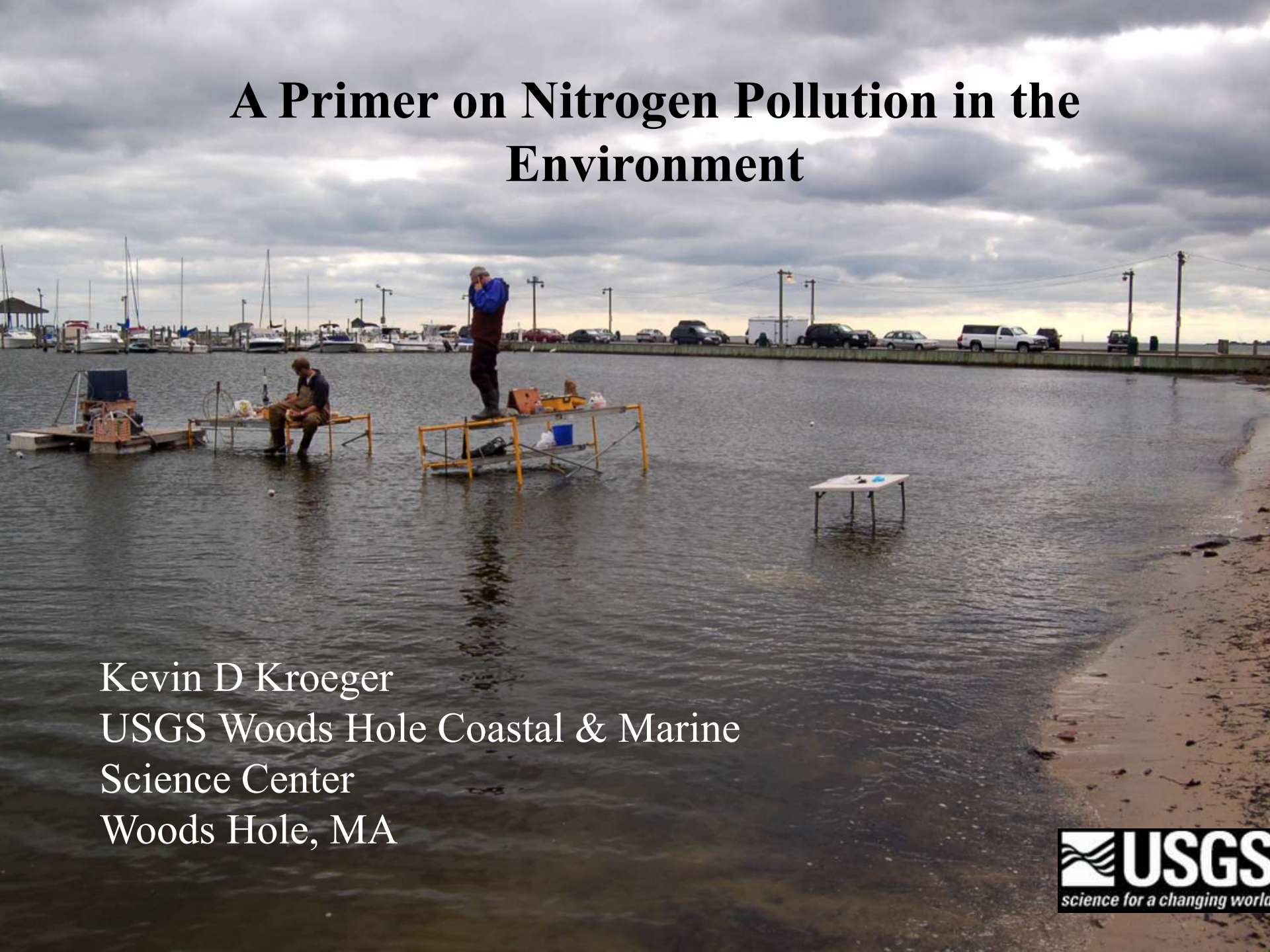
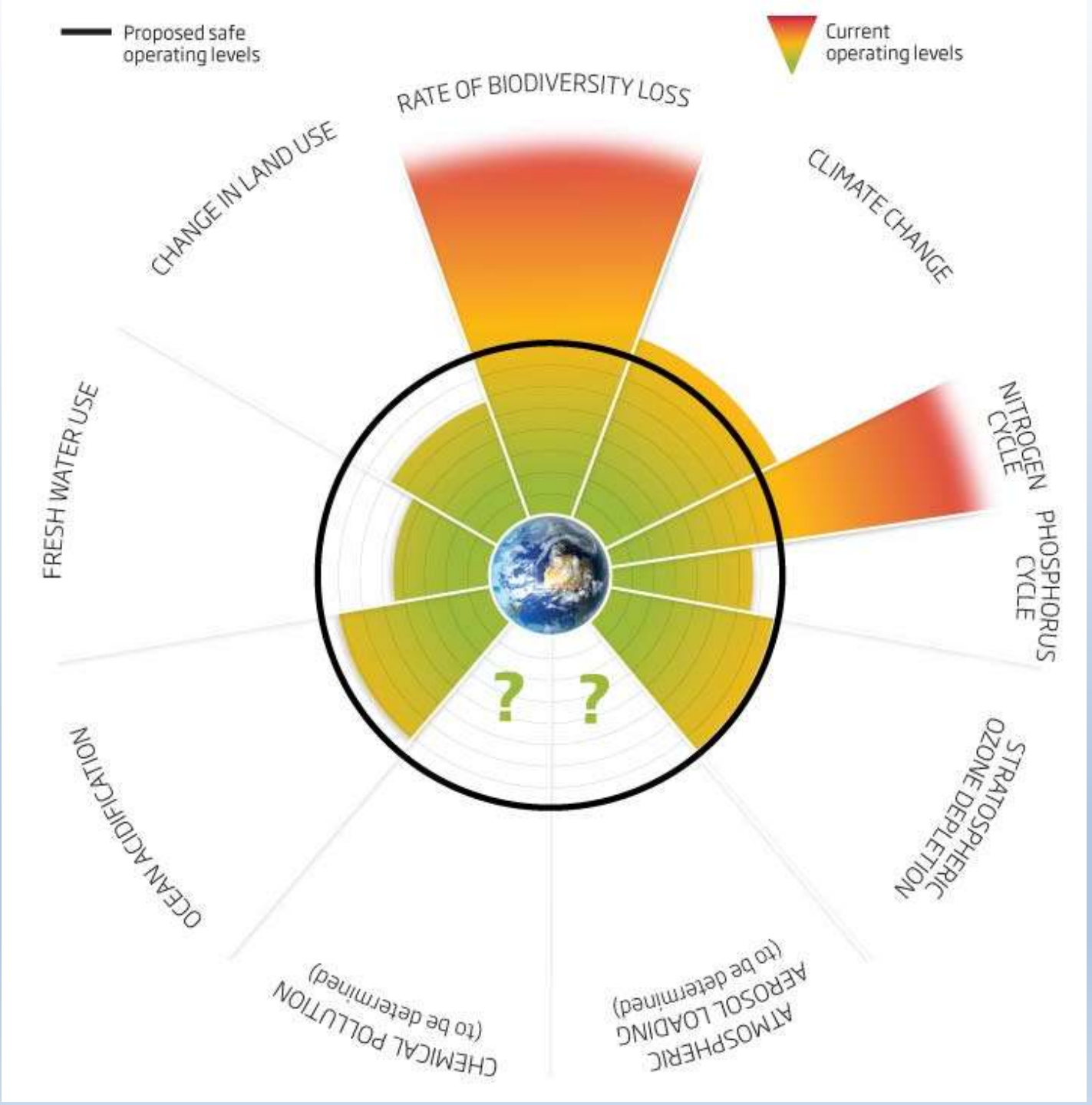
A Primer on Nitrogen Pollution in the Environment



Kevin D Kroeger
USGS Woods Hole Coastal & Marine Science Center
Woods Hole, MA

USGS
science for a changing world



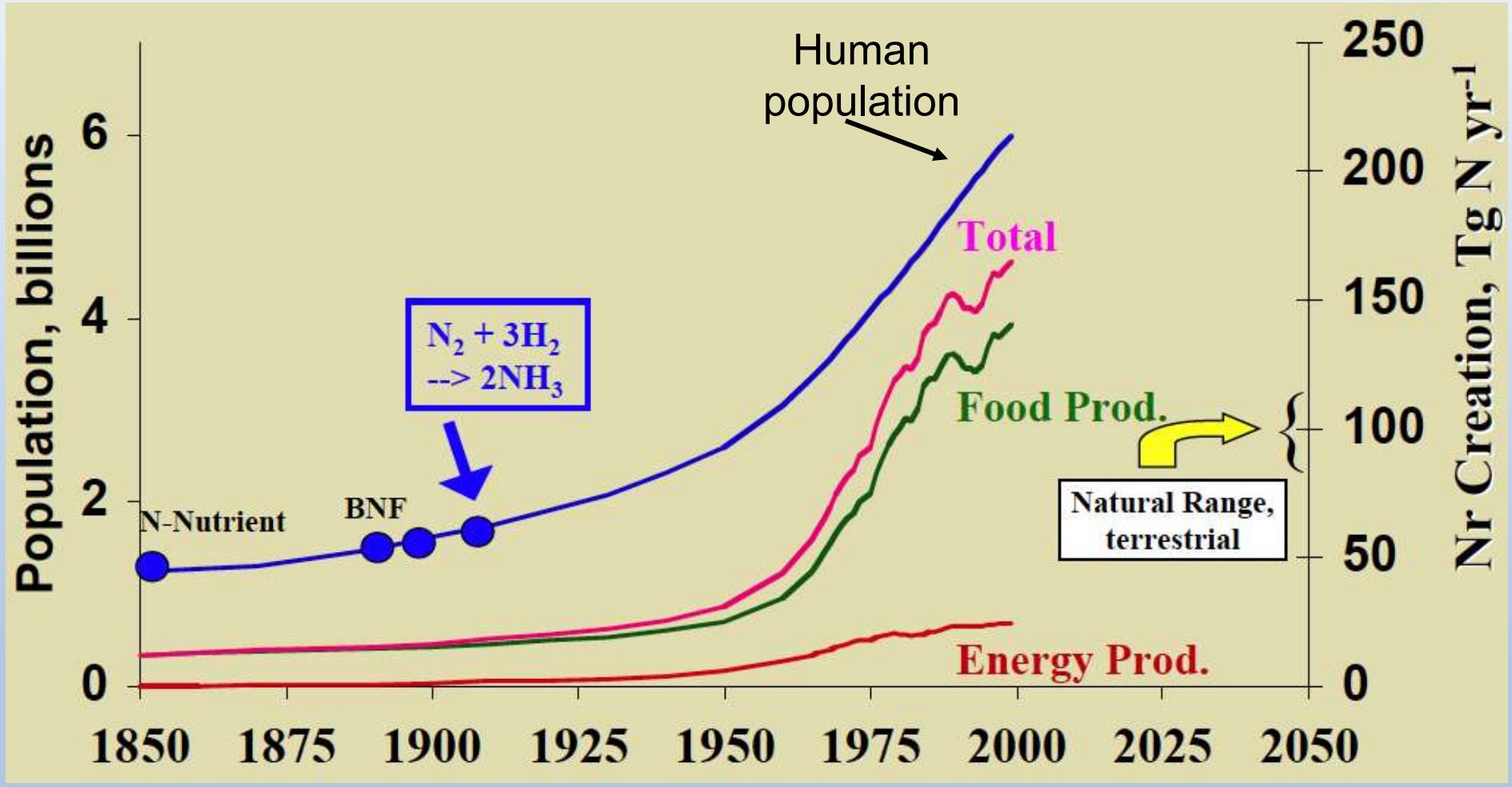
Beyond the Boundaries

We have already overstepped 3 of 9 planetary boundaries and are at risk of transgressing several others

