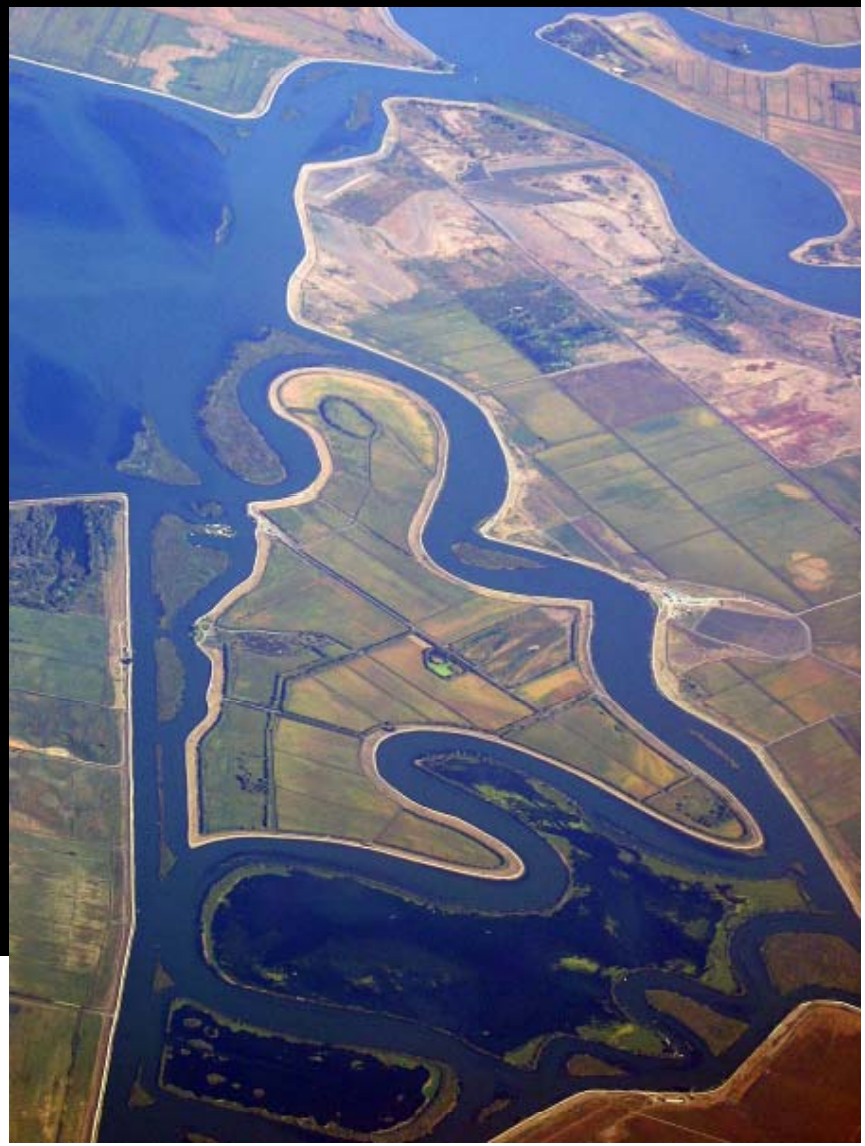
# Ammonium-Global trends, issues on the east coast, and implications for plankton dynamics



