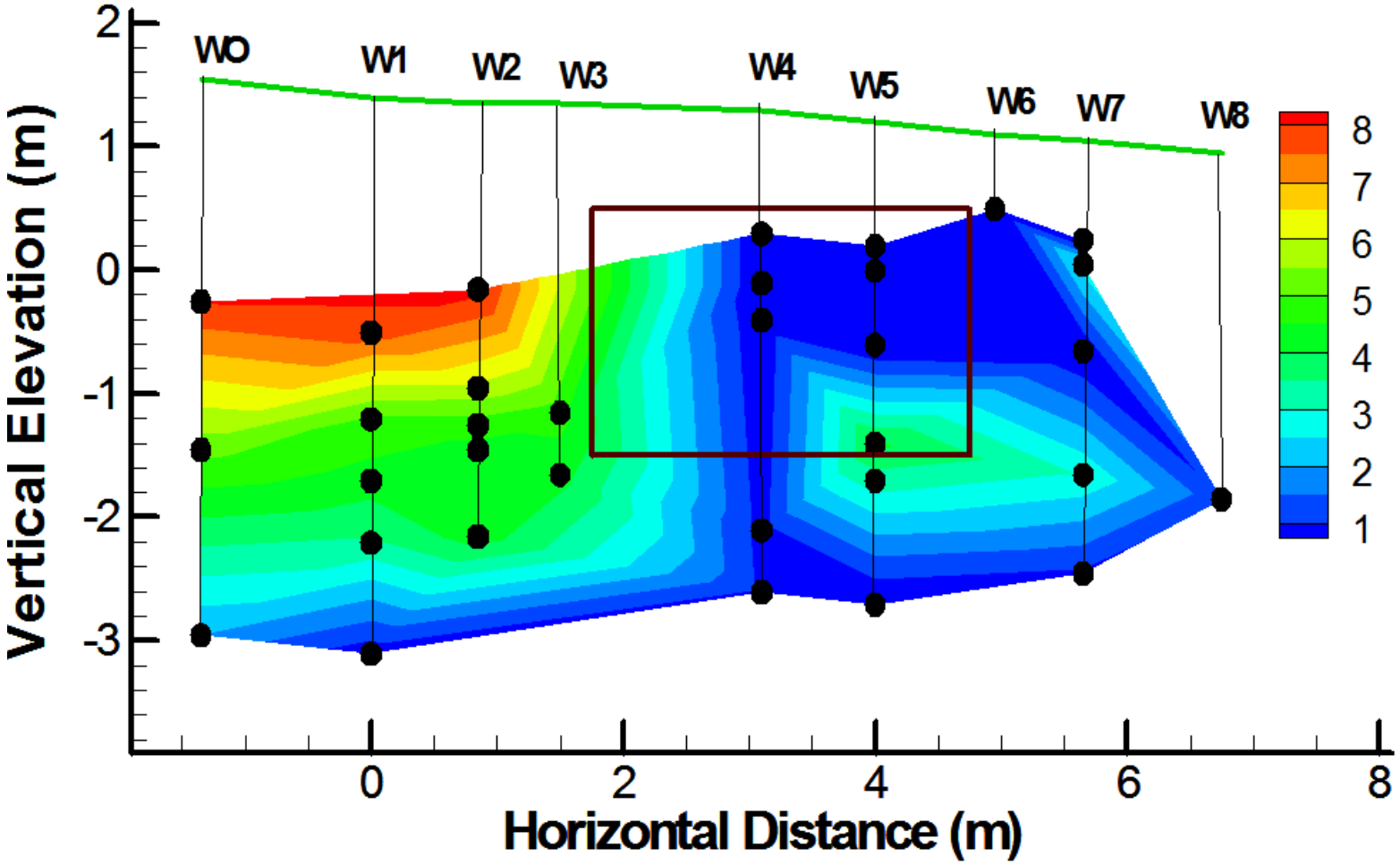
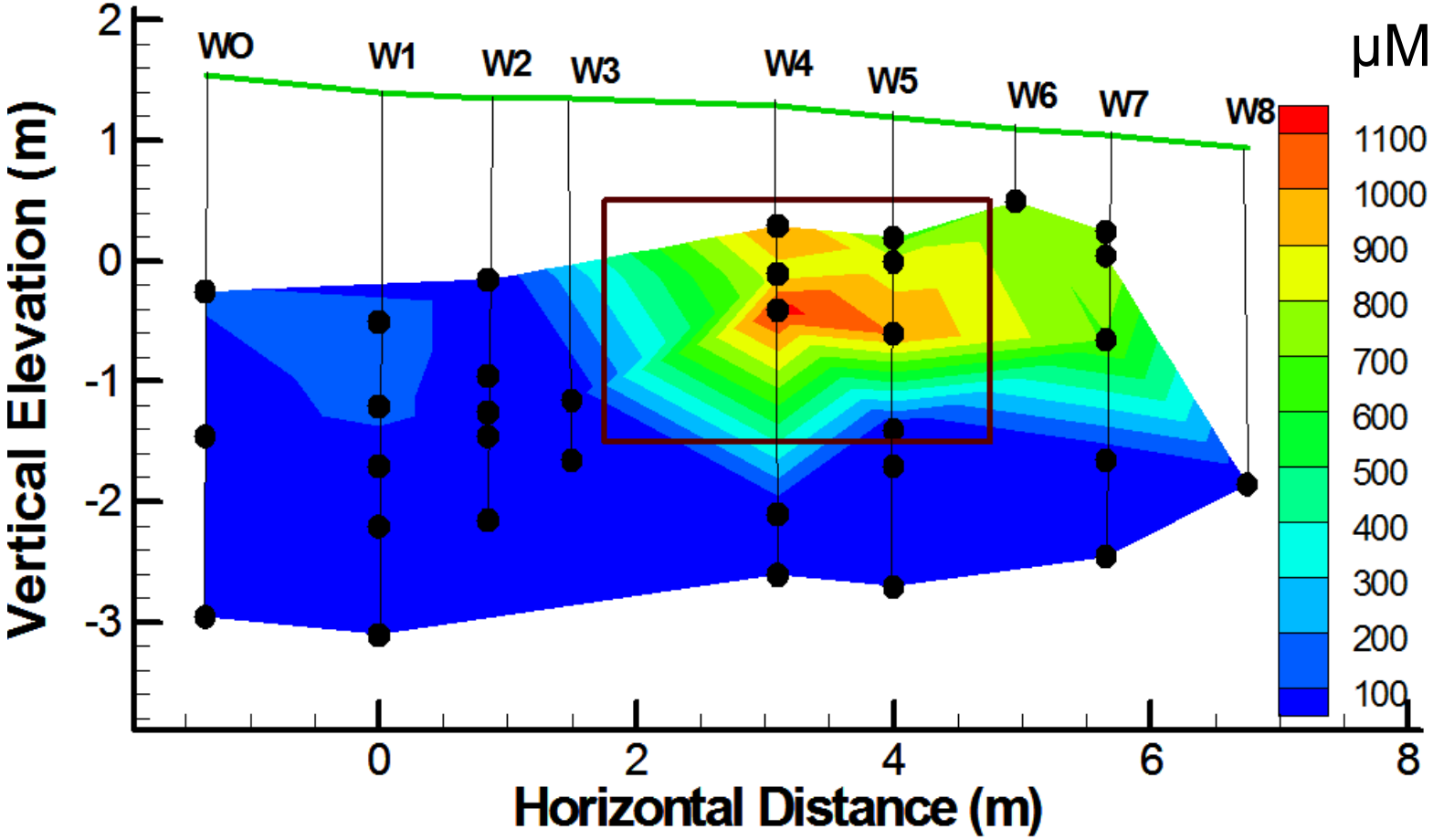
November 2011 ~Six years after installation

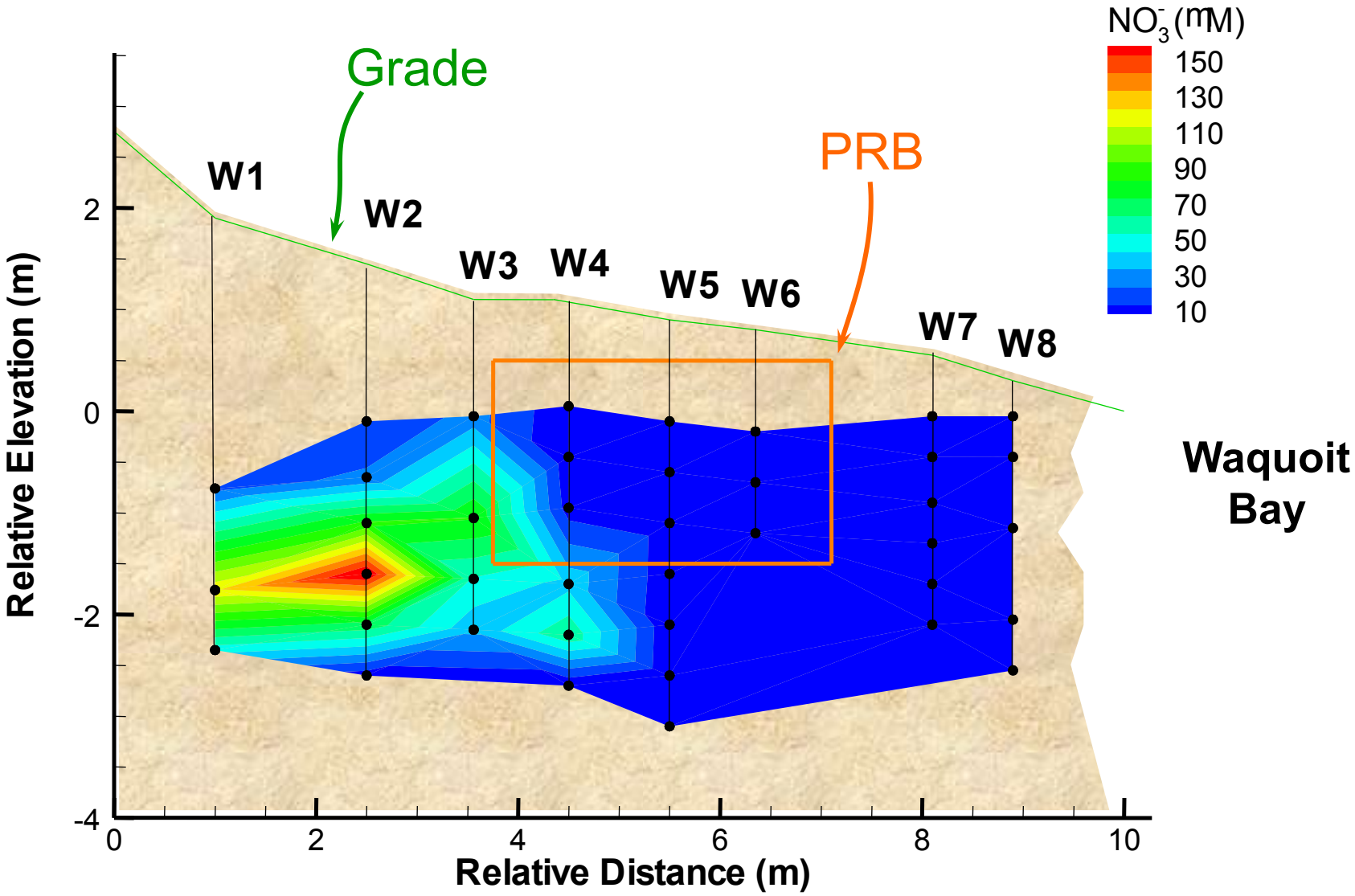
Dissolved Oxygen (mg/L)



Excess Dissolved Inorganic Carbon from decay of wood to CO_2



Disappearance of Nitrate Plume at Barrier - 2005



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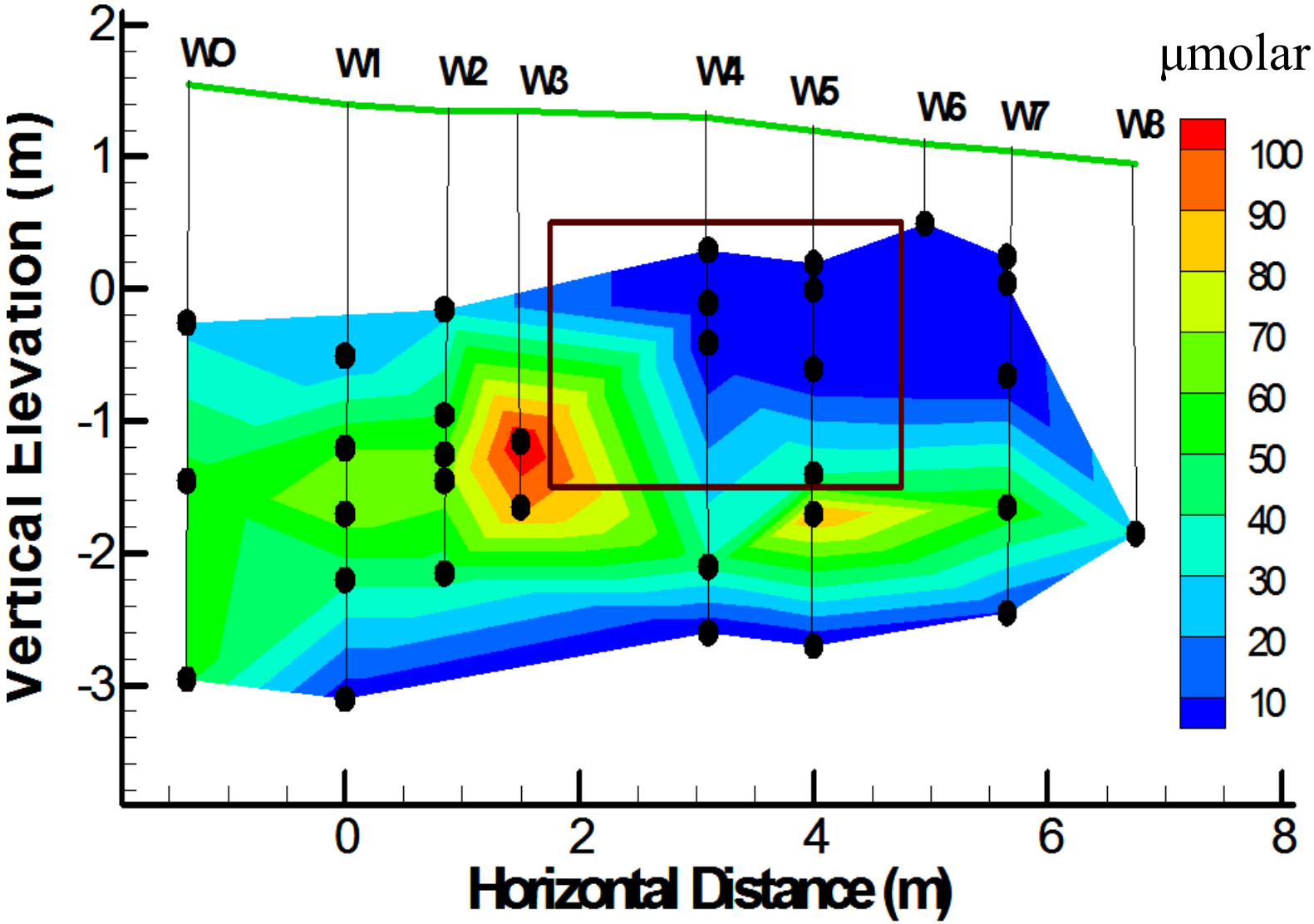
Disappearance of Nitrate Plume at Barrier - 2012



July 2009, algal growth along seepage face inhibited down-gradient from barrier

Photo by Chris Weidman, WBNERR; K. Foreman MBL, Woods Hole, MA 02543

Where did the Nitrate Go?