NewScientist©

USGS science for a changing world

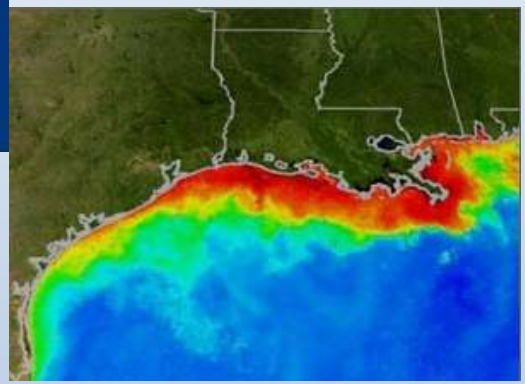
Sources of nitrogen pollution in the environment



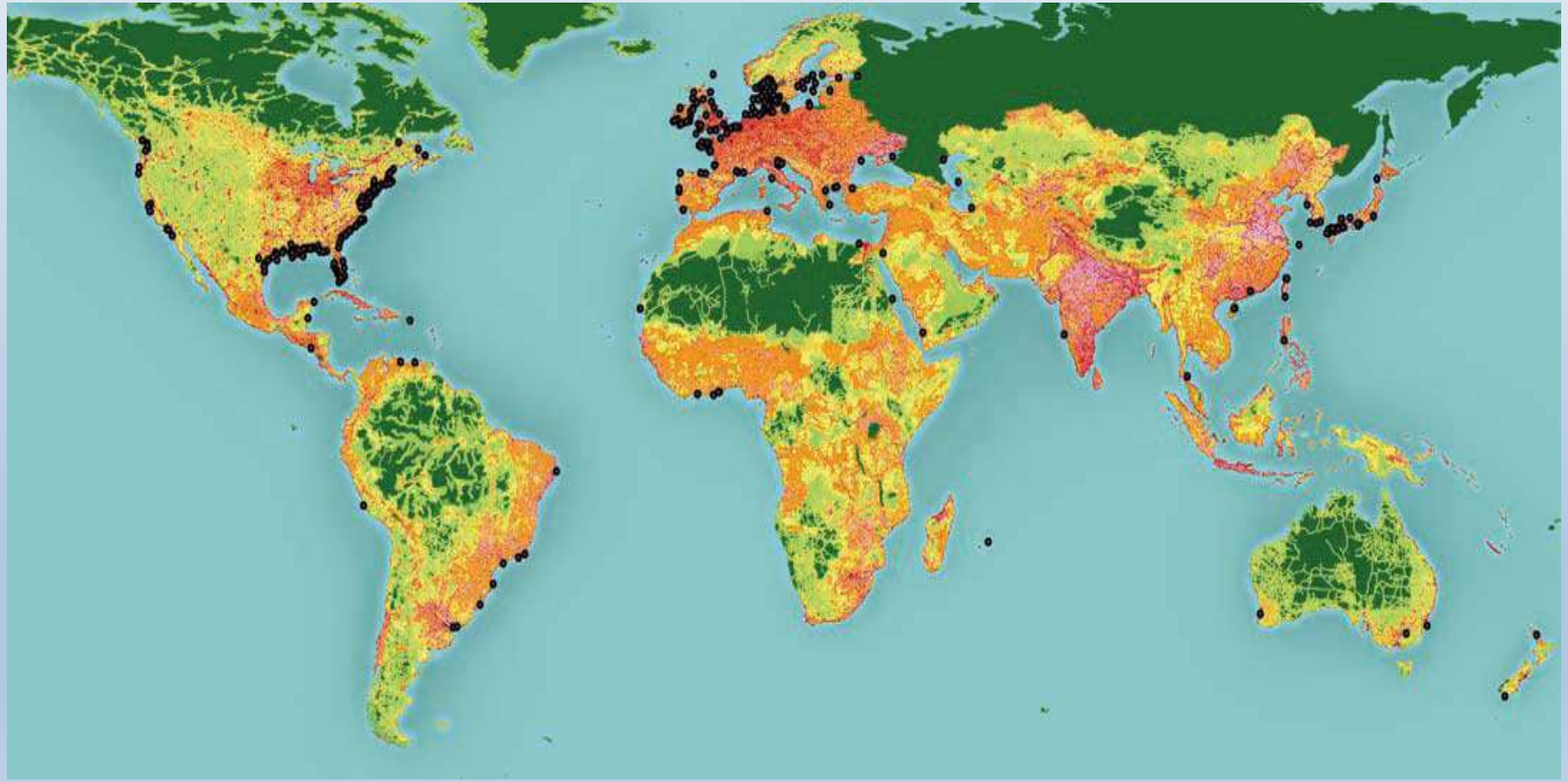
Galloway *et al.* 2003

USGS science for a changing world

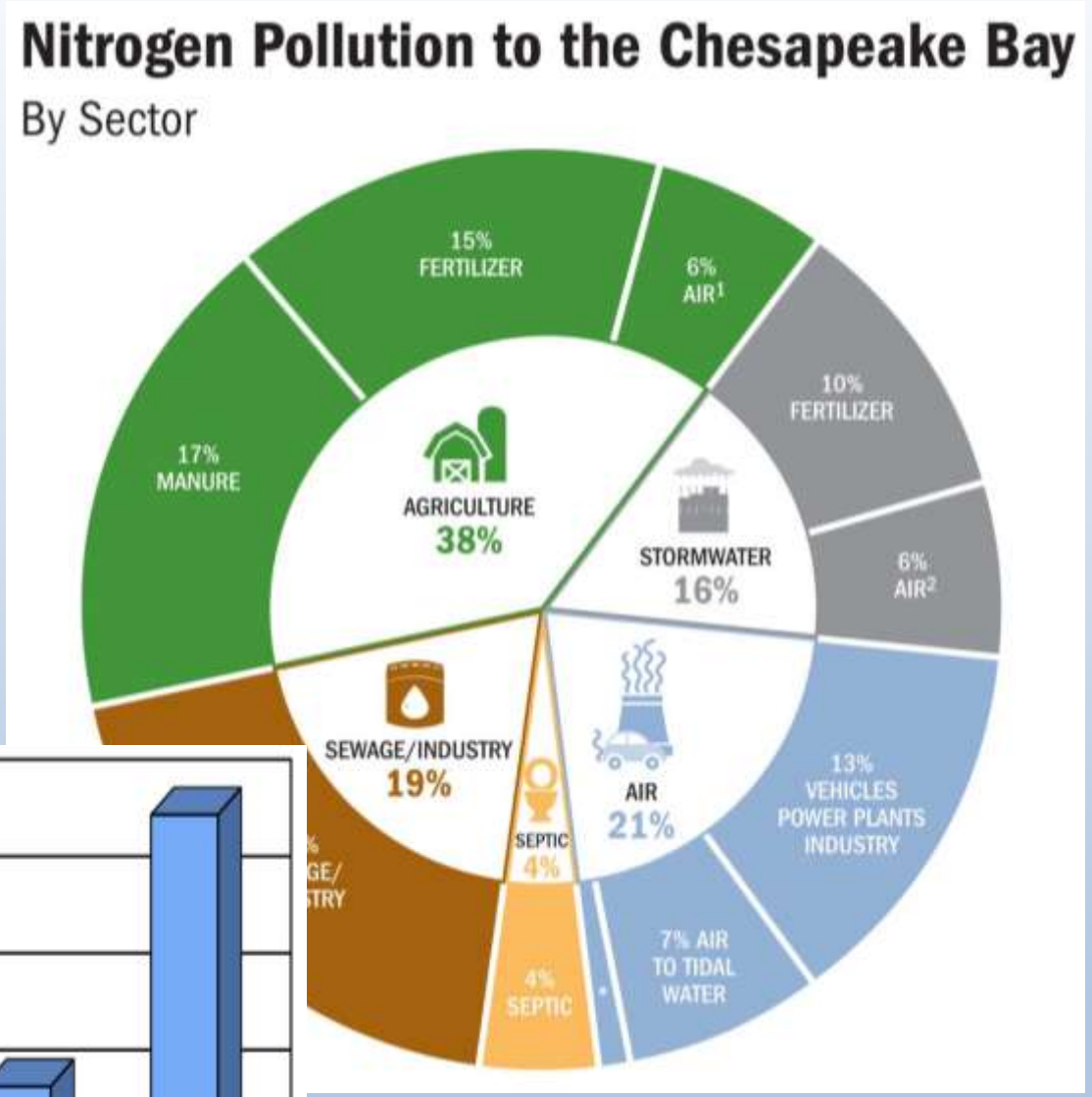
Gulf of Mexico Dead Zone: Agricultural fertilizer travels in groundwater and streams to the coast. Impacts include low oxygen, harmful algal blooms, fish kills

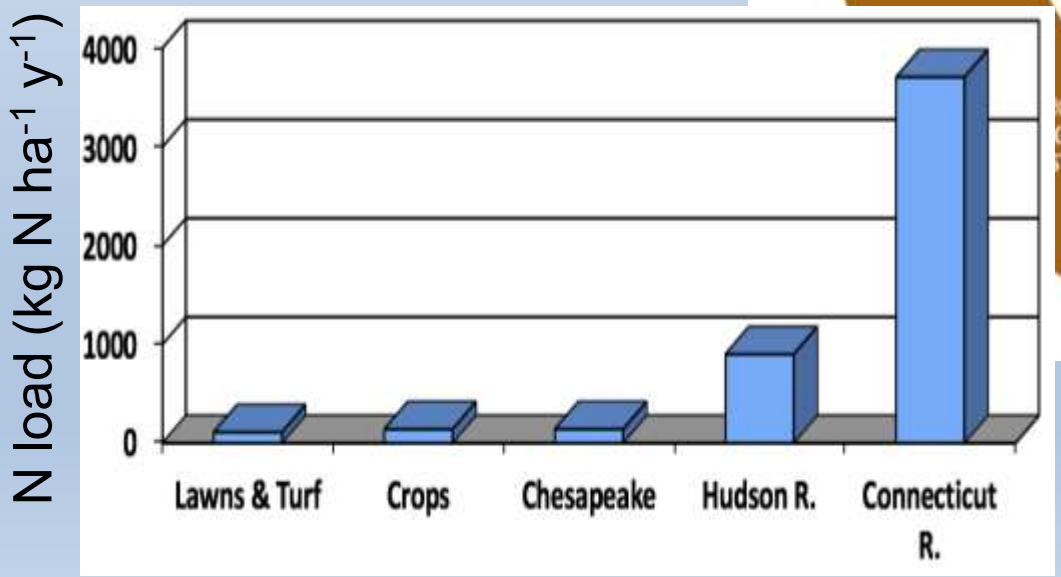


Global Increase in Coastal Dead Zones: More than 400 dead zones worldwide, caused by Nitrogen pollution from agriculture, wastewater, air pollution



Excess nitrogen added to coastal waters





Data from Bricker et al. 2007

USGS science for a changing world

The New York Times

Asia Pacific

To Save Olympic Sailing Races, China Fights Algae

EyePress, via Associated Press

A barge at Qingdao, site of the Olympic sailing regatta in August, was surrounded by algae last week. The Chinese have begun a huge cleanup effort.