Patricia M. Glibert

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Horn Point Laboratory

# Outline

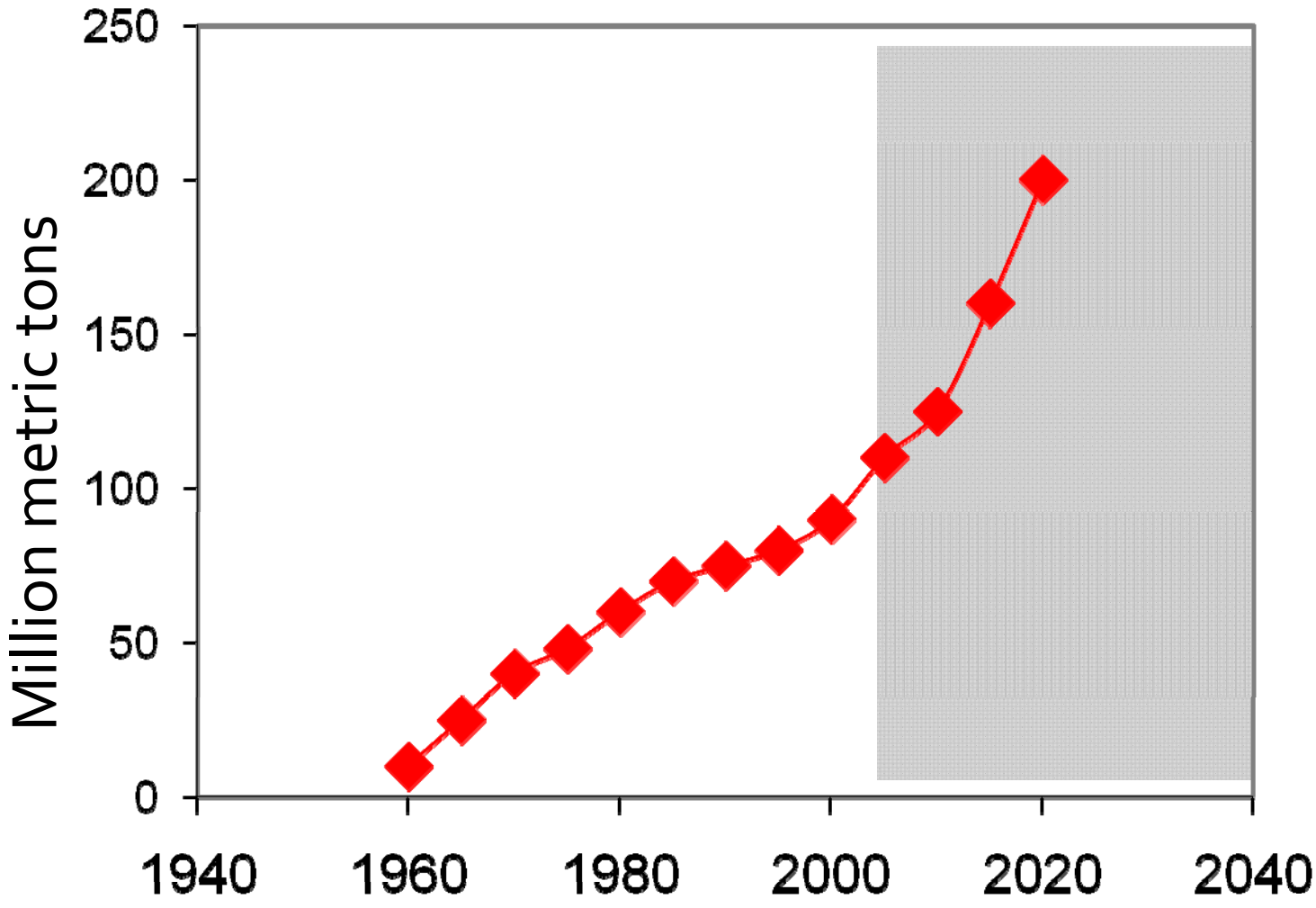
Global overview