Three possible fates:

1. Denitrification

$$5CH_2O + 4NO_3^- \longrightarrow 5CO_2 + 2N_2 + 3H_2O + 4OH^-$$

2. Dissimilatory Nitrate Reduction to Ammonia (DNRA)

$$NO_3^- + 2H^+ + 2CH_2O \longrightarrow 2CO_2 + NH_4^+ + H_2O$$

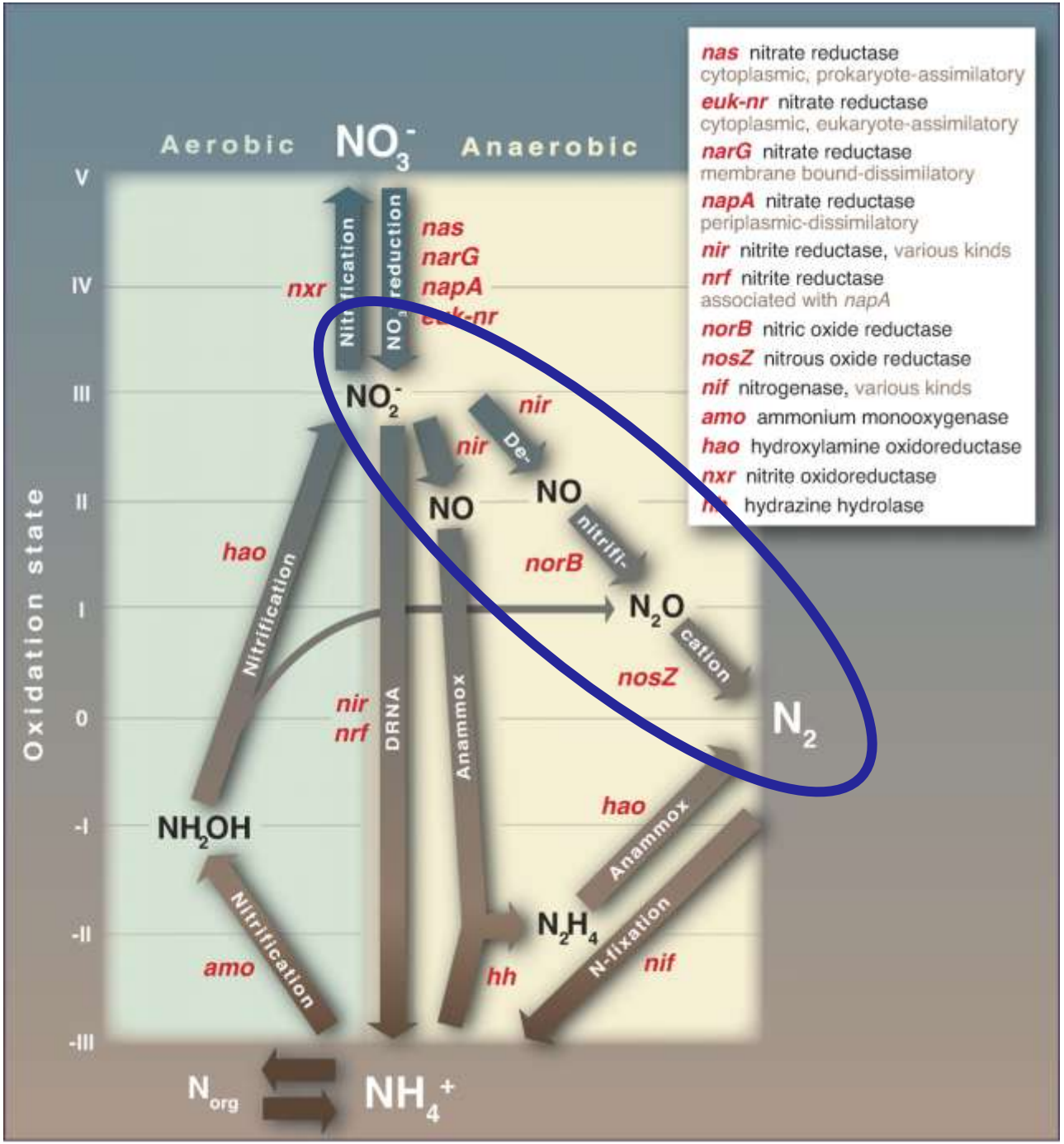
3. N-immobilization in microbial biomass and complexation of N in refractory organic compounds

Complex Biological Nitrogen Transformation Pathways

A great diversity of organisms and enzymes

Aerobic Processes

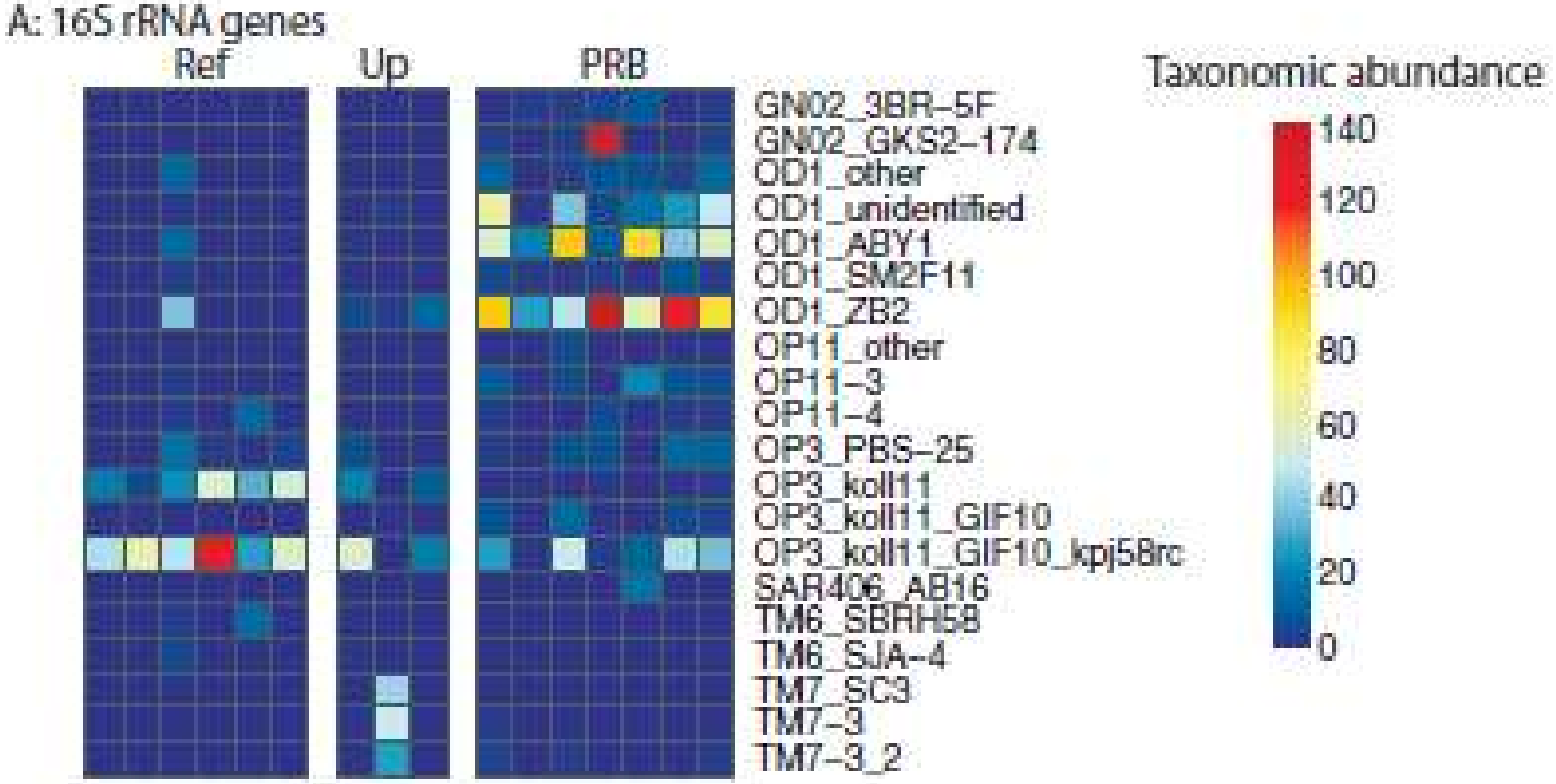
Anaerobic Processes



Science
AAAS

D E Canfield et al.
Science
2010;330:192-196

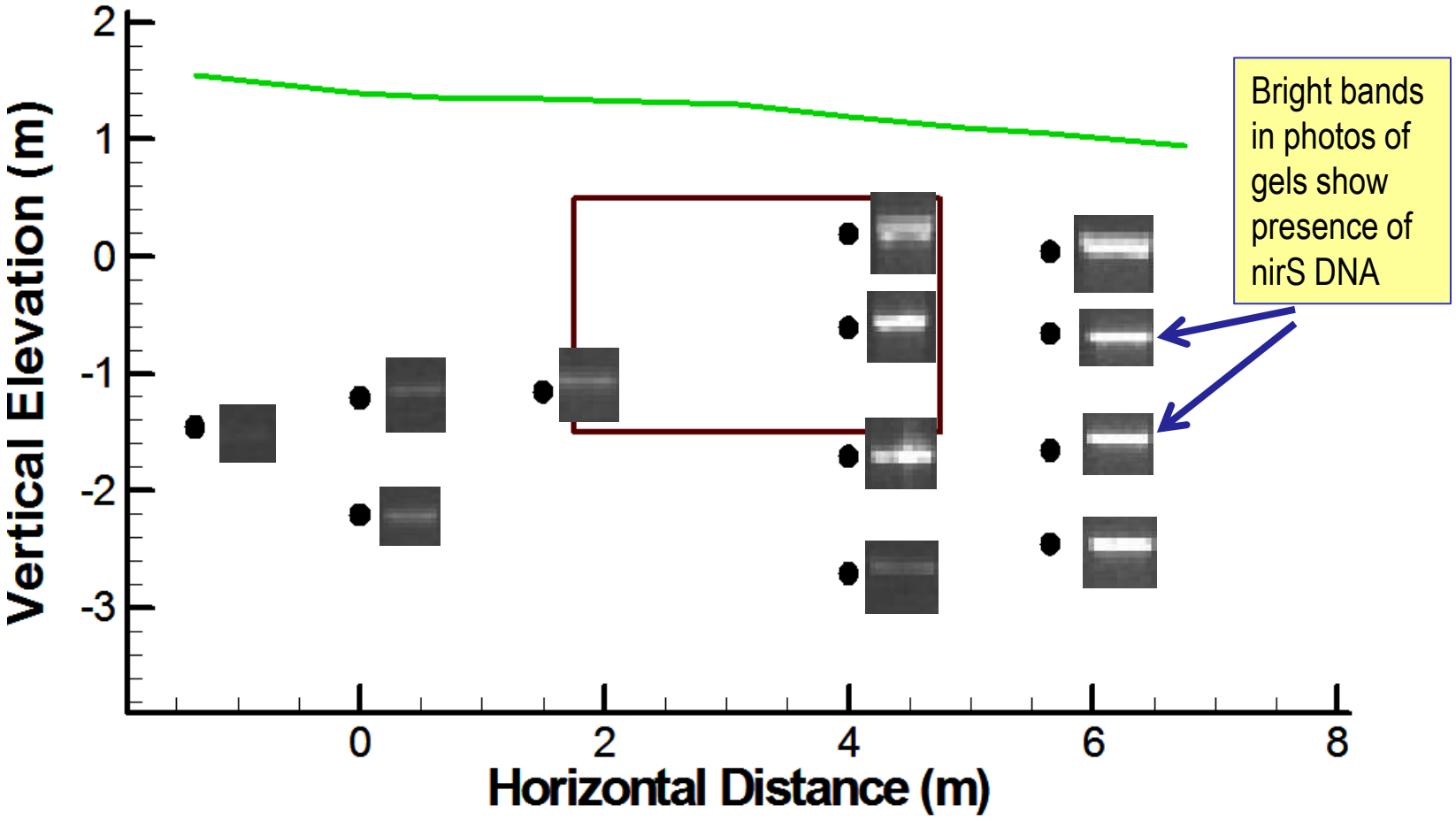
Distinctive Microbial Community Found in PRB
What are they doing?