By JIM YARDLEY
Published: July 1, 2008

USGS
science for a changing world

Plain Dealer file

Former reporter Richard Ellers says he didn't appreciate the thickness of the pollution on Cuyahoga River until he dipped his hand into it. The photo was taken in the 1960s.

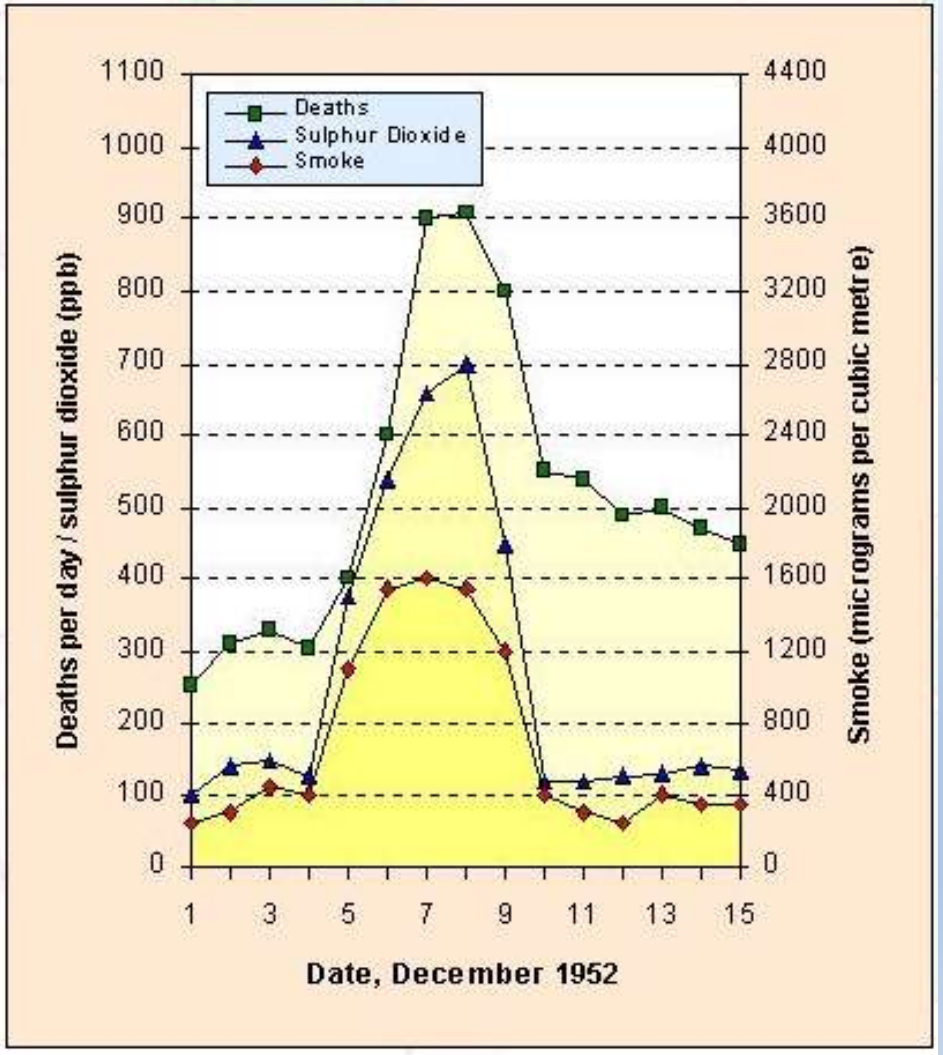
But even recently, water pollution has been much worse…

And so the current problems can be dealt with, just as these were in the past.

On June 22, 1969, the Cuyahoga River caught on fire. This blot on the American environment actually led to positive results, including creation of the U.S. Environmental Protection Agency and passage of major environmental laws such as the Clean Water Act in 1972.

Deaths due to Great London Smog of 1952

Over 4,000 deaths were attributable to the **Great London Smog** of December 1952



CLINICAL REVIEW

CLINICIAN'S CORNER

Main Air Pollutants and Myocardial Infarction

A Systematic Review and Meta-analysis

Context Short-term exposure to high levels of air pollution may trigger myocardial infarction (MI), but this association remains unclear.

Objective To assess and quantify the association between short-term exposure to major air pollutants (ozone, carbon monoxide, nitrogen dioxide, sulfur dioxide, and particulate matter ≤10 μm [PM_{10}] and ≤2.5 μm [$PM_{2.5}$] in diameter) on MI risk.

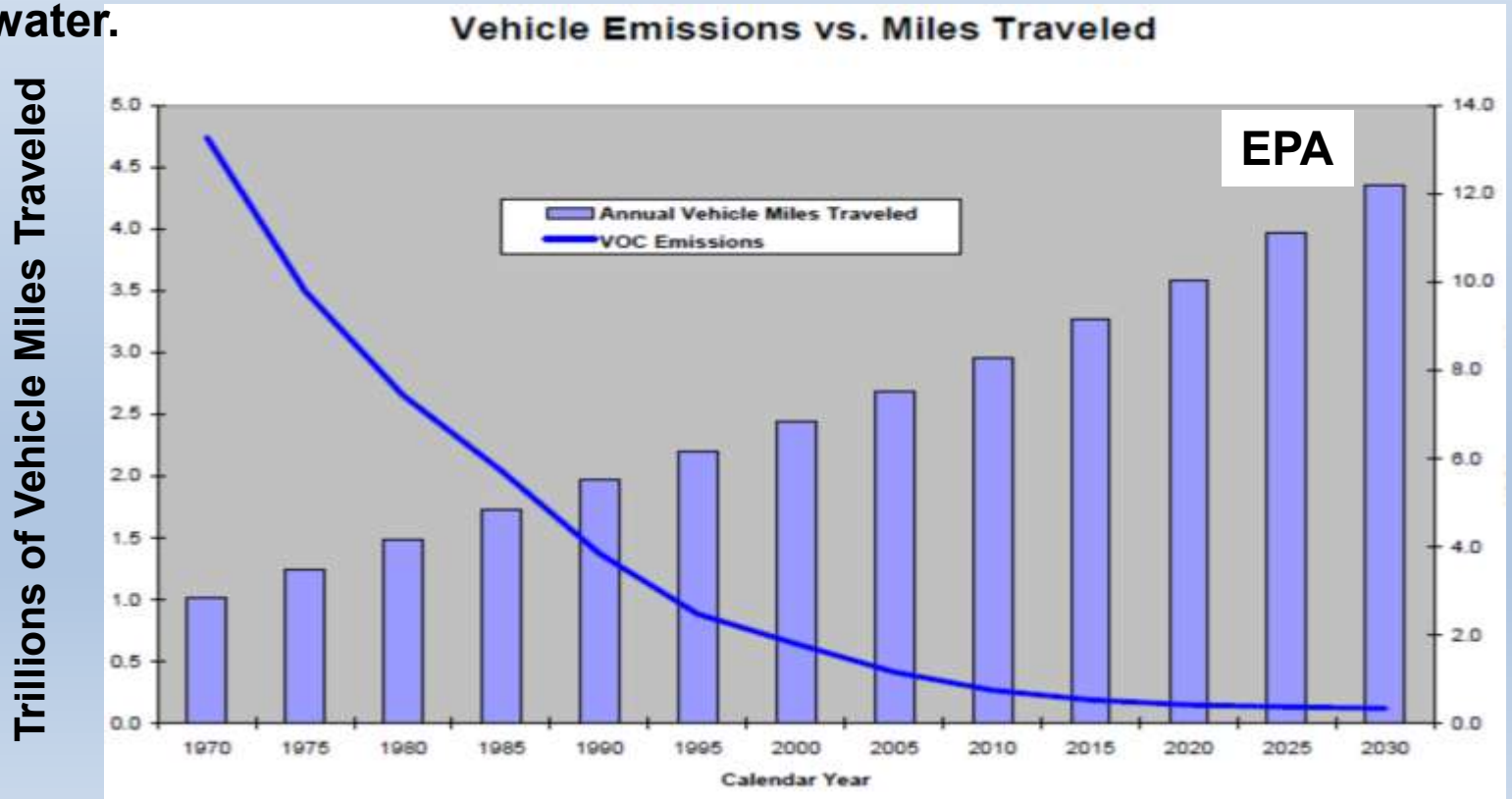
Conclusion All the main air pollutants, with the exception of ozone, were significantly associated with a near-term increase in MI risk.