Some examples of ammonium increases from the east coast

Algal physiological basis for nutrient preferences

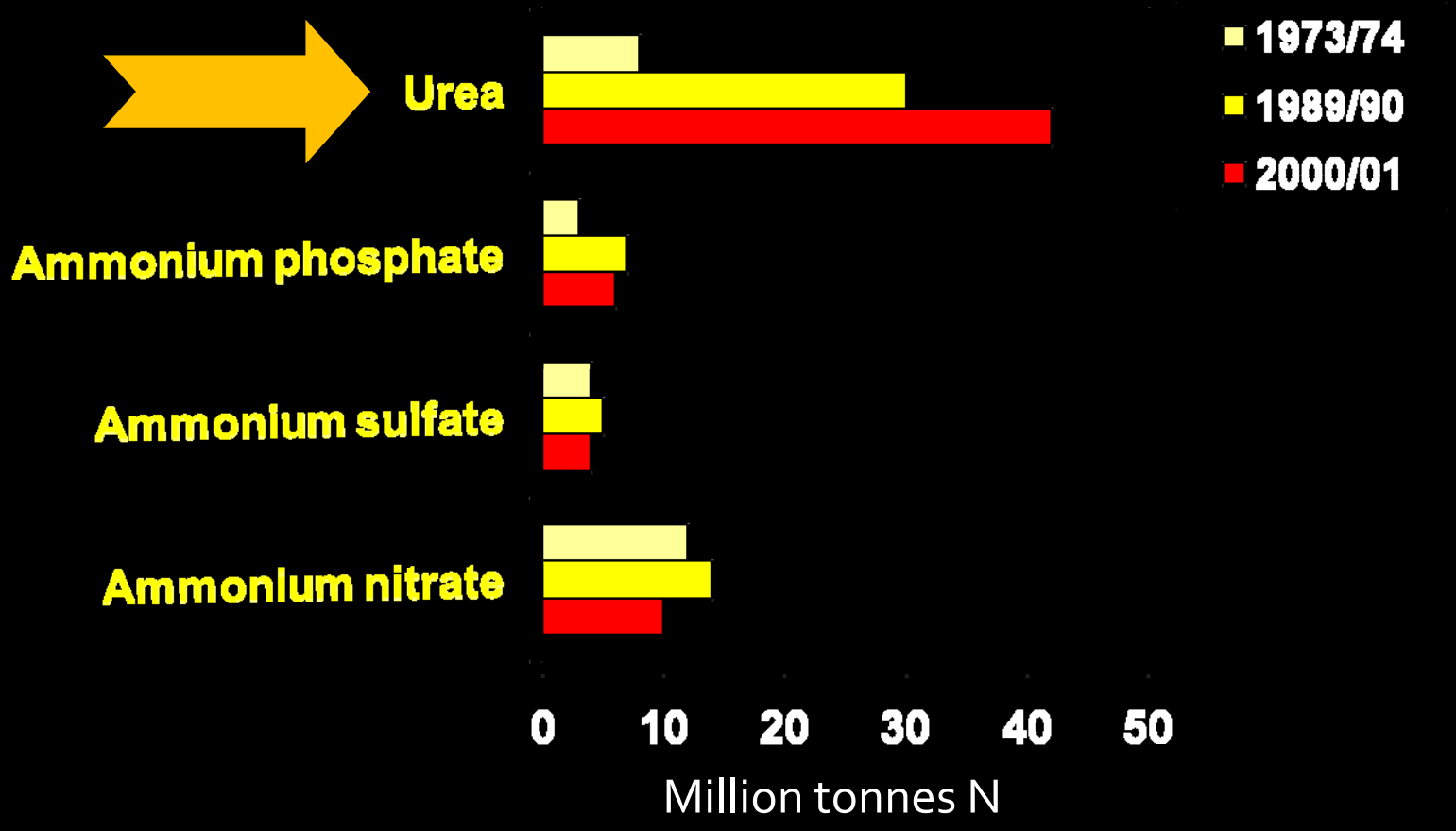
Implications for the Delta region