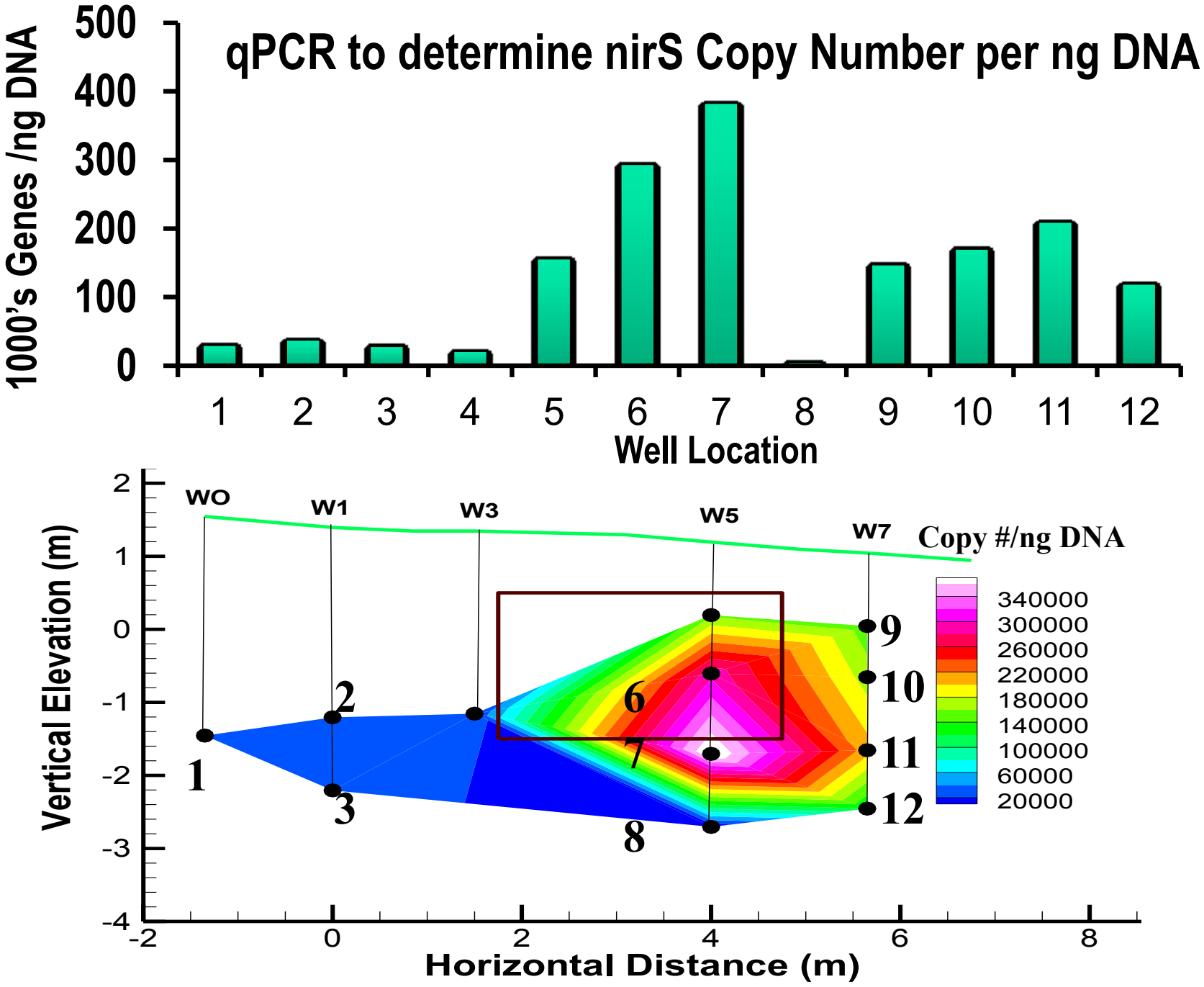


From Hiller et al. 2015

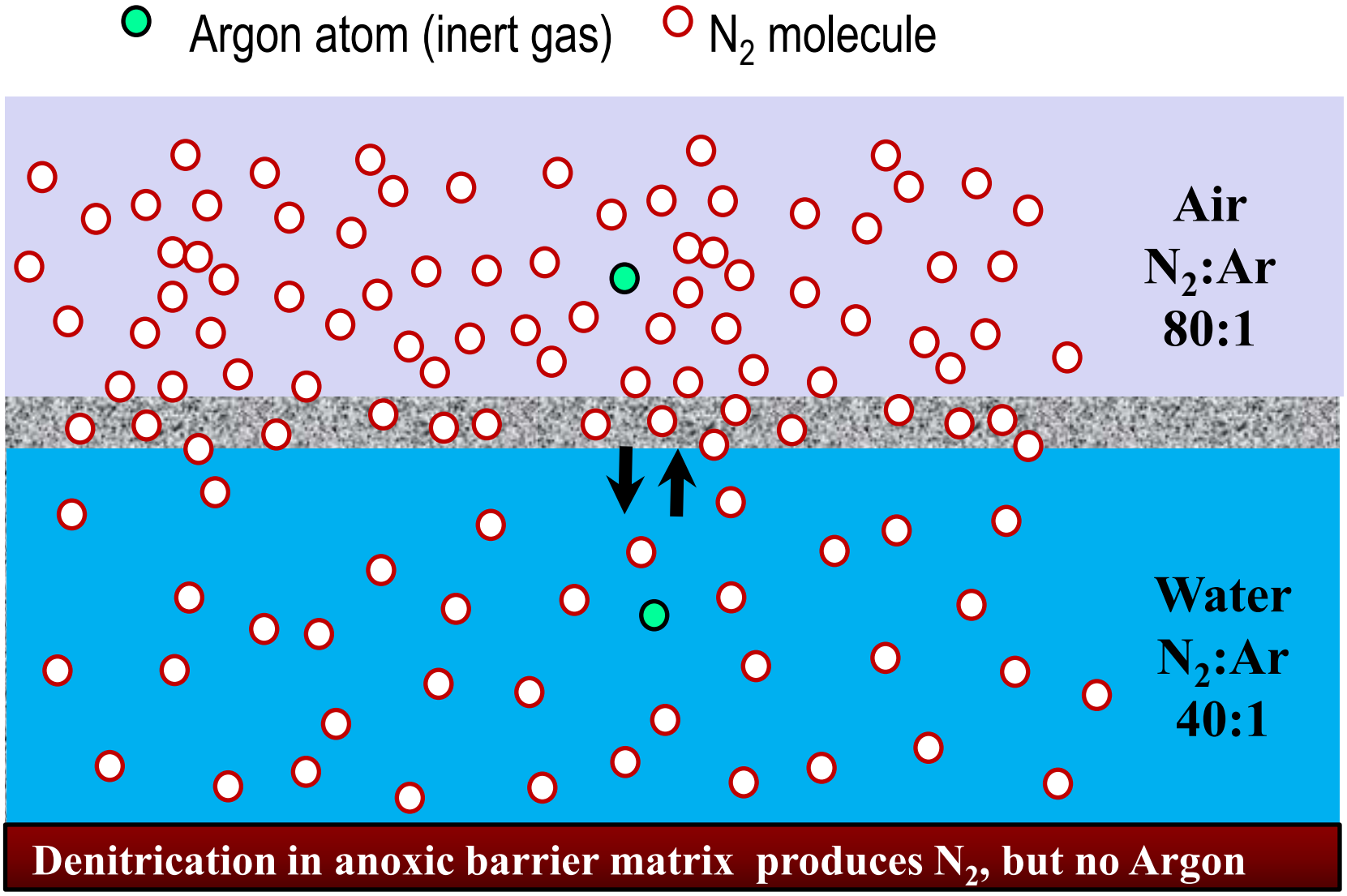
Are the Denitrifying Bacteria there?

Using PCR, amplify DNA from microbes in groundwater sampled from the wells for the nirS (denitrifying) gene.



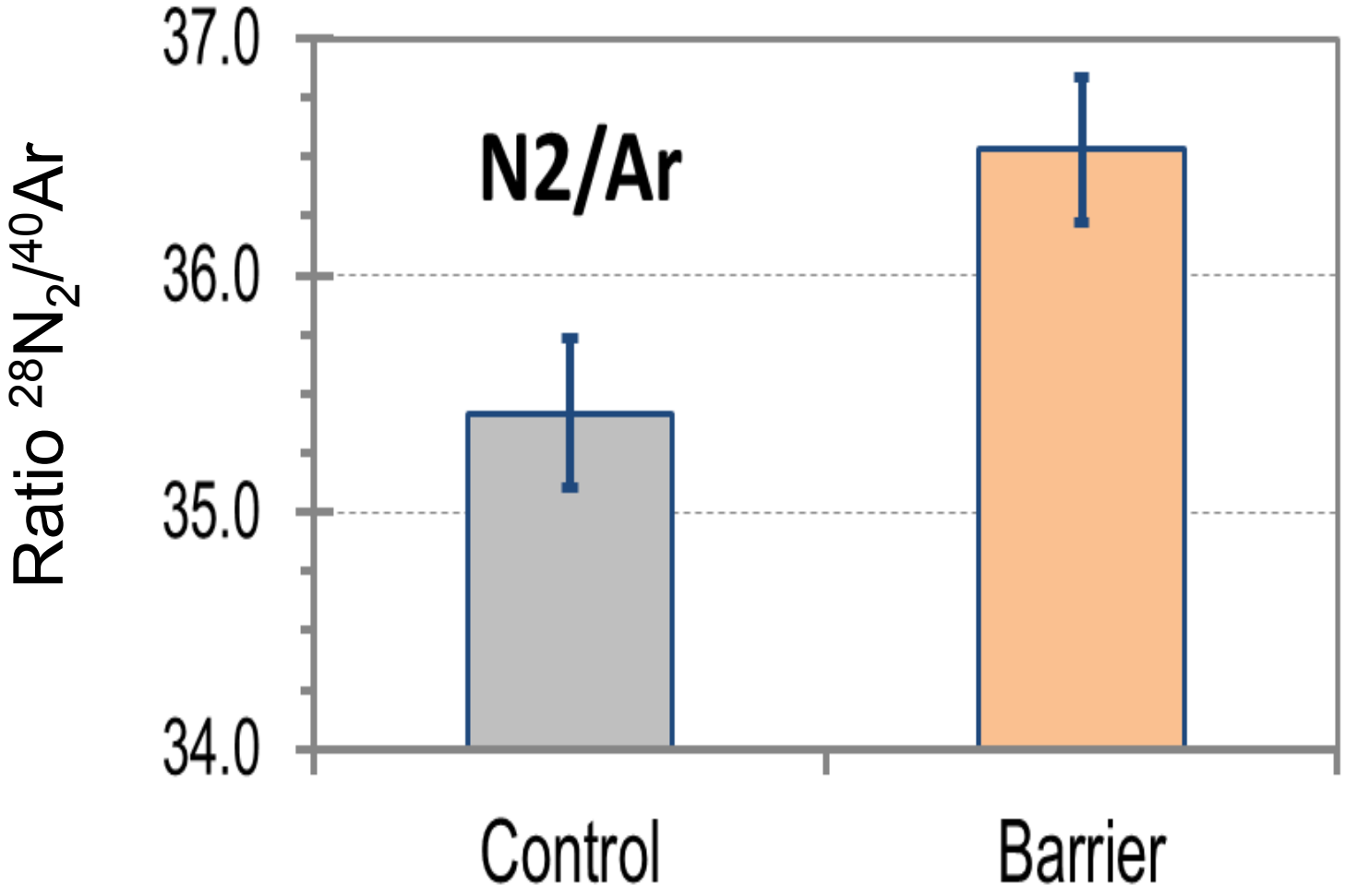

qPCR to determine nirS Copy Number per ng DNA
1000's Genes /ng DNA
500
400
300
200
100
0
1
2
3
4
5
6
7
8
9
10
11
12
Well Location
Vertical Elevation (m)
2
1
0
-1
-2
-3
-4
-2
0
2
4
6
8
Horizontal Distance (m)
WO
W1
W3
W5
W7
Copy #/ng DNA
340000
300000
260000
220000
180000
140000
100000
60000
20000
1
2
3
6
7
8
9
10
11
12

Evidence for and Quantificaton of Denitrification
N_2 / Ar Equilibrium and Ratio



Excess N_2 in Groundwater at PRB from Denitrification

Quantified by Membrane Inlet Mass Spectrometry (MIMS)