JAMA. 2012;307(7):713-721

www.jama.com

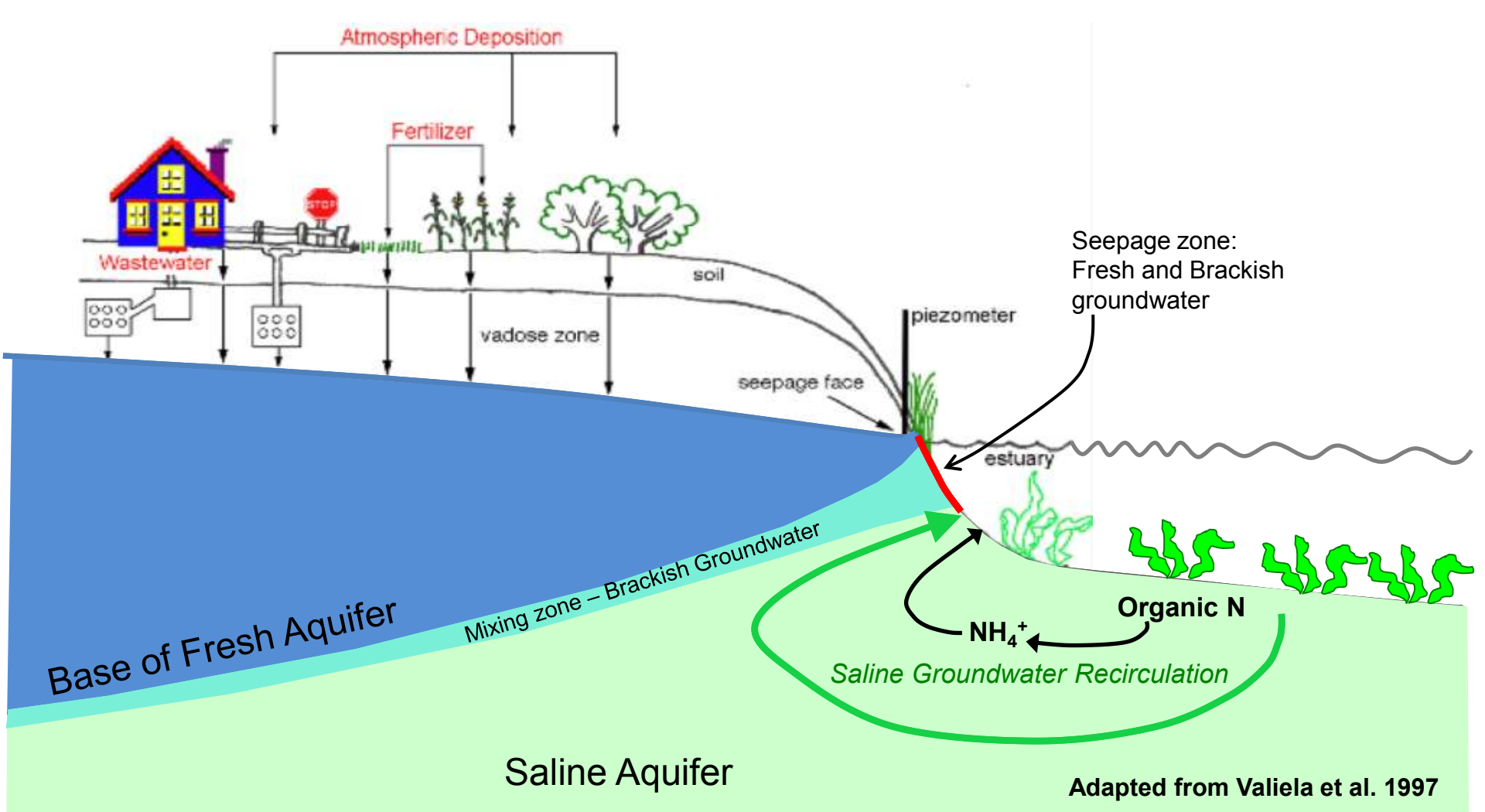
The heart is the most sensitive organ to air pollution, and the effects are not a subtle, far off, cumulative impact, but rather a higher risk of immediate illness or death even after just a day or a few days of exposure.

- **Regulations have been extremely effective at reducing some kinds and sources of pollution, such as automobile emissions and power plant emissions.**
- **The current situation is that we've significantly addressed disposal of many pollutants, but our main two problems are among the most difficult: CO_2 and fixed N in atmosphere and water.**



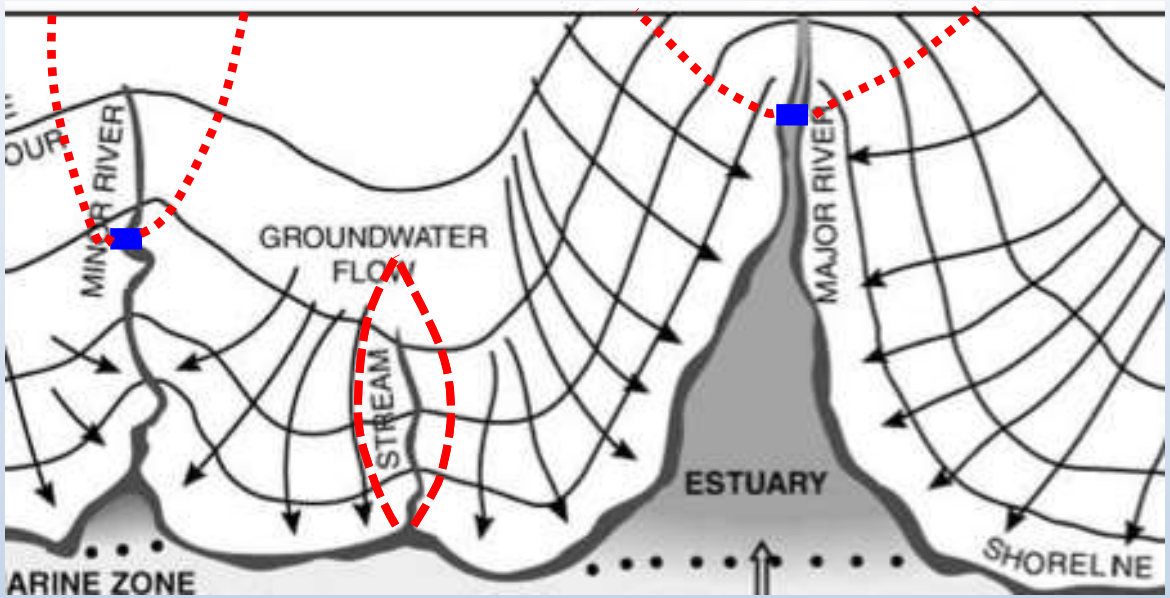
Movement of nitrogen through the environment locally here on Cape Cod:

- **3 main sources**
- **Groundwater is the primary route to sea**
- **Chemical and microbial transformations and removal can occur at several points**



Adapted from Valiela et al. 1997

Why is groundwater the main pathway of transport on Cape Cod?



Sandy soils allow rapid percolation of water, so that surface runoff is minimal.

Septic systems dispose wastewater directly to the aquifer.

The near-shore portions of the landscape commonly have particularly high population density, and the transit distances from lawns and septic systems to the estuary are relatively short.

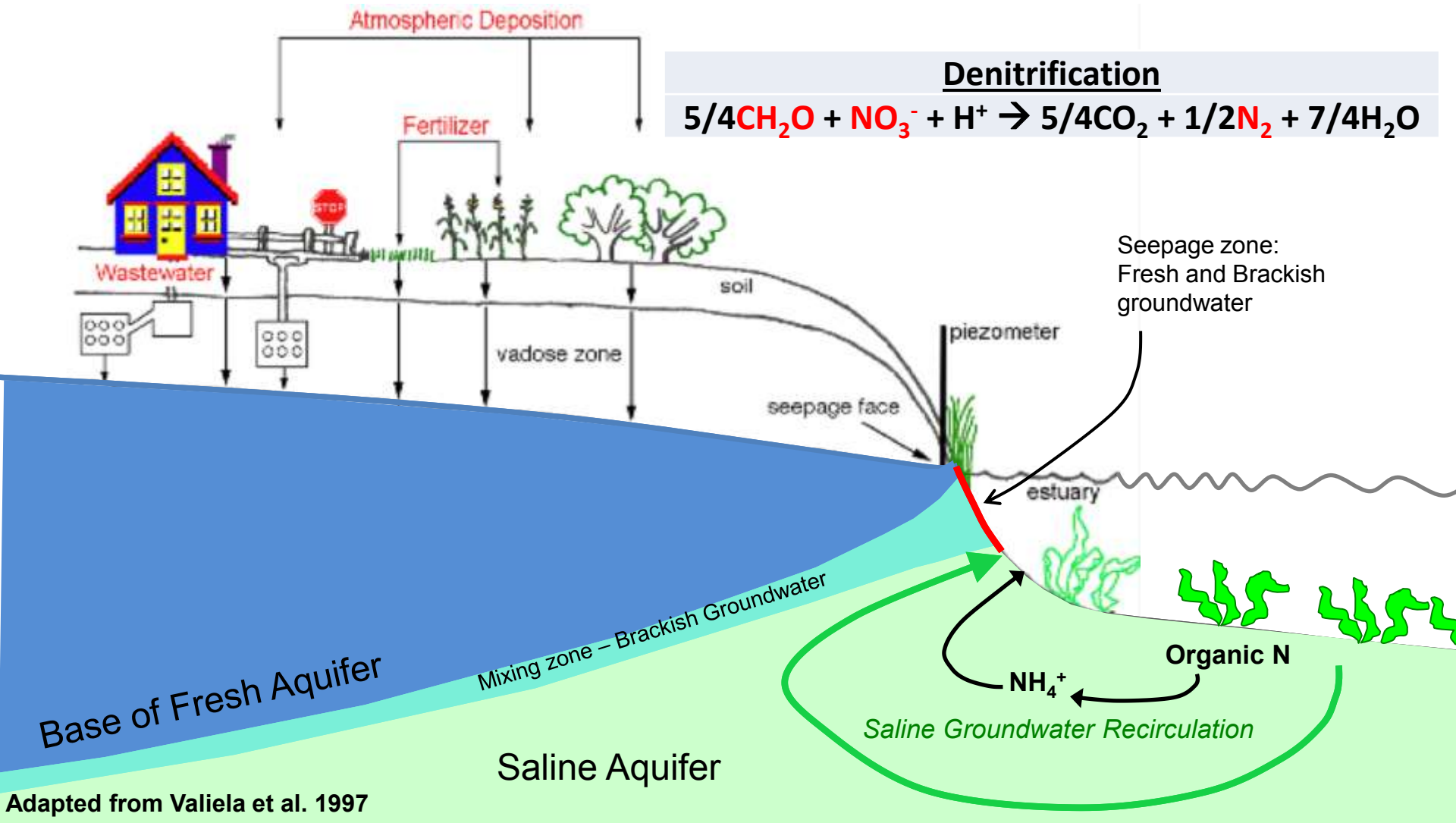
Why are the different forms and transformations of nitrogen important?