# World consumption of N fertilizers



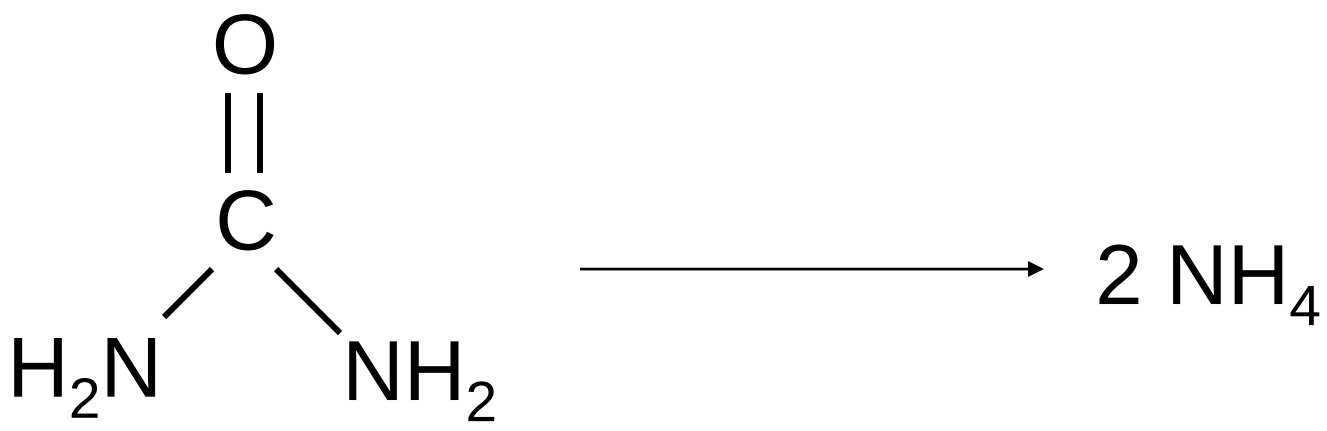
# World Nitrogen Fertilizer Consumption

World N fertilizer increases have