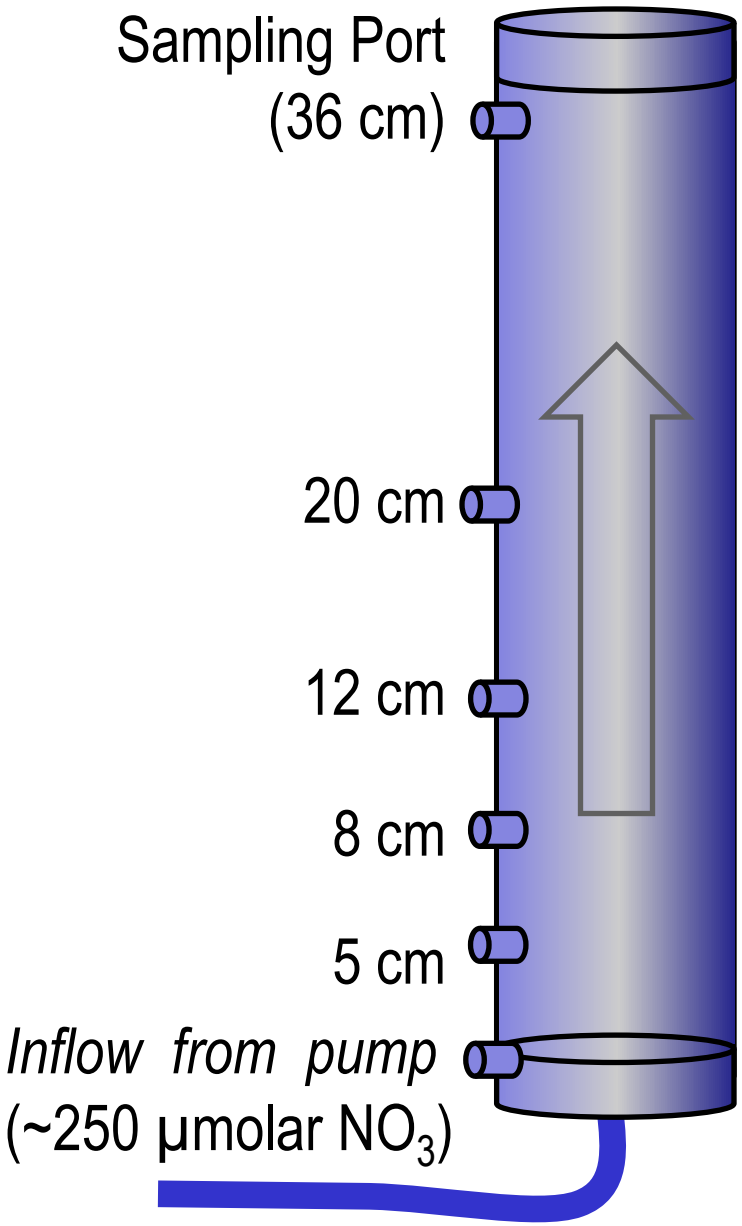
Core Microcosm Experiments 2015

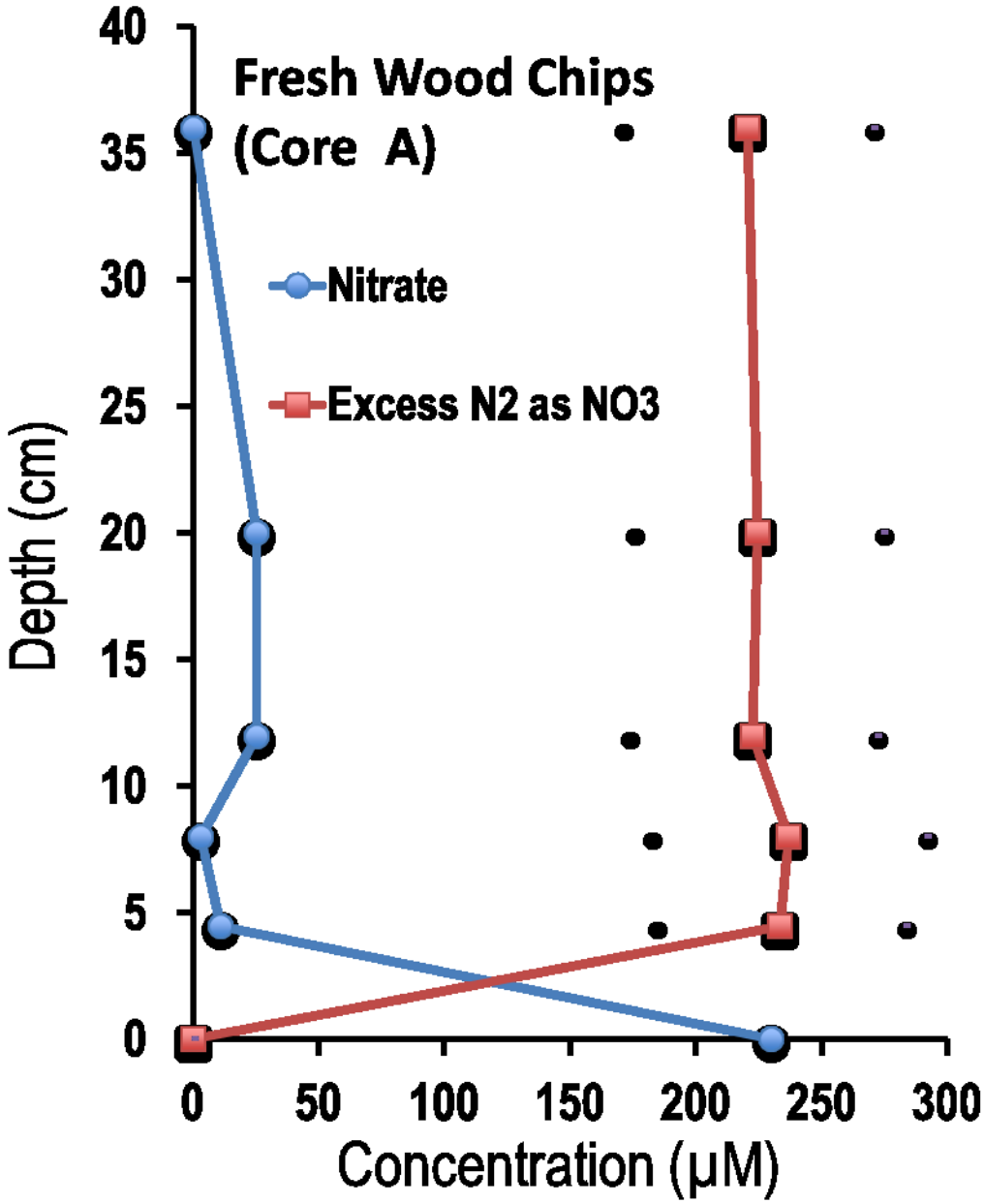
Excavate wood chips from PRB after 10 years

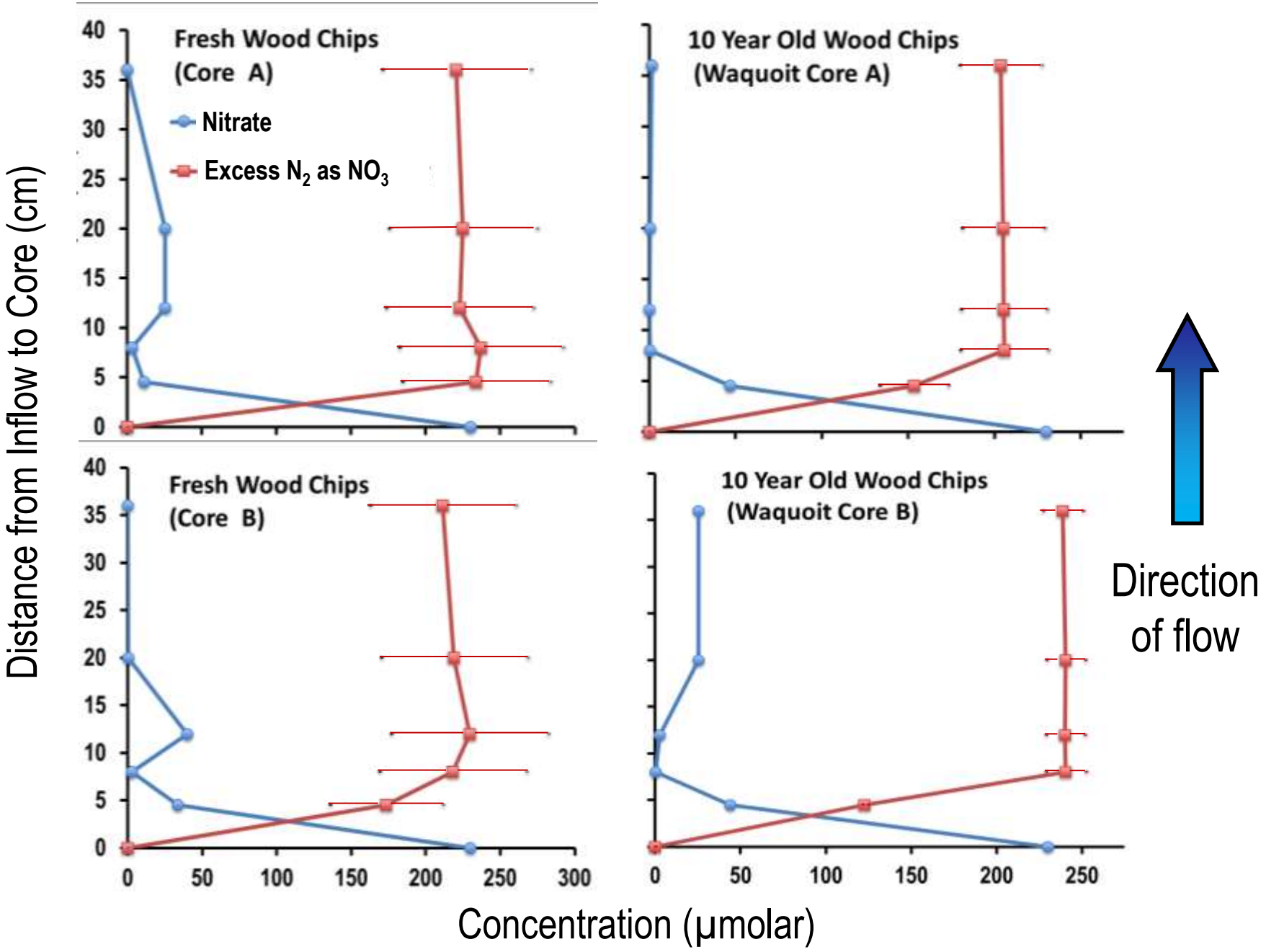
Incubate in cores with groundwater amended with Nitrate (final concentration ~250 µmolar, approx. 3.5 mg/l) flowing through cores

Measure **Nitrate *inflow*** and **Nitrate *outflow***

Core Microcosm






Fresh Wood Chips
(Core A)
Nitrate
Excess N_2 as NO_3
10 Year Old Wood Chips
(Waquoit Core A)
Fresh Wood Chips
(Core B)
10 Year Old Wood Chips
(Waquoit Core B)
Distance from Inflow to Core (cm)
Concentration (µmolar)
Direction of flow
0
5
10
15
20
25
30
35
40
0
50
100
150
200
250
300

On-Going Questions / Problems?

- What components of the microbial community are altered and how can their function be optimized
- How long will the PRB last?
- How to deal with permitting issues / property rights?
- Will barrier capture most of groundwater flow at shore in most settings?
- What are best engineering strategies for placement and construction?

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Thanks to:

Co-Investigators:

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(Lombardo Associates, Newton, MA)

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Dan Feinberg (Hamilton College)
Kenly Hiller (Connecticut College)
Collin Knauss (Colorado College)
Jesse Kunke (Northwestern University)
Kaitlyn Lucey (Wellesley College)
Sarah Messenger (Trinity College)
Kim Meneo (Connecticut College)
Sabrina Moreau (Hampshire College)
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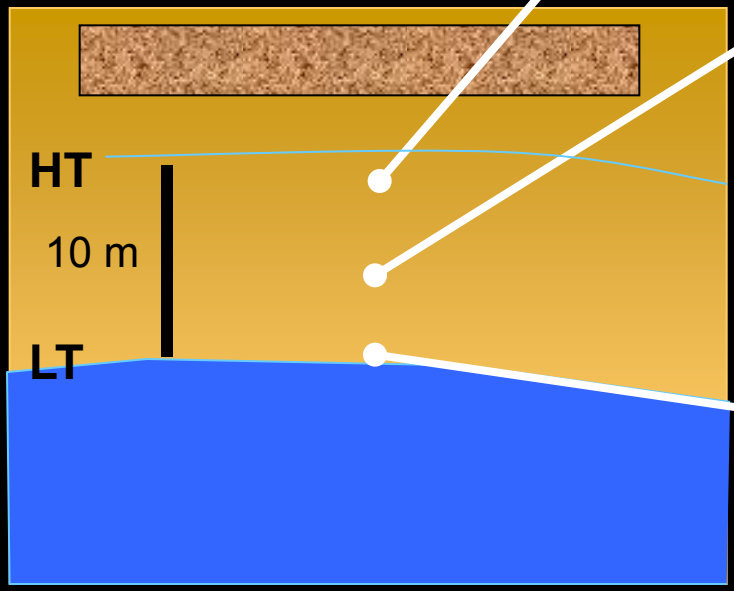
Jen Reimer (Clark University)
Angela Vincent (Grinnell College)
Maggie Waldron (Lawrence University)

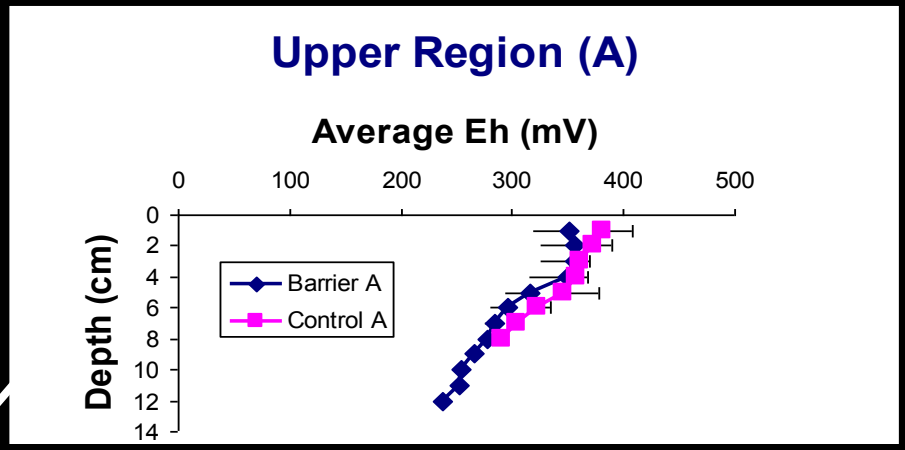
Funded by:
***C**ooperative **I**nstitute for **C**oastal and **E**stuarine **E**nvironmental **T**echnology (CICEET) and*
The National Science Foundation

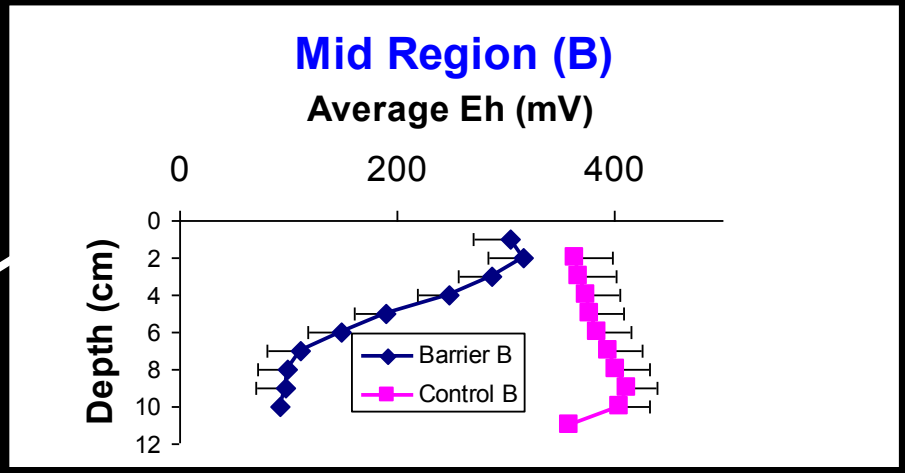
Down-gradient Effects of Barrier

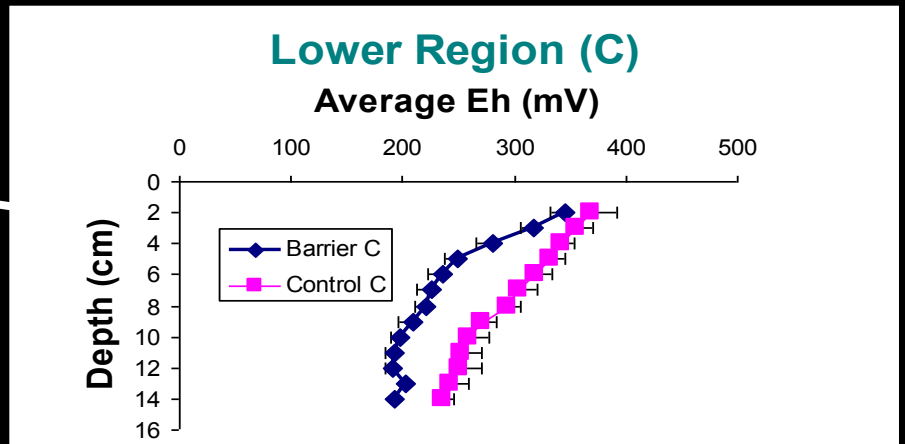
Pt electrode measurements of Redox Potentional (Eh)