Nitrate = NO_3^- = oxidized, occurs where have oxygen present

Ammonium = NH_4^+ = reduced, occurs where oxygen absent or limited

Dissolved organic nitrogen = DON = common under many conditions

Total dissolved nitrogen = TDN = NO_3^- + NH_4^+ + DON



Denitrification

$5/4CH_2O + NO_3^- + H^+ \rightarrow 5/4CO_2 + 1/2N_2 + 7/4H_2O$

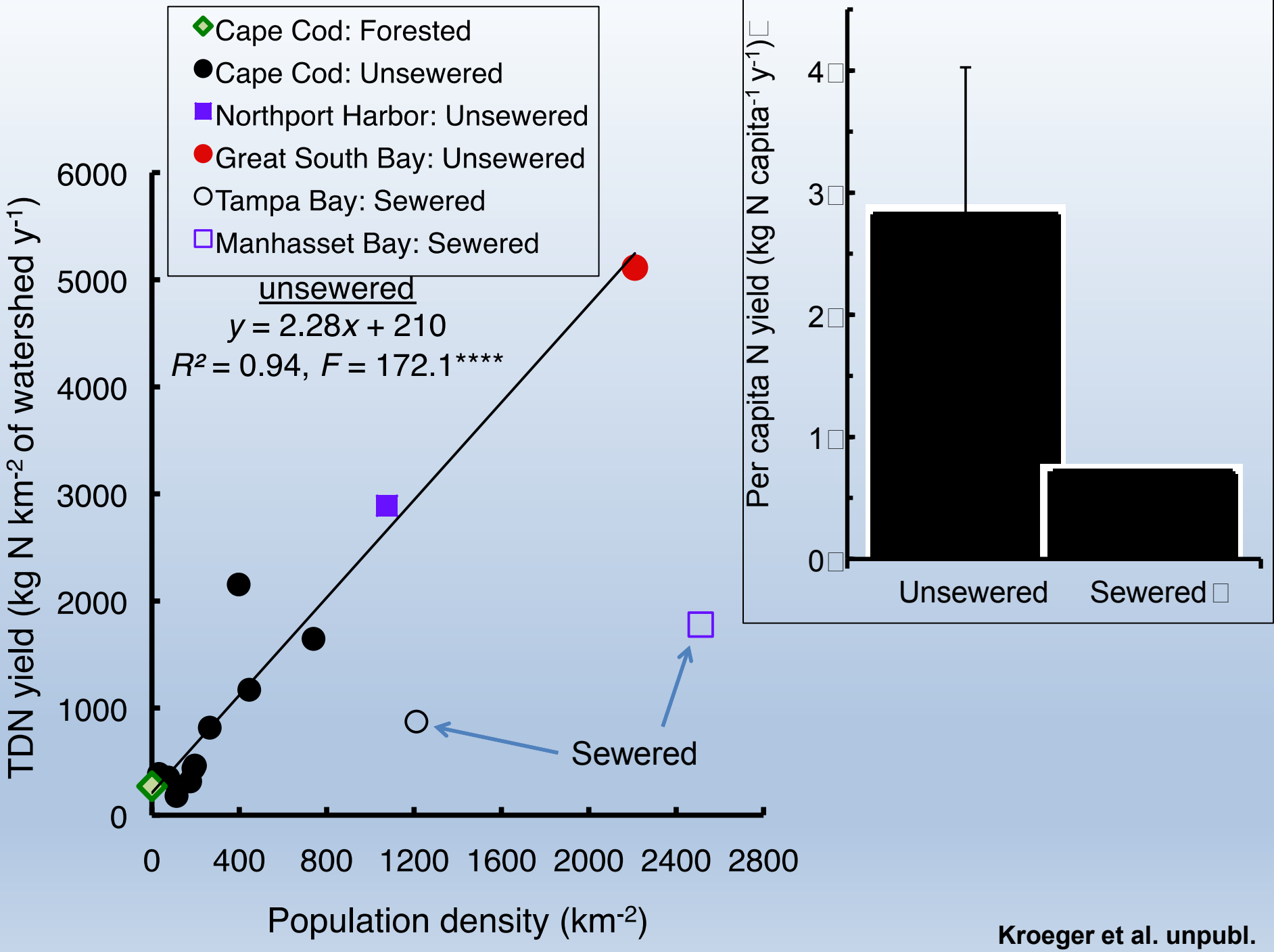
Adapted from Valiela et al. 1997

How can we manage nitrogen loading?

- **Maintain low to moderate population densities, and preserve green spaces**
- **Sewer where population densities are high**

Long Island, NY: Urban, intense eutrophication

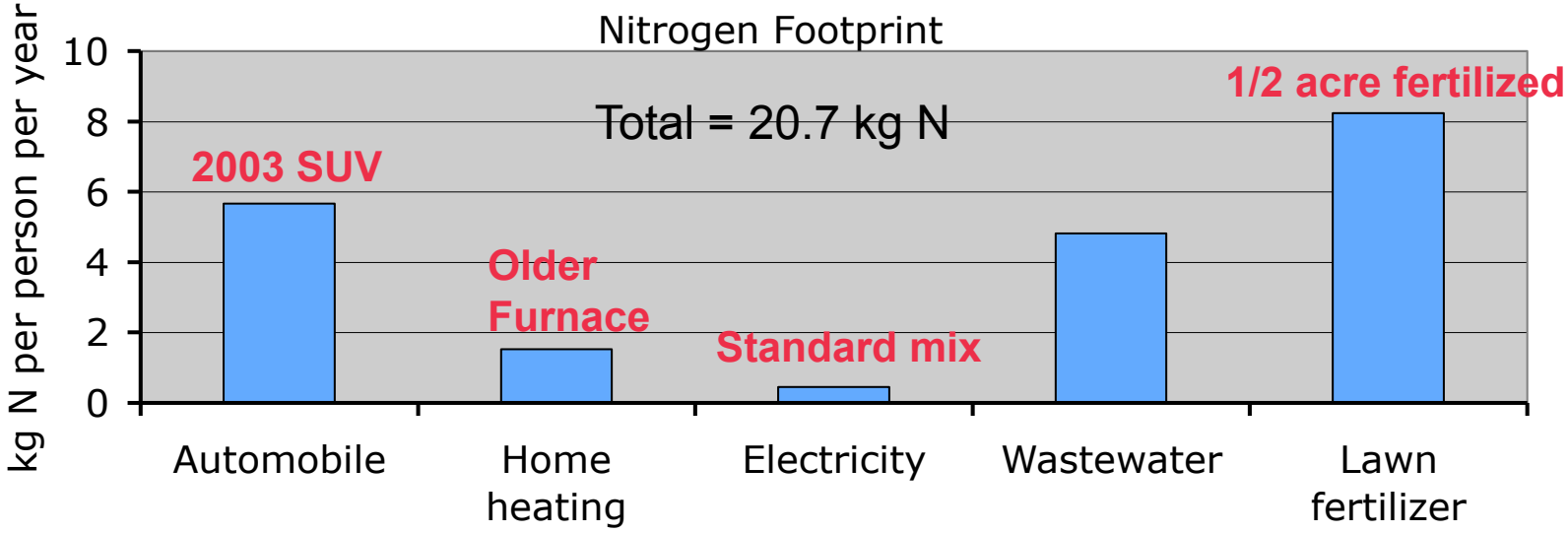
Cape Cod: Mix of forest & residential

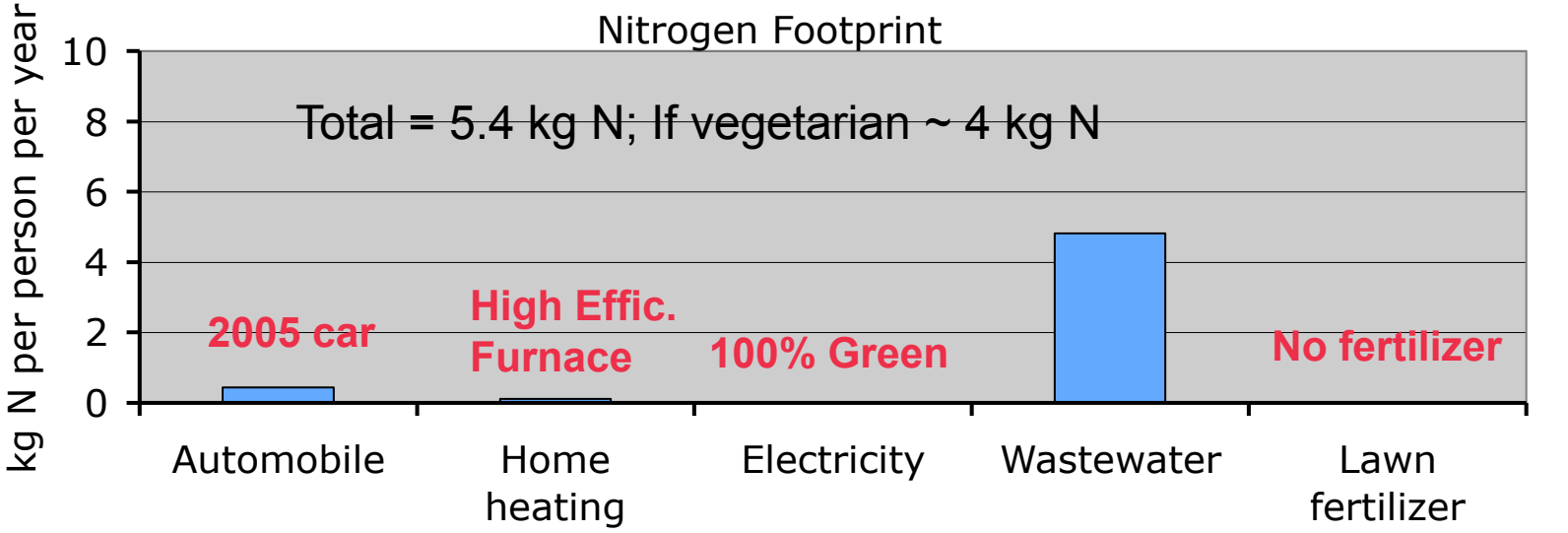


Kroeger et al. unpubl.

How can we manage nitrogen loading?

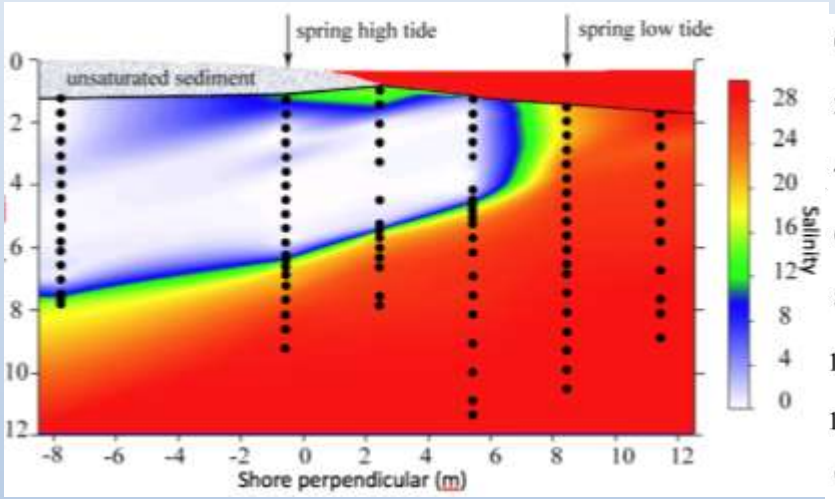
- **Individual choices have a large impact**

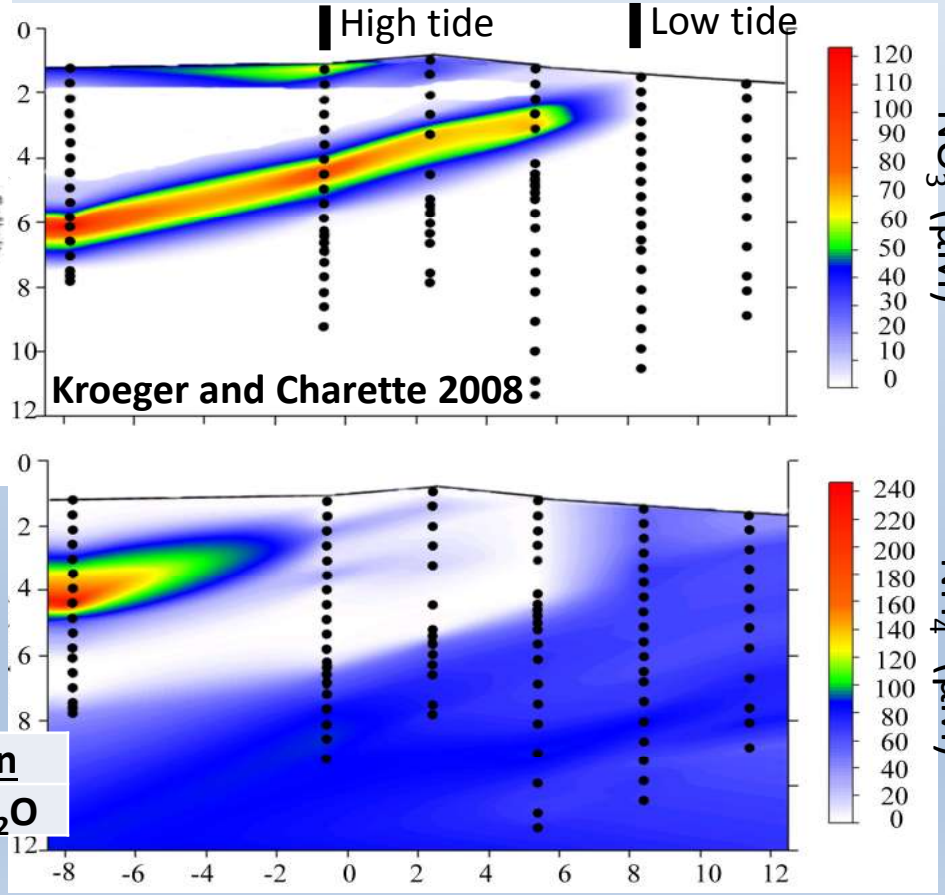




Identify and take advantage of locations where natural N removal occurs

- **Aquifer: We can't readily manage, but can prioritize other actions in areas where removal in the aquifer is minimal**
- **Seepage face: Amenable to management through PRB or similar technologies**
- ***Careful evaluation of chemical and hydrological conditions are required**