primarily been in the form of urea

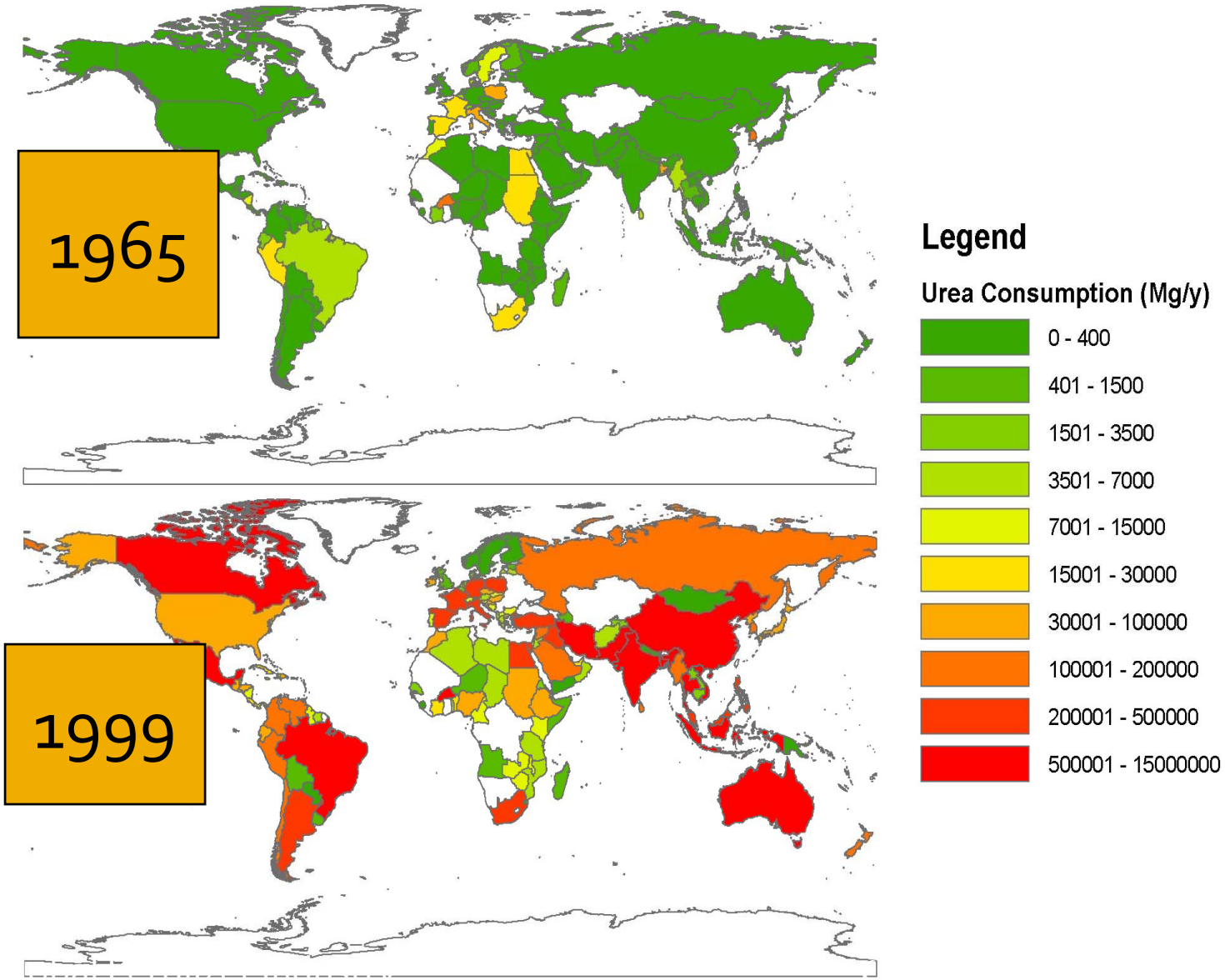



International Fertilizer Industry

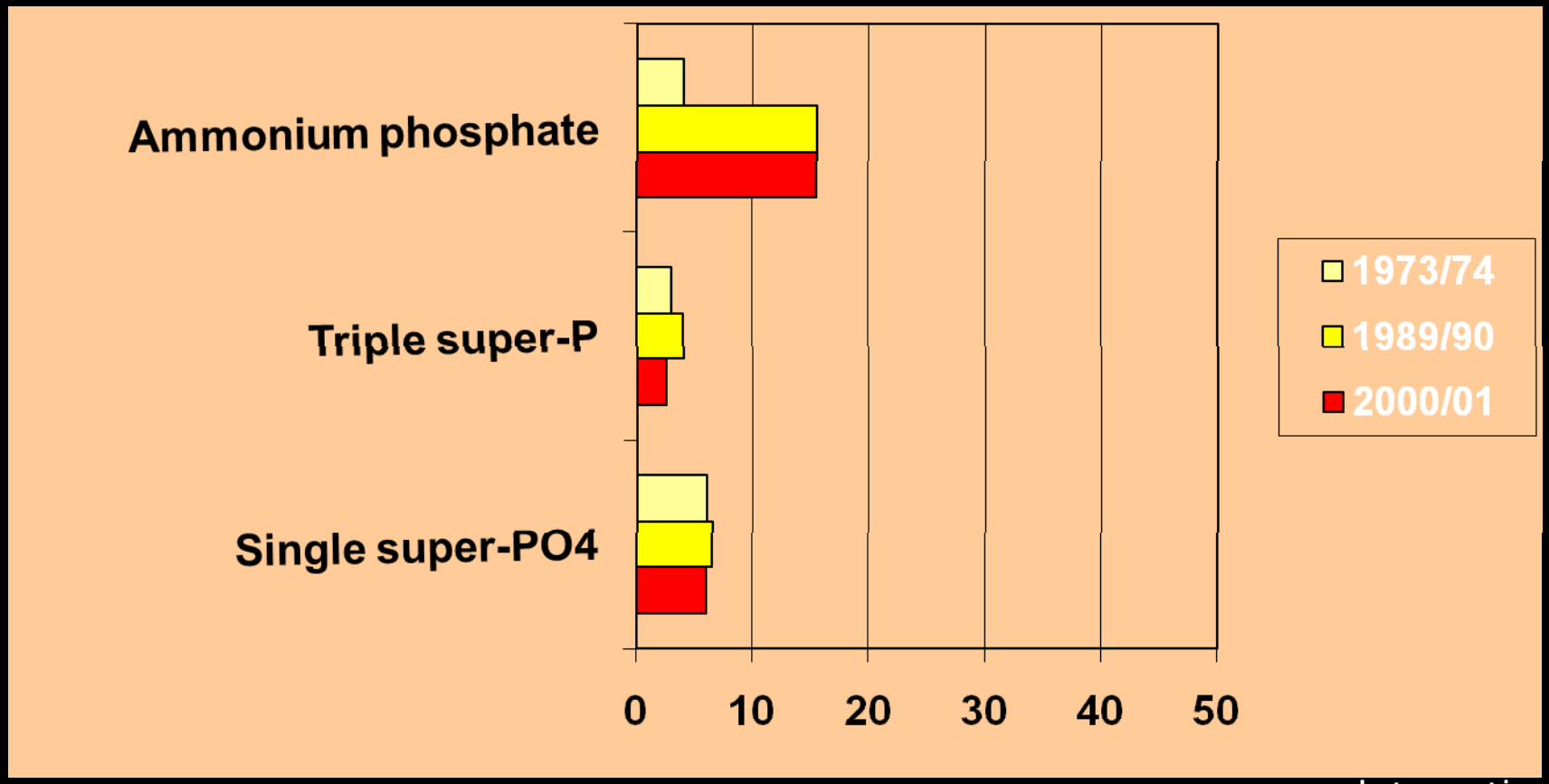
# What is urea?