lower Eh values = high sulfide activities - indicates anoxia

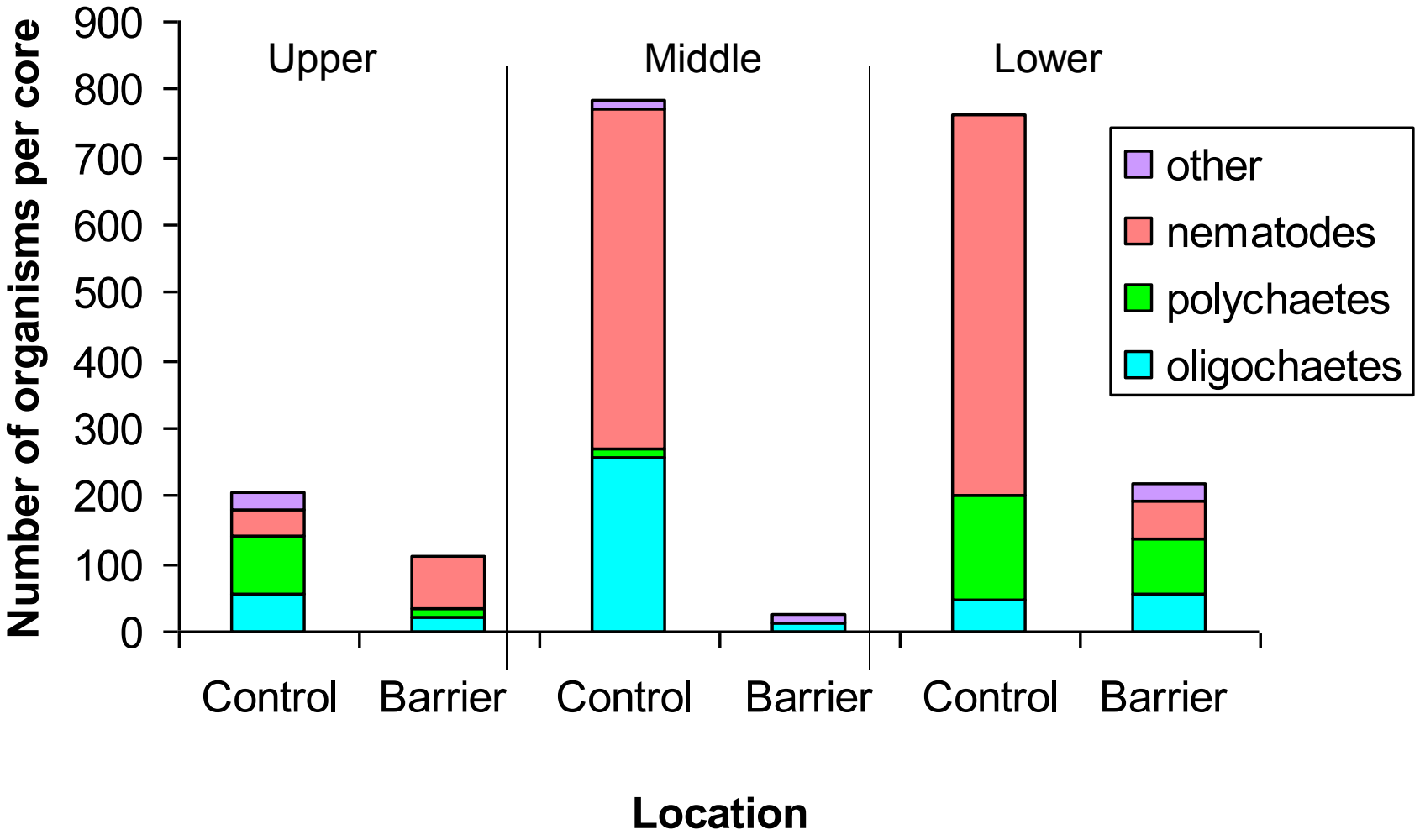




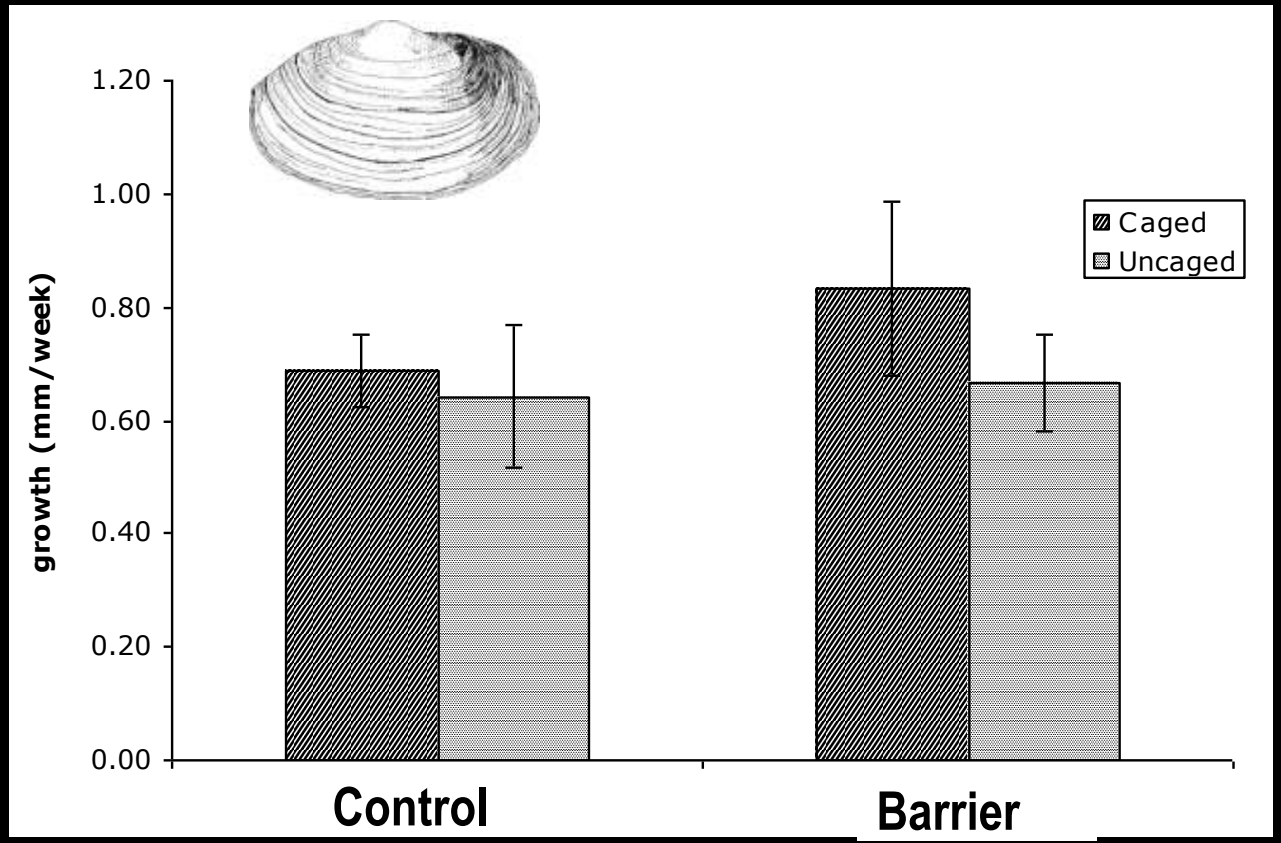




Benthic Infauna Abundance



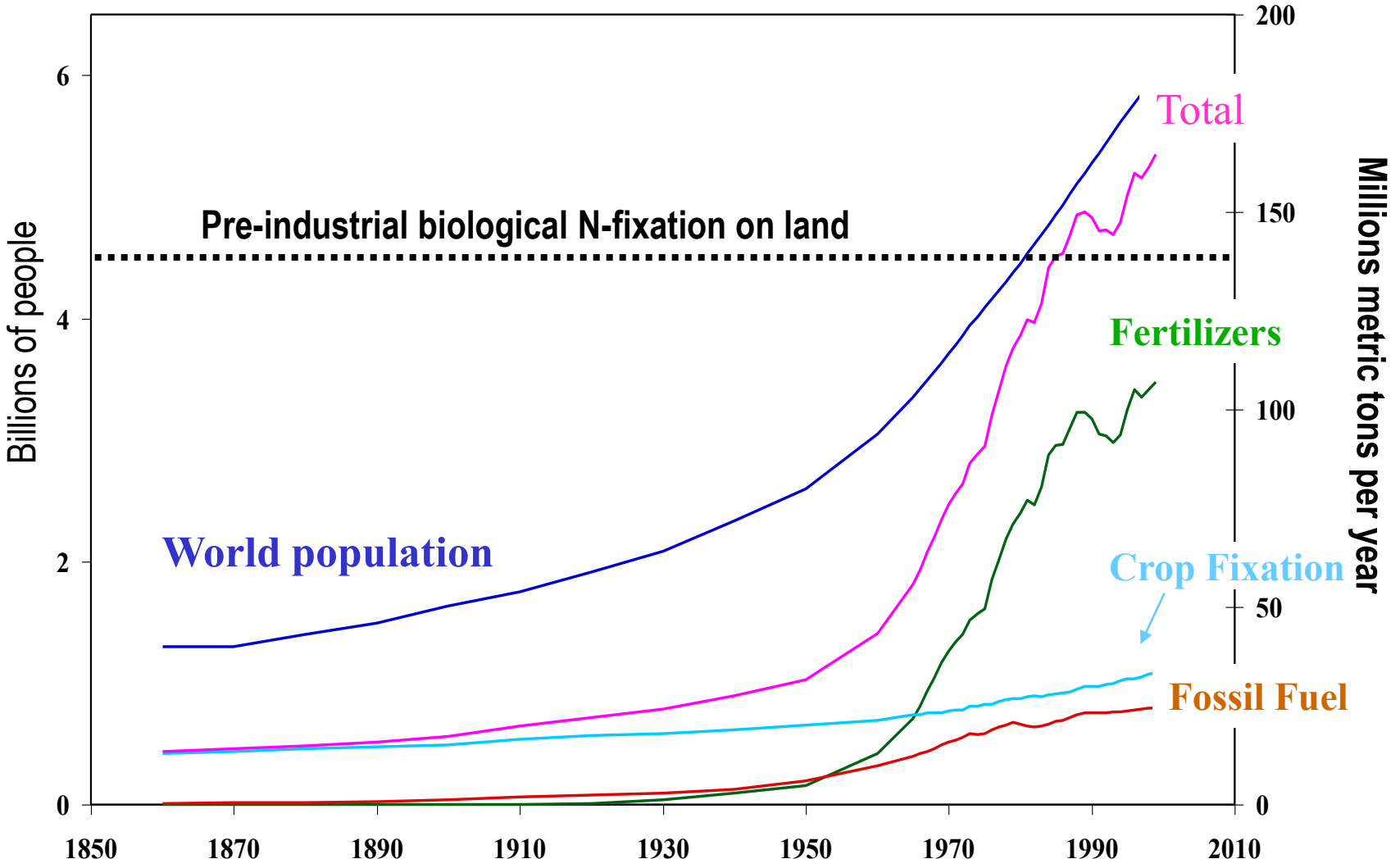
Down-gradient effects of barrier on soft-shell clam growth



Average linear growth of clam *Mya arenaria* per week was **not different** when compared by site and treatment, in October 2007 after ~3.0 months in Waquoit Bay. Error bars indicate +/- 1 standard error for the growth period.

Data courtesy Maggie Waldron (Lawrence University), K. Foreman (MBL)

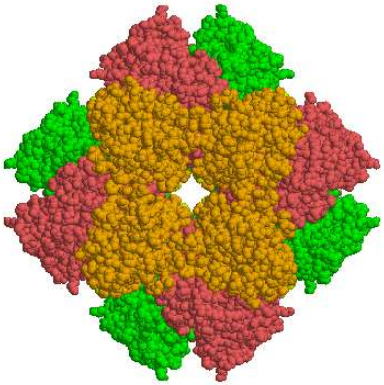
Anthropogenic Sources of New Reactive Nitrogen



Galloway et al. 2002

Living things need Nitrogen to grow and flourish

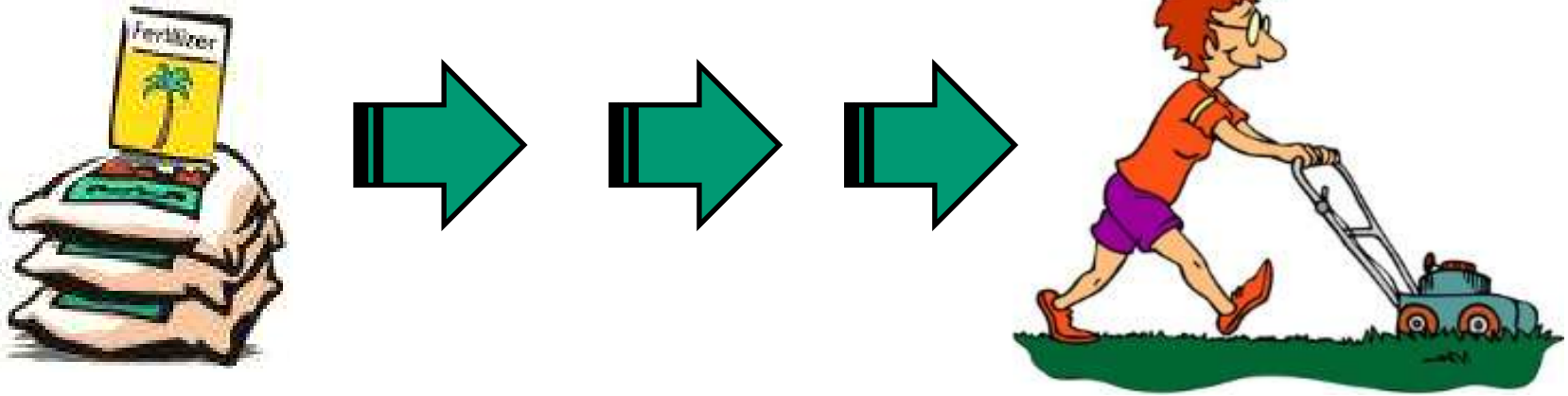
Proteins made up of amino acids are generally ~17% N by weight.