1. Nitrification: Requires Oxygen

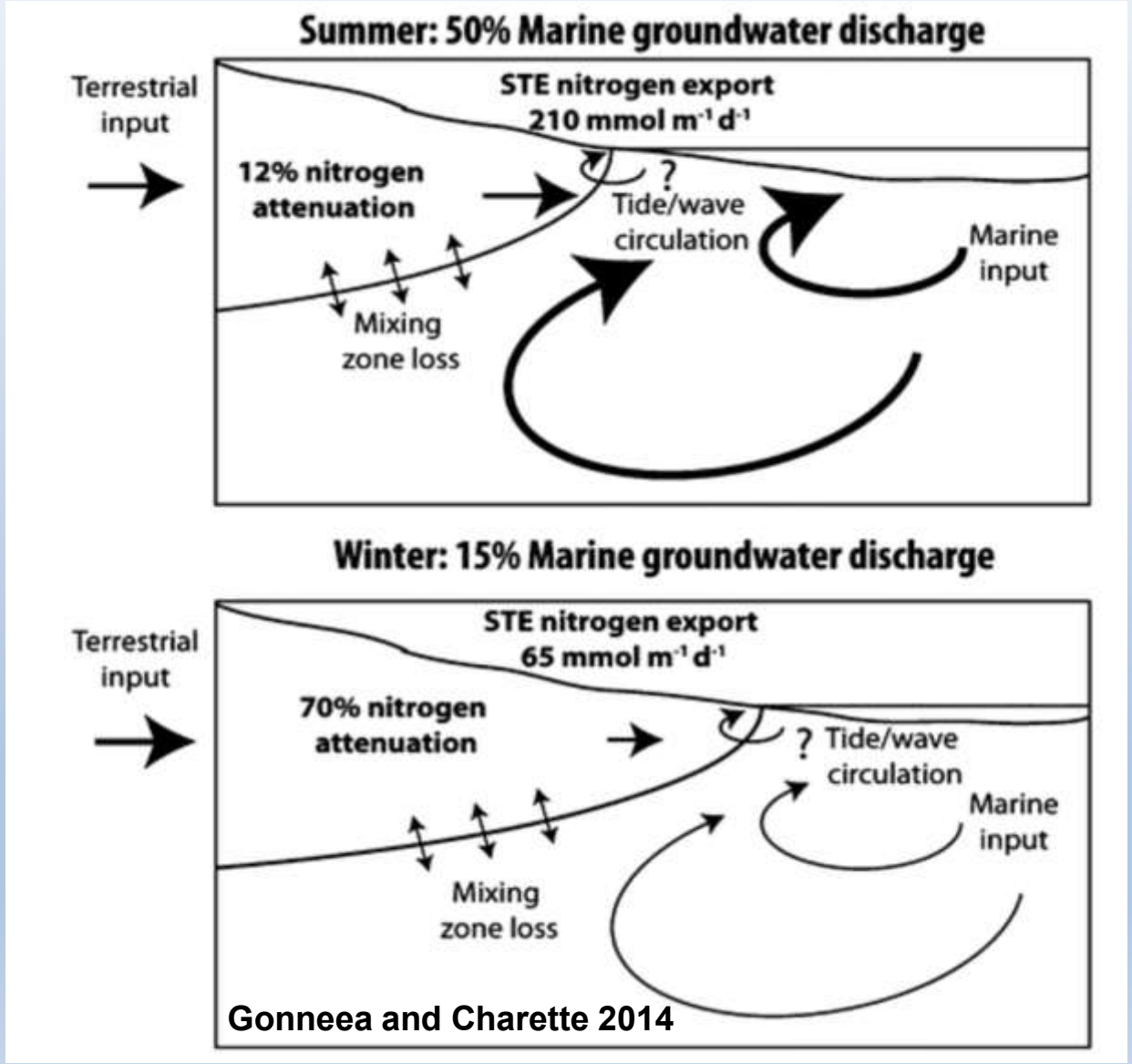
$2O_2 + NH_4^+ \rightarrow 2H^+ + NO_3^- + H_2O$

2. Denitrification: Requires Absence of Oxygen

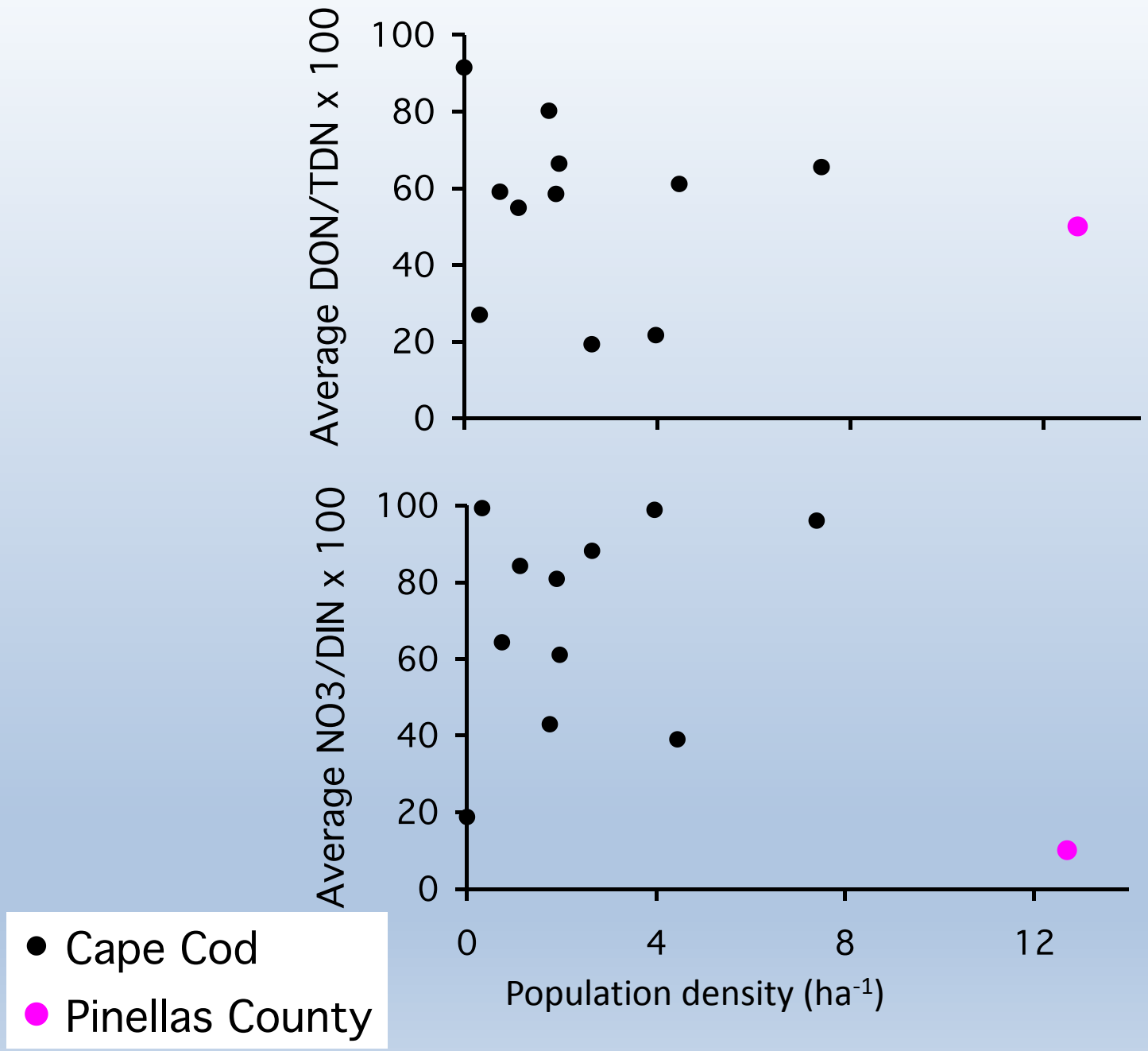
$5/4CH_2O + NO_3^- + H^+ \rightarrow 5/4CO_2 + 1/2N_2 + 7/4H_2O$