# Virtually every country has dramatically increased Urea use since 1965



# World Phosphate Fertilizer Consumption



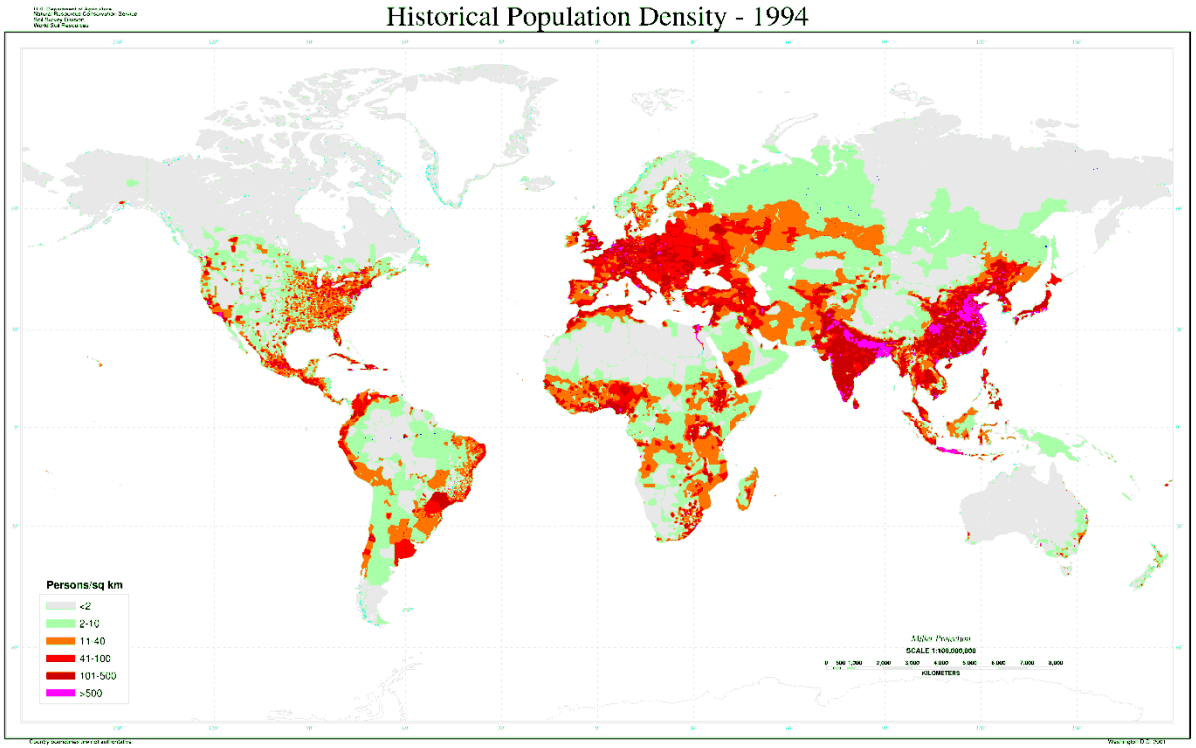

Million tonnes $P_2O_5$

International Fertilizer Industry

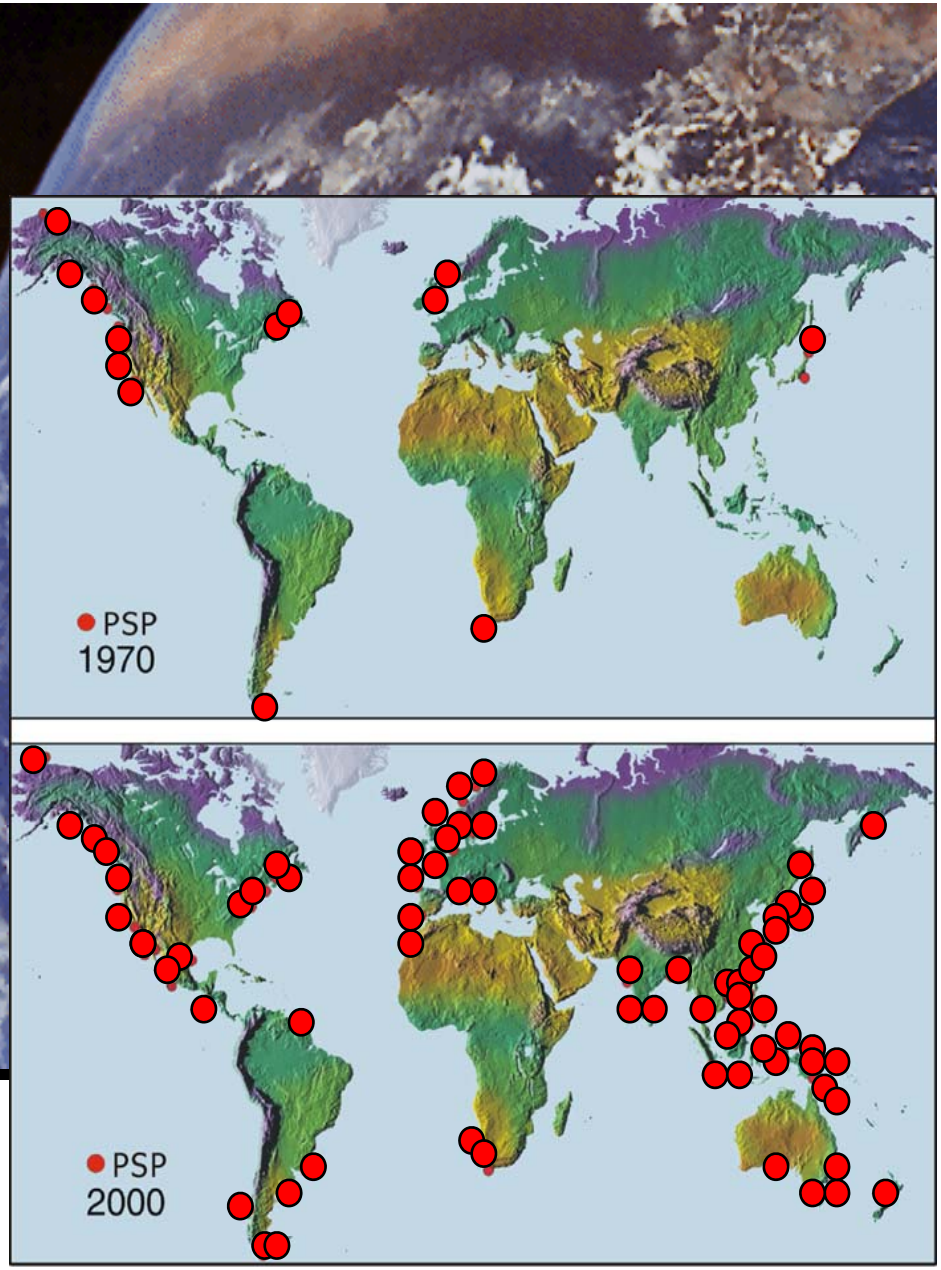
The increase in N fertilizers
is about double that of P fertilizers since 1973