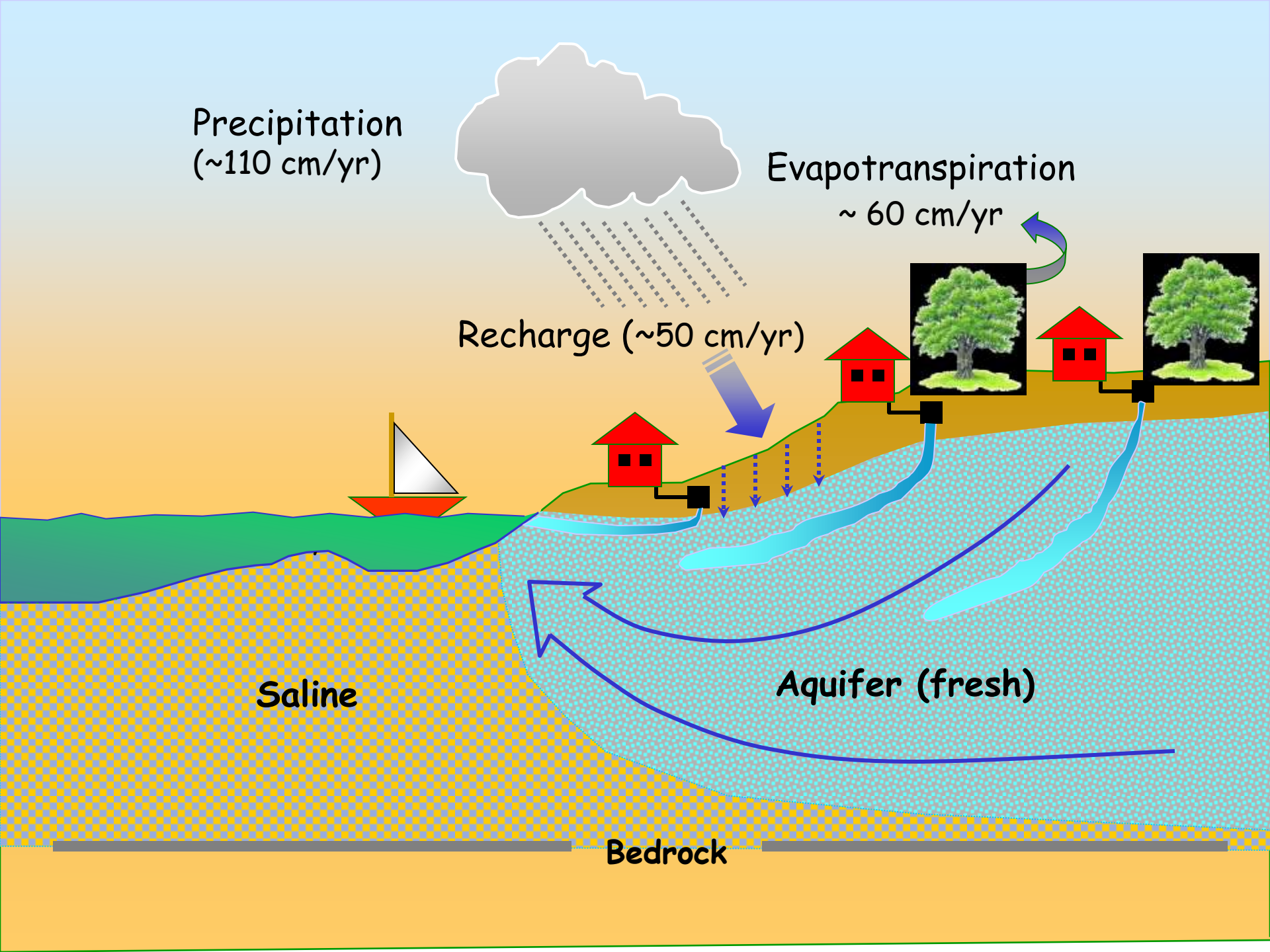
RUBISCO -- the enzyme that catalyzes the fixation of carbon dioxide and is present in all photosynthetic organisms.

Most abundant protein on Earth (~ 40 million tons globally).

Leaves of land plants typically contain 2-5% N by weight, and most of this is Rubisco. Phytoplankton 8% N by weight, half of this Rubisco.



Waquoit Bay and tributary estuaries


Precipitation
(~110 cm/yr)
Evapotranspiration
~ 60 cm/yr
Recharge (~50 cm/yr)
Saline
Aquifer (fresh)
Bedrock

Massive algal blooms fueled by excess nutrients

Photo C. Weidman

History of Development on Seacoast Shores Peninsula

1938

History of Development on Seacoast Shores Peninsula

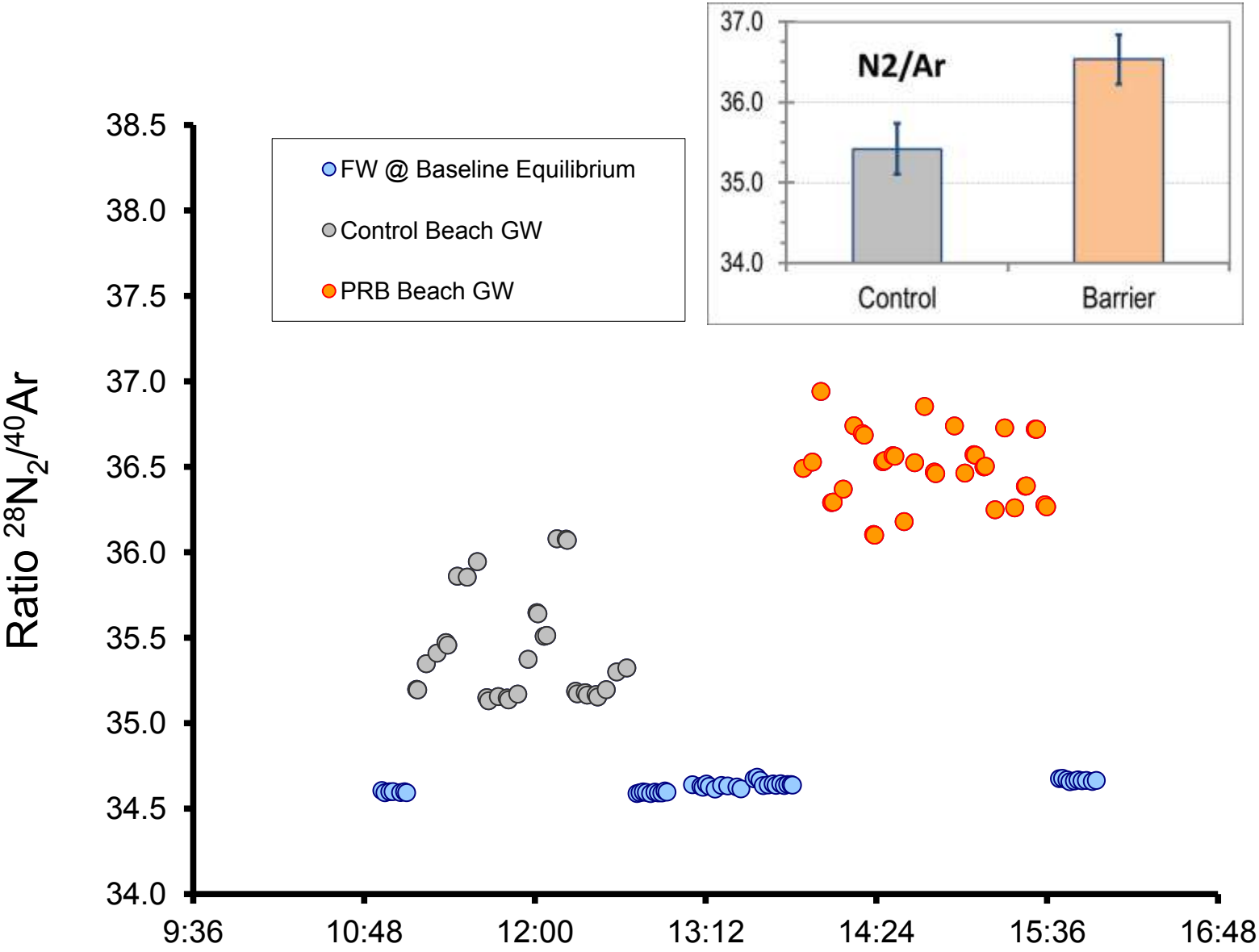
1950's

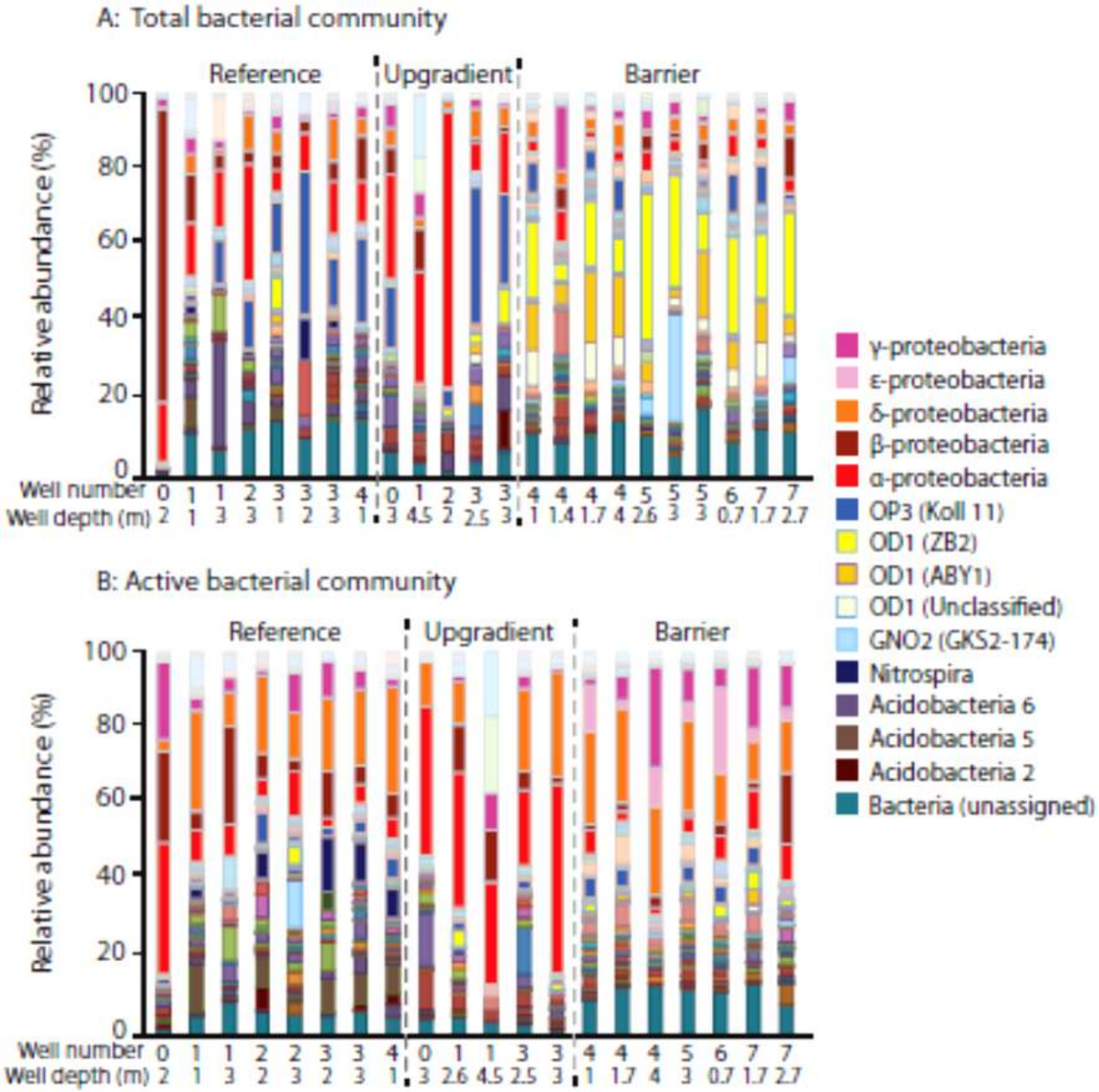
History of Development on Seacoast Shores Peninsula

1990's

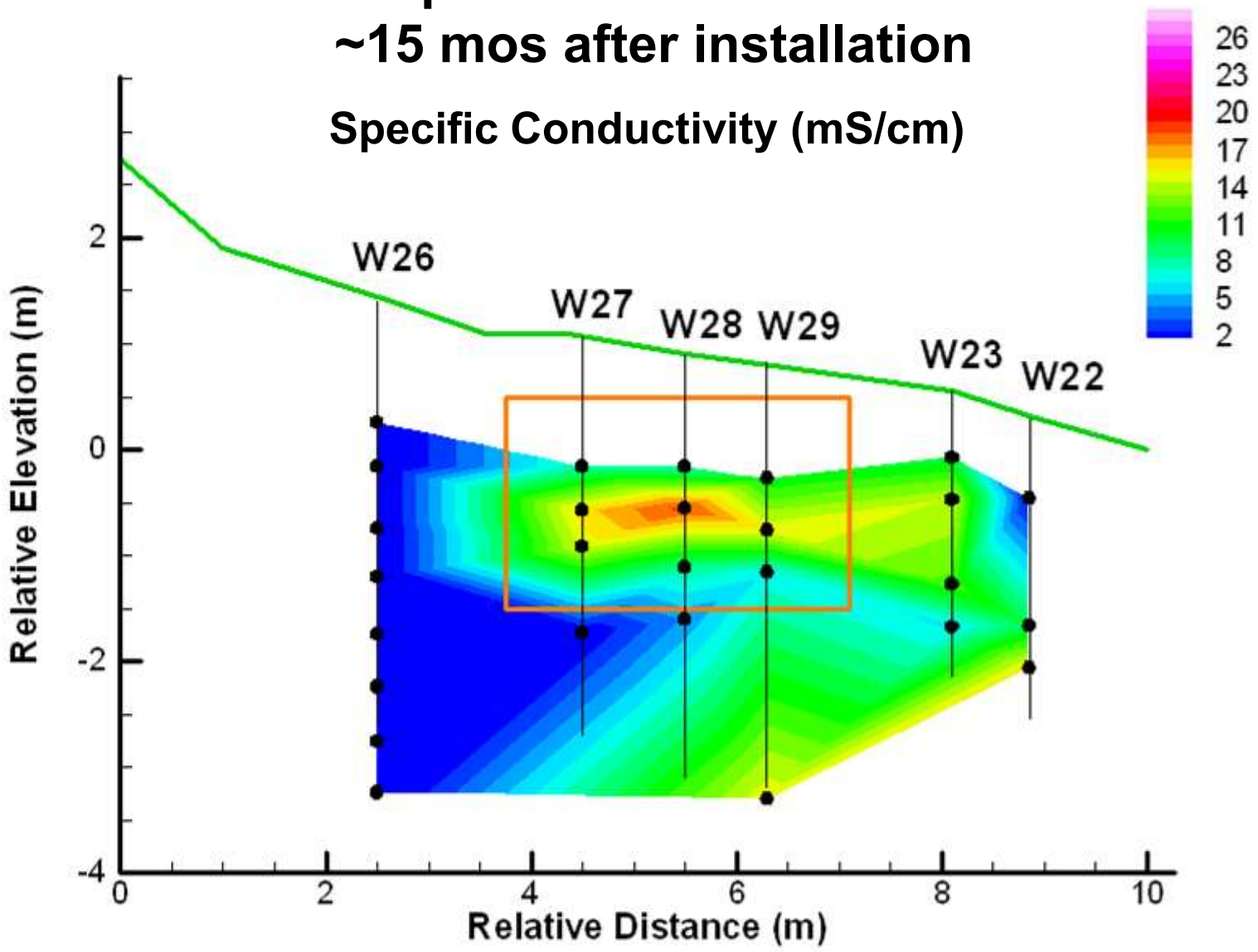
>1000 homes and individual on-site septic systems