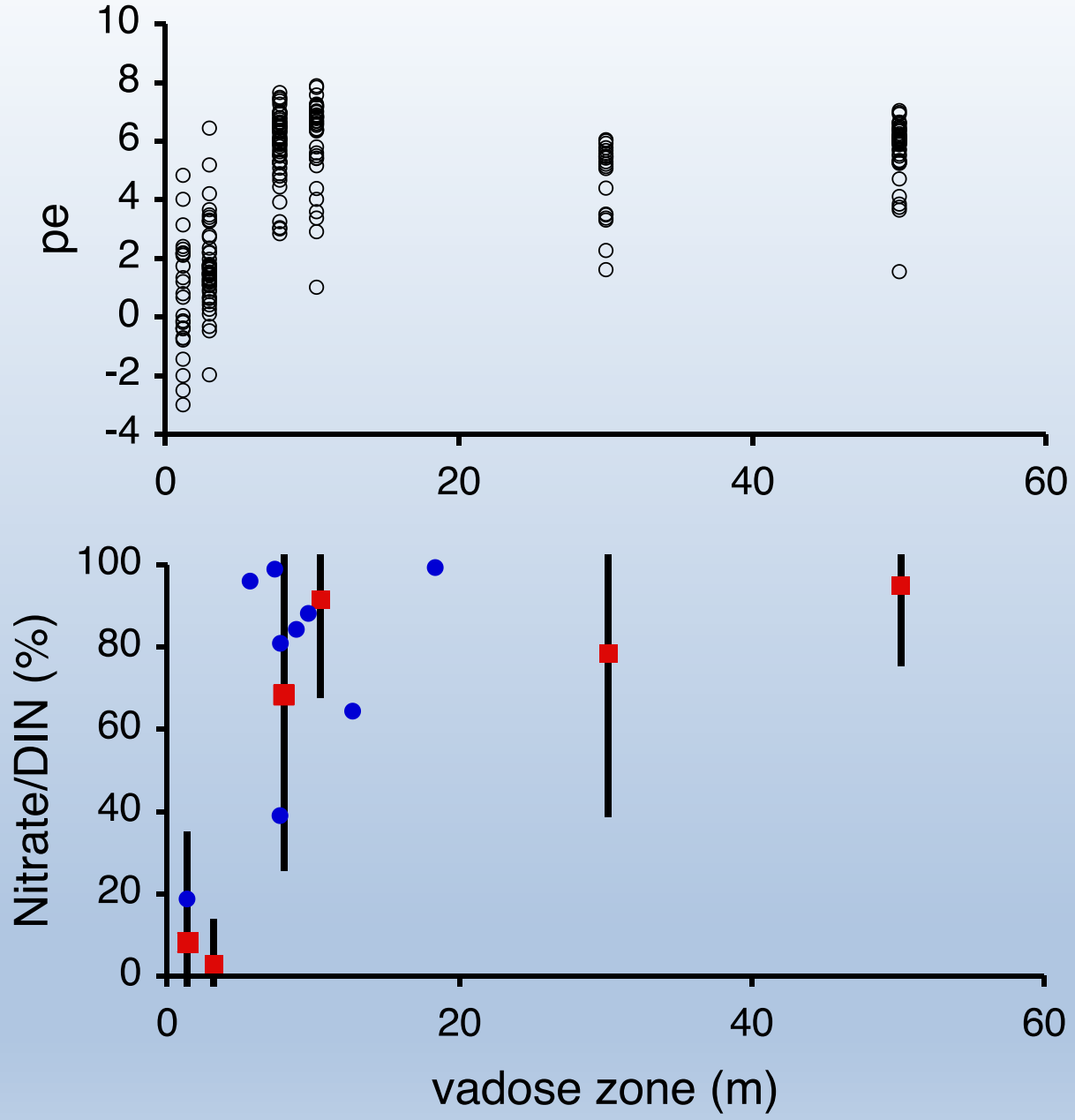
The freshwater/saltwater interface can move seasonally

- May interfere with the goal of promoting delivery of freshwater-borne nitrate to the PRB



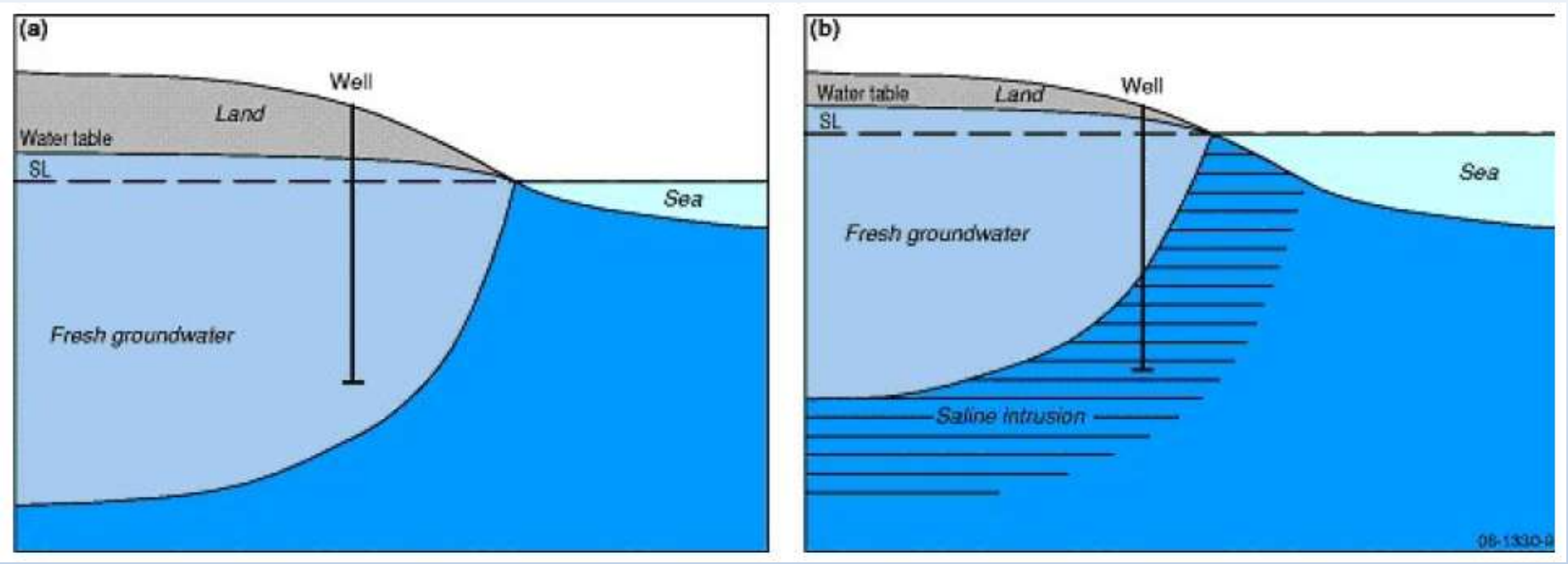
Questions?


Average DON/TDN x 100
100
80
60
40
20
0
Average NO3/DIN x 100
100
80
60
40
20
0
0
4
8
12
Population density (ha-1)
Cape Cod
Pinellas County



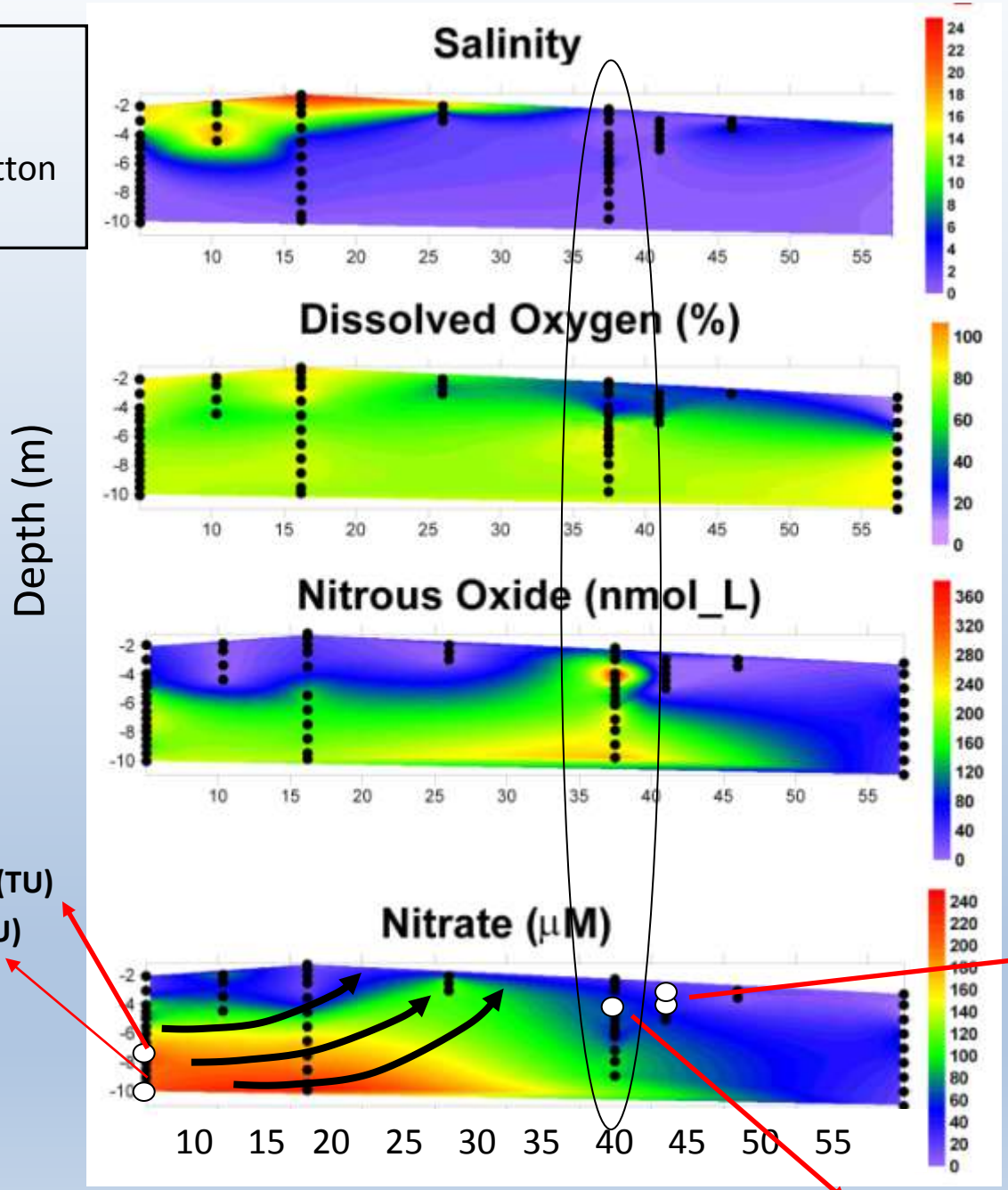
Data: Kroeger et al. 1999, Kroeger 2003, Kroeger et al. 2006a, Kroeger et al. 2007, Kroeger & Charette 2008, unpub.

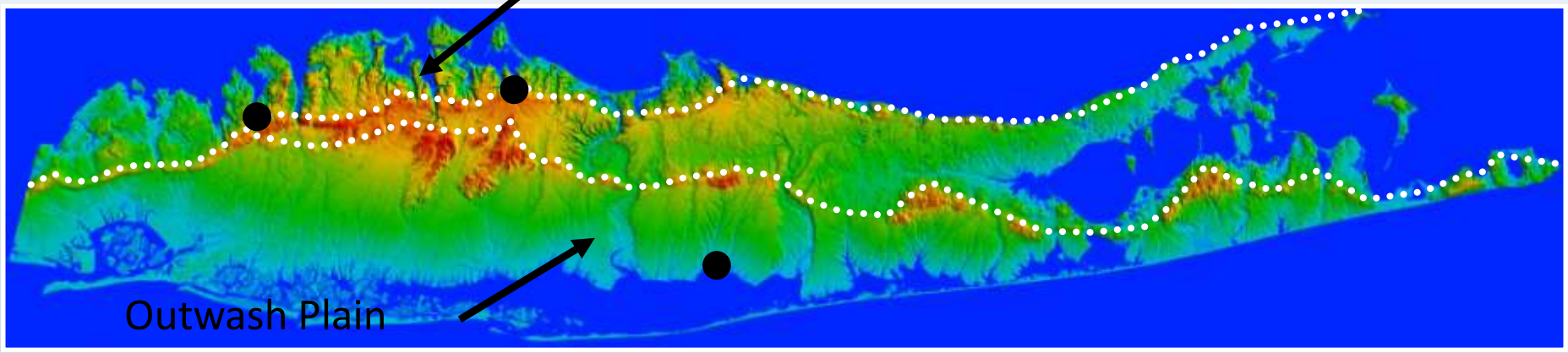
USGS science for a changing world

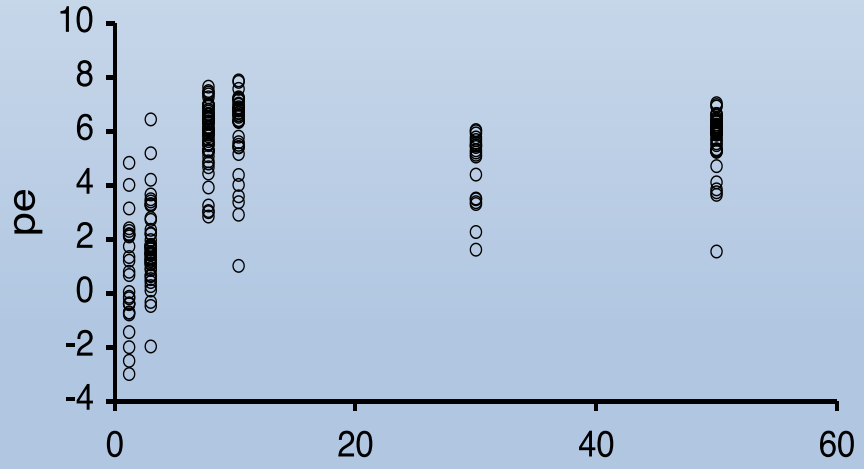

(a)
Well
Land
Water table
SL
Sea
Fresh groundwater
(b)
Water table
Land
Well
SL
Sea
Fresh groundwater
Saline intrusion
08-1330-0