# Population growth also contributes to N and P pollution

World Population



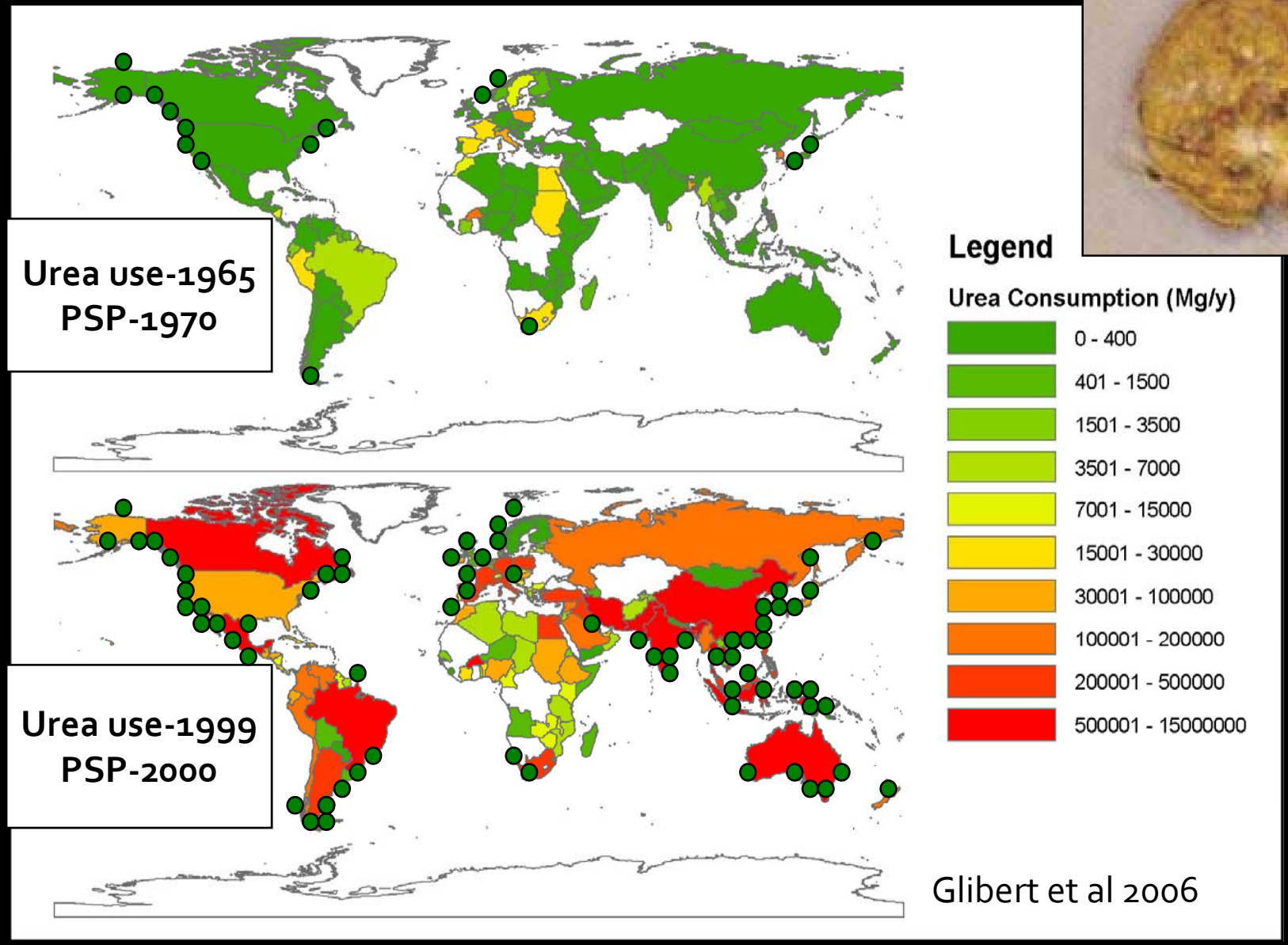
# Do these global changes relate to global increases in HABs?