MIMS data on N_2/Ar Ratios

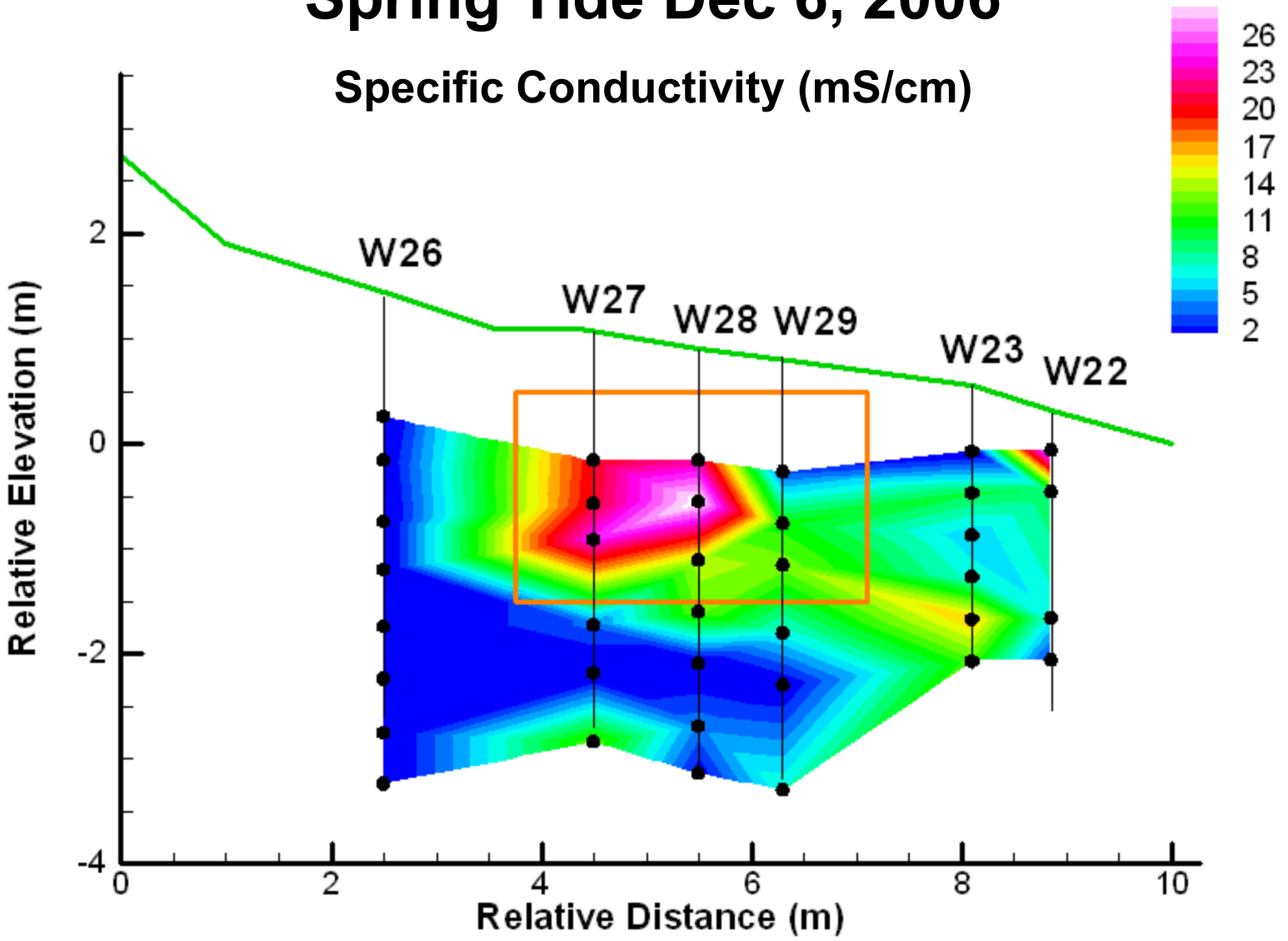



A: Total bacterial community
Reference
Upgradient
Barrier
Relative abundance (%)
100
80
60
40
20
0
Well number 0 1 1 2 3 3 3 4 0 1 2 3 3 4 4 4 4 5 5 5 6 7 7
Well depth (m) 2 1 3 3 1 2 3 1 3 4.5 2 2.5 3 1 1.4 1.7 4 2.6 3 3 0.7 1.7 2.7
B: Active bacterial community
Reference
Upgradient
Barrier
Relative abundance (%)
100
80
60
40
20
0
Well number 0 1 1 2 2 3 3 4 0 1 1 3 3 4 4 4 5 6 7 7
Well depth (m) 2 1 3 2 3 2 3 1 3 2.6 4.5 2.5 3 1 1.7 4 3 0.7 1.7 2.7
γ-proteobacteria
ε-proteobacteria
δ-proteobacteria
β-proteobacteria
α-proteobacteria
OP3 (Koll 11)
OD1 (ZB2)
OD1 (ABY1)
OD1 (Unclassified)
GNO2 (GKS2-174)
Nitrospira
Acidobacteria 6
Acidobacteria 5
Acidobacteria 2
Bacteria (unassigned)

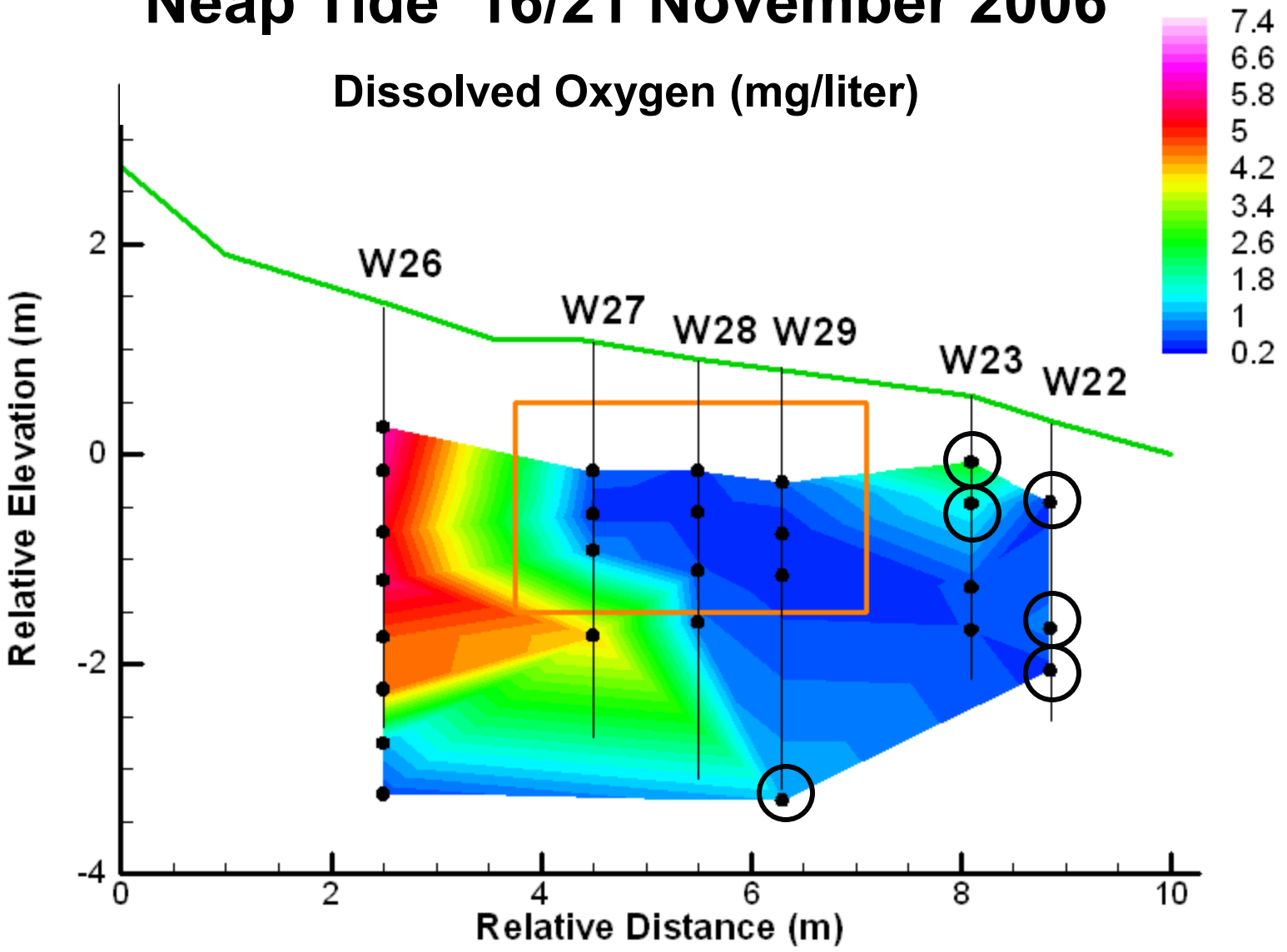
Neap Tide Nov 16/21 2006
~15 mos after installation