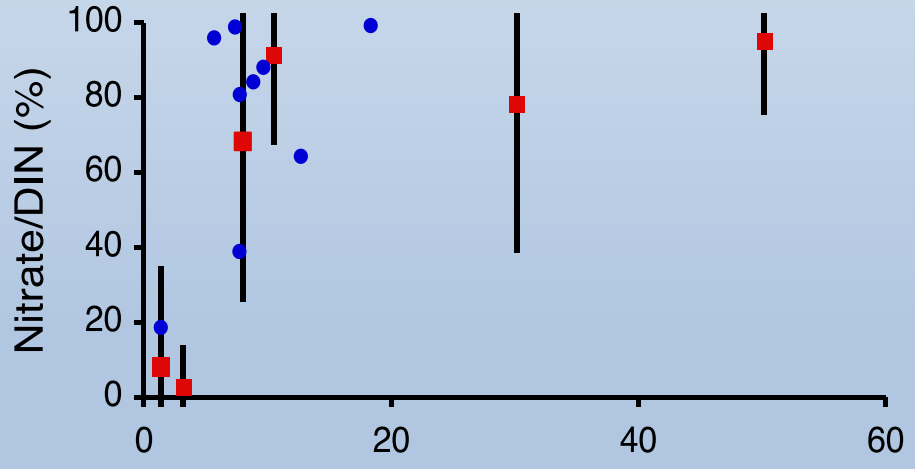
Northport Harbor
Long Island, NY

Kroeger, Crusius, Bratton unpubl.







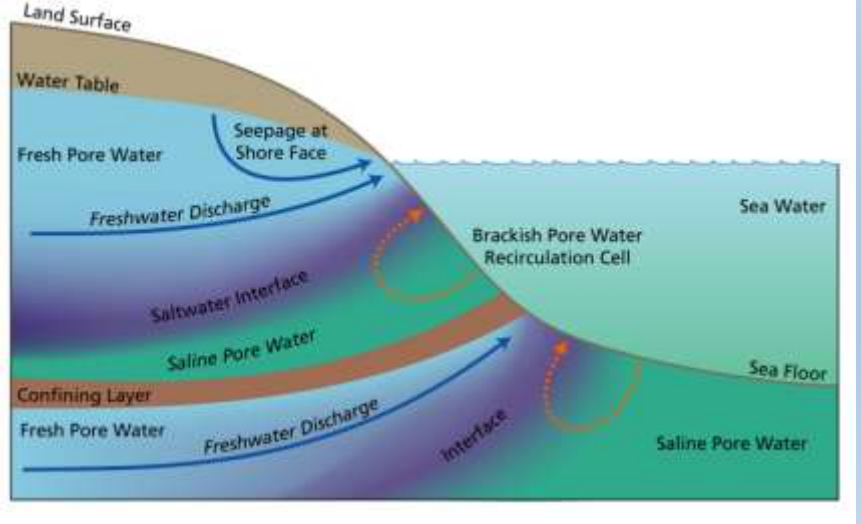


Vadose Zone (m)

Data from Kroeger et al., unpublished; Kroeger et al., 2006, 2007: Kroeger and Charette, 2008.

Management Options

- Reduce Sources:
  - Wastewater-Sewering
  - Atmospheric deposition-Reduce combustion of all types; Regulate NOx from trucks & SUVs
  - Fertilizer-Encourage or mandate reductions & changes in type (slow release, organic)
- Remediate N at the seepage face:
  - Addresses all 3 sources
  - Addresses "legacy" N
  - Economical relative to sewering



Nitrification

1 $2O_2 + NH_4^+ \rightarrow 2H^+ + NO_3^- + H_2O$

2 $4MnO_2 + NH_4^+ + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O$

Ammonium oxidation to N_2

3 $3/2MnO_2 + NH_4^+ + 2H^+ \rightarrow 3/2Mn^{2+} + 1/2N_2 + 3H_2O$

4 $MnOOH + 1/3NH_4^+ + 5/3H^+ \rightarrow Mn^{2+} + 1/6N_2 + 2H_2O$

5 $5/8\ FeS + 4MnO_2 + NH_4^+ + 7H^+ \rightarrow$
$1/2N_2 + 4Mn^{2+} + 5/8\ SO_4^{2-} + 5/8\ Fe^{2+} + 1\ 1/2H_2O$

Denitrification

6 $5/4CH_2O + NO_3^- + H^+ \rightarrow 5/4CO_2 + 1/2N_2 + 7/4H_2O$

7 $I^+ + 1/5NO_3^- + 6/5H^+ \rightarrow 1/10N_2 + 1/2I_2 + 3/5H_2)$

8 $NO_3^- + 5/8FeS + H^+ \rightarrow 1/2N_2 + 5/8SO_4^{2-} + 5/8Fe^{2+} + 1/2H_2O$

9 $NO_3^- + 5Fe^{2+} + 12H_2O \rightarrow 5Fe(OH)_3 + 1/2N_2 + 9H^+$

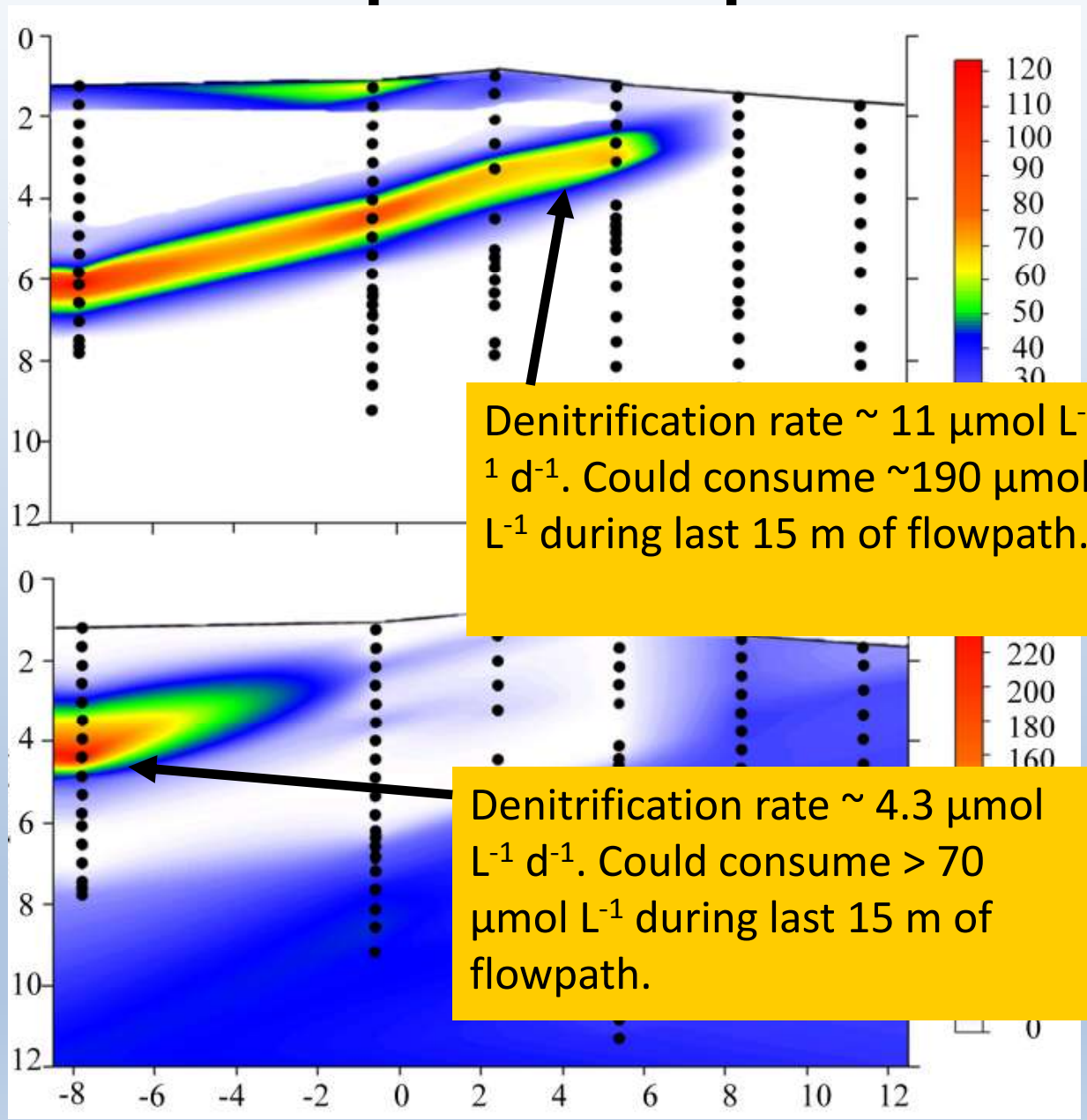
10 $5/2Mn^{2+} + NO_3^- + 2H_2O \rightarrow 5/2MnO_2 + 1/2N_2 + 4H^+$

Anammox

11 $NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$

12 $NH_3 + 1.5O_2 \rightarrow NO_2^- + H_2O + H^+$

$NH_3 + 1.32NO_2^- + H^+ \rightarrow 1.02N_2 + 0.26NO_3^- + 2H_2O$



Denitrification rate ~ 11 µmol L^{-1} d^{-1}. Could consume ~190 µmol L^{-1} during last 15 m of flowpath.

Denitrification rate ~ 4.3 µmol L^{-1} d^{-1}. Could consume > 70 µmol L^{-1} during last 15 m of flowpath.

Despite very low organic matter content, the extent of N loss in the seepage face is likely limited by limited mixing of fresh and saline groundwater.

Likely that commonly the majority of the N survives transit through the seepage zone, and enters the estuary.