Spring Tide Dec 6, 2006

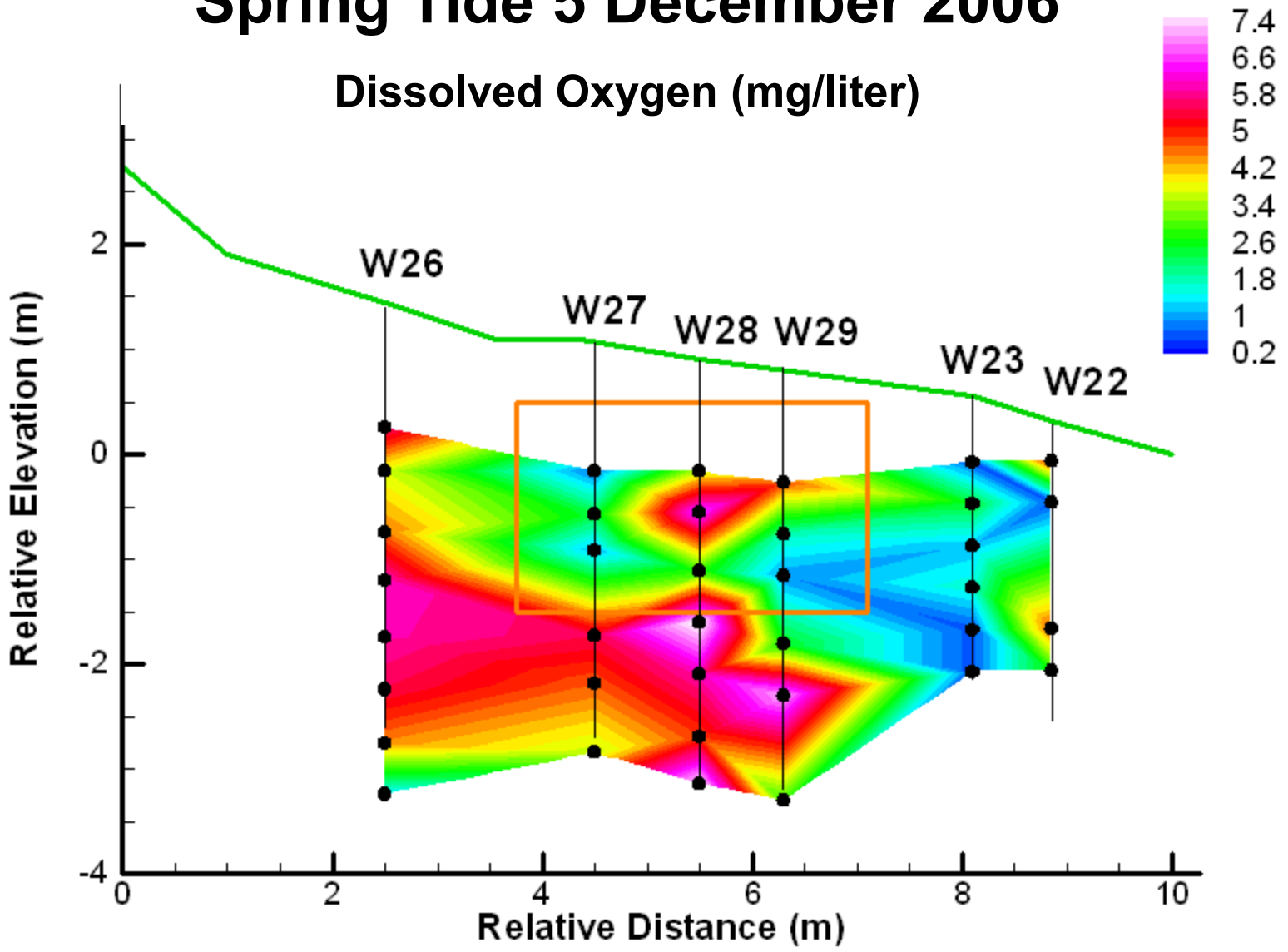


Neap Tide 16/21 November 2006



NOTE: Black circle around data point denotes sample taken 21 Nov 06

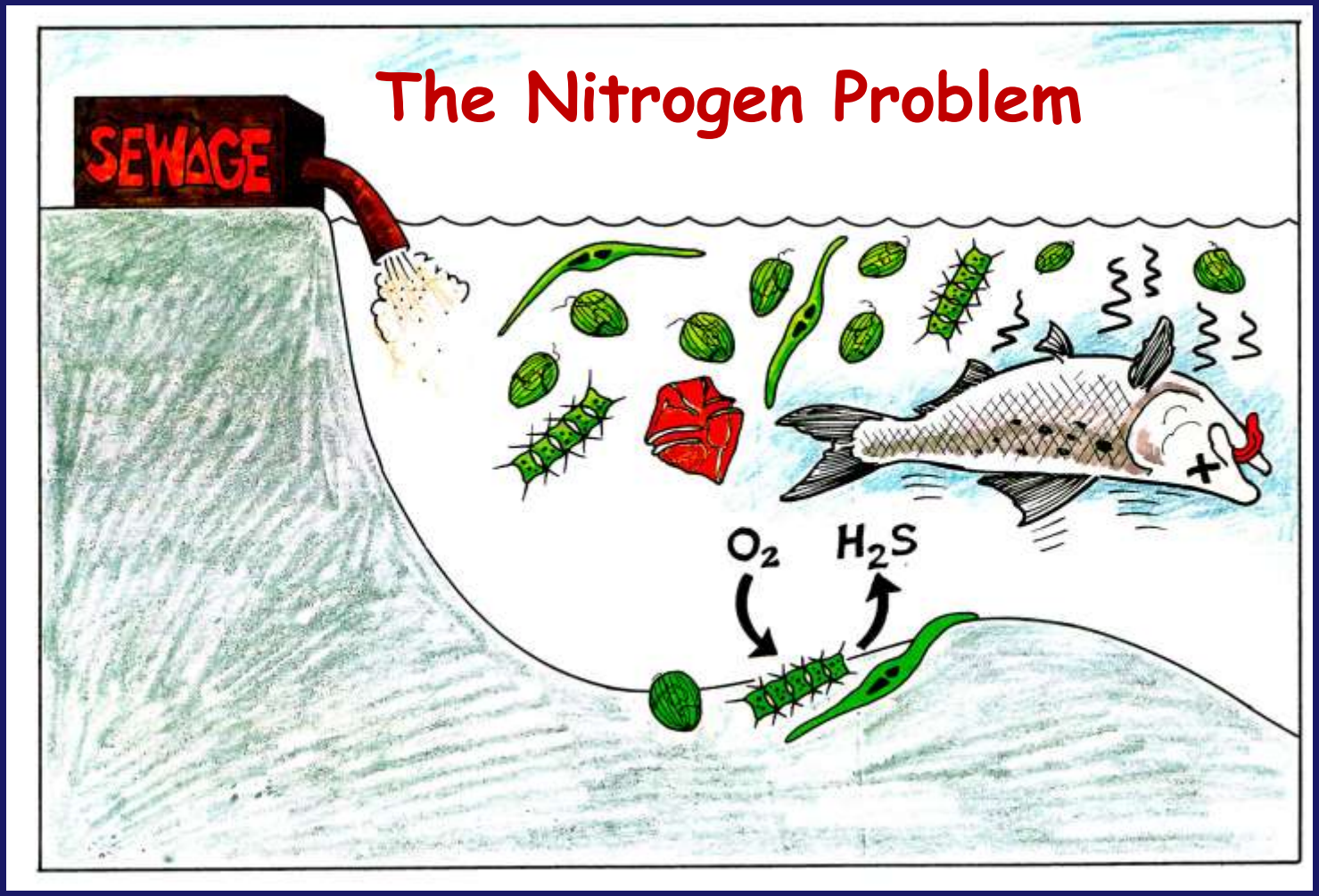
Spring Tide 5 December 2006



From the perspective of Biology we can distinguish two general forms of Nitrogen

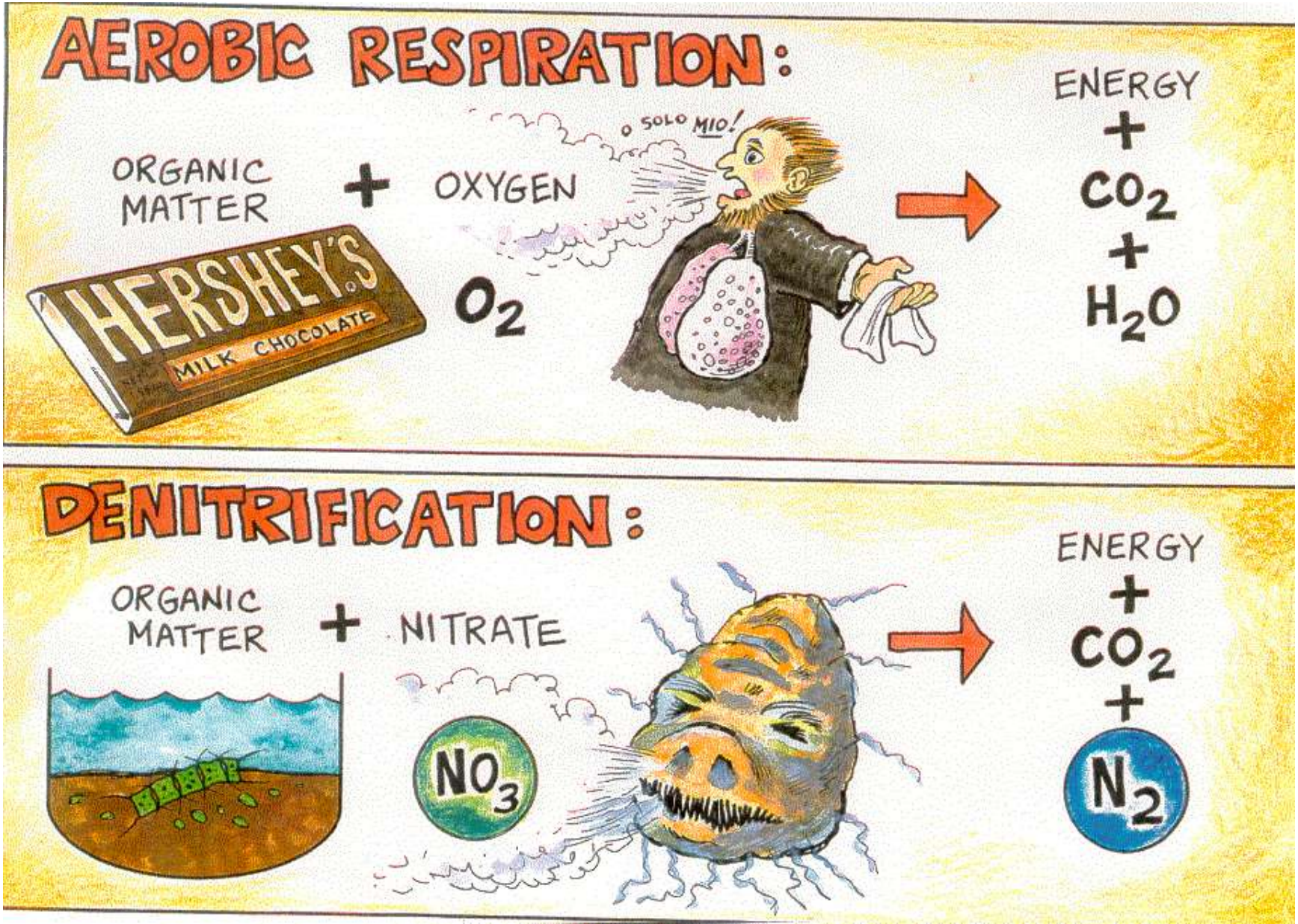
- **Reactive (Nr for short)**
  - ✓ Mineral forms: e.g. Ammonia NH_3, Nitrite (NO_2), Nitrous Oxide (N_2O), Nitrate (NO_3);
  - ✓ Organic forms: Nitrogen bonded to Carbon and Hydrogen (amino acids, nucleic acids, etc.)
- **Less Reactive**
  - ✓ Di-nitrogen gas (N_2) making up ~78% of the atmosphere (can only be used by a few types of microbes at high energy cost)

Conversion of N_2 (non-reactive) to reactive form = "N-Fixation"



- ✓ Excess N can stimulate blooms of harmful or undesirable species
- ✓ When the organic matter produced dies & decomposes, dissolved O_2 can be depleted in surface waters
- ✓ Causing fish kills and so-called Dead Zones

In contrast, denitrification is a heterotrophic process carried out when oxygen is low or absent.



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Gossie McKissick, who lives along Arey's Pond in Orleans, Mass., said the problems from nitrogen levels on Cape Cod waterways run deep. "It looks beautiful, but it's all dead underneath," she said of the pond. Below, a sign on Pleasant Pond warns of dangers of shellfishing there.

Cape Cod Waterways Face Pollution Crisis

Disputes Stall Cleanup Plans

By KATIE ZEZIMA

ORLEANS, Mass. — Rising nitrogen levels are suffocating the vegetation and marine life in salt water ponds and estuaries on Cape Cod, creating an environmental and infrastructure problem that, if left unchecked, will threaten the shellfishing industry, the tourist economy and the beaches that here on many summer visitors.

Many of the 60 ponds and estuaries on the cape and a few elsewhere in the region have been clouded by algae and seaweed. The culprit is nitrogen, much of it leaching out of septic systems that runs through sandy soil into the

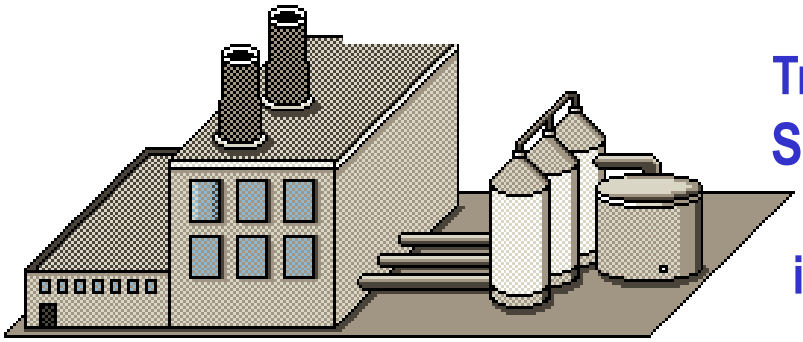
virtual concern.

Here in Orleans, wastewater has been a divisive subject for years. Some residents say the town should put in place a $150 million plan that was drafted two years ago and approved at a town meeting, while others are calling for additional review before it is financed by taxpayers.

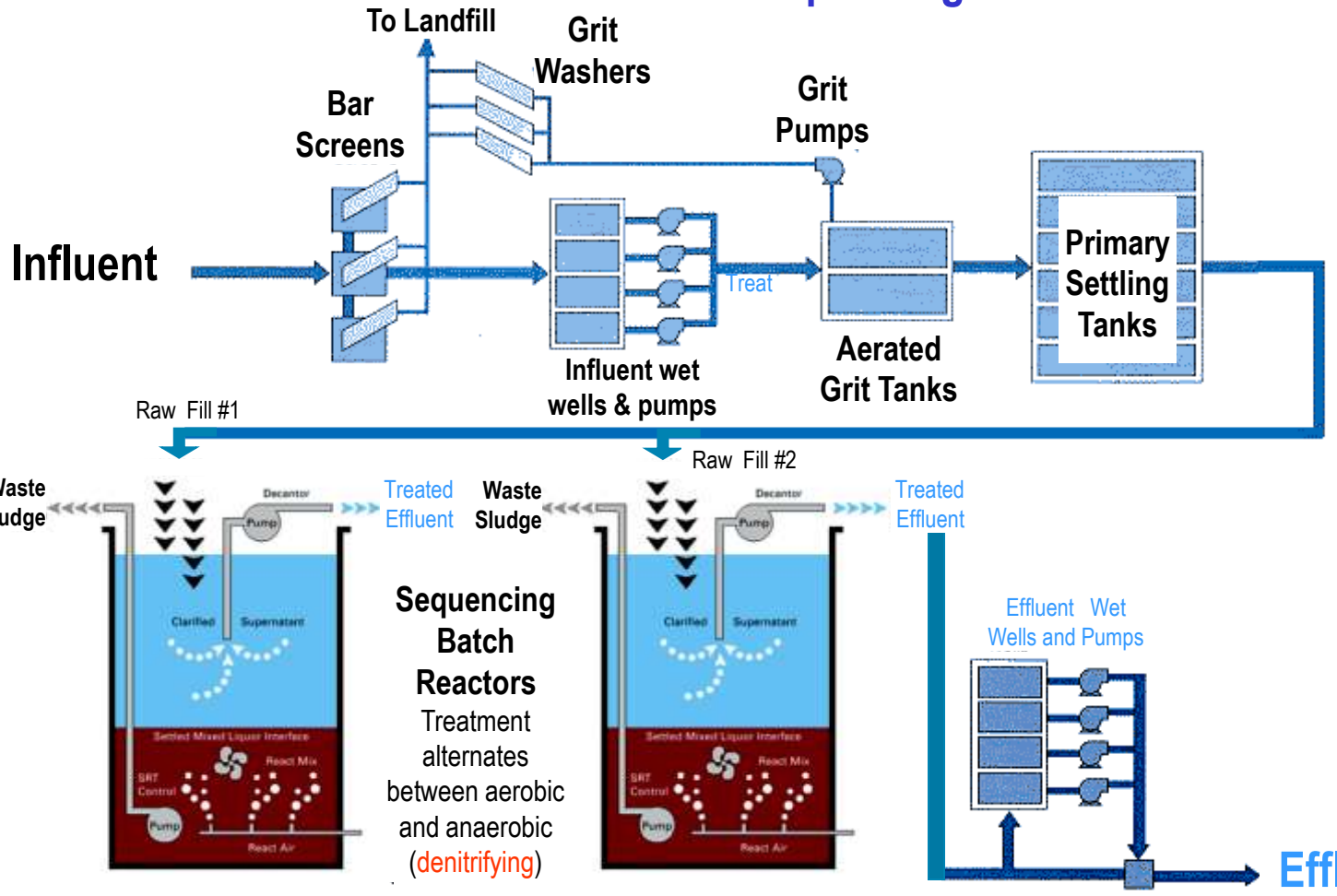
The problem is not always immediately apparent. From a distance, one saltwater pond here looks pristine, the summer sun bouncing off its placid waters and boats bobbing in the salt breeze.

"It's deceiving," said Gossie McKissick, who lives alongside the pond. "It looks beautiful, but it's all dead underneath."

Septic systems deposit wastewater, a mixture of urine and water, into a leach field. Because the



Traditional Approach to clean up is Centralized Sewering – Collect and pipe effluent to facility for Advanced Wastewater Treatment (e.g. including SBR's for N-removal), with on-going operating and maintenance costs



Is centralized sewering the best solution?

- A permeable reactive barrier (PRB), if it works, would capture all sources of groundwater-borne N to the estuary.
- If it is placed at the shore just before contaminated groundwater enters the estuary, it becomes effective immediately.
- Discharge is at the site of origin.
- A PRB would be cheaper to build and operates passively; has no annual O & M cost.

K. Foreman MBL, Woods Hole, MA 02543

Is centralized sewering the best solution?

Will treating just the wastewater input be sufficient to cure the eutrophication problem?

What about the multi-year legacy of contaminated groundwater ?

K. Foreman MBL, Woods Hole, MA 02543

Title V Septic Systems:

Nitrogen removal is three step process:

1. Convert organic N to mineral N (e.g. ammonia, NH_4) - **Mineralization**
2. Convert NH_4 to Nitrate (NO_3). **Nitrification** requires oxygen.
3. ***Denitrification*** - convert to stable, unreactive N_2 gas (as in atmosphere).

Title V systems accomplish much of step 1 in the holding tank.

Percolation of liquid via the leach field through the air-filled (unsaturated) soils to the water table accomplishes step 2, and also removes pathogens.

Title V systems are not designed to remove nitrogen however.

Wood chip nitrate barriers are intended to accomplish step 3 by providing a decomposable carbon source that consumes oxygen in groundwater creating conditions ideal for denitrification.