# What are harmful algal blooms?

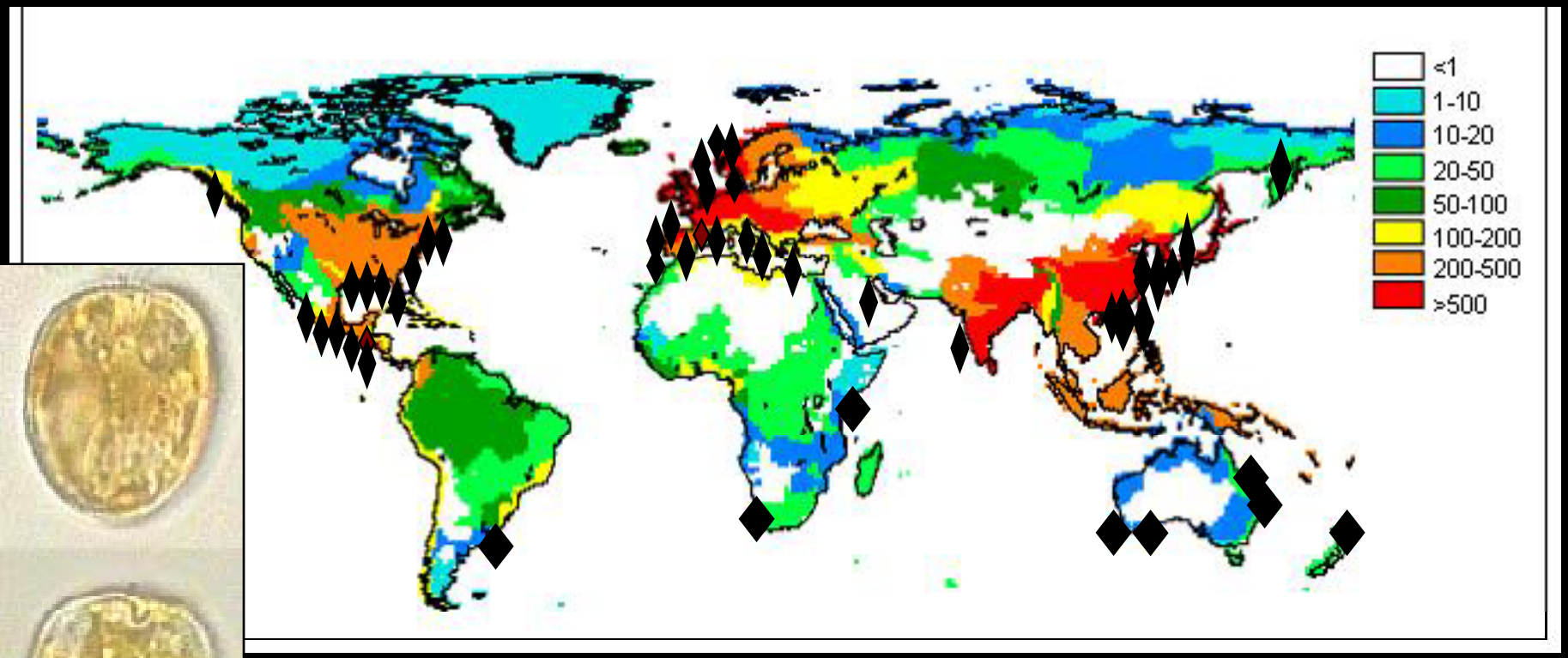
HABs are algae that contaminate seafood with toxins, cause fish and shellfish kills, affect human health, or alter ecosystems in detrimental ways

# Harmful blooms that produce PSP have paralleled urea increases




Glibert et al 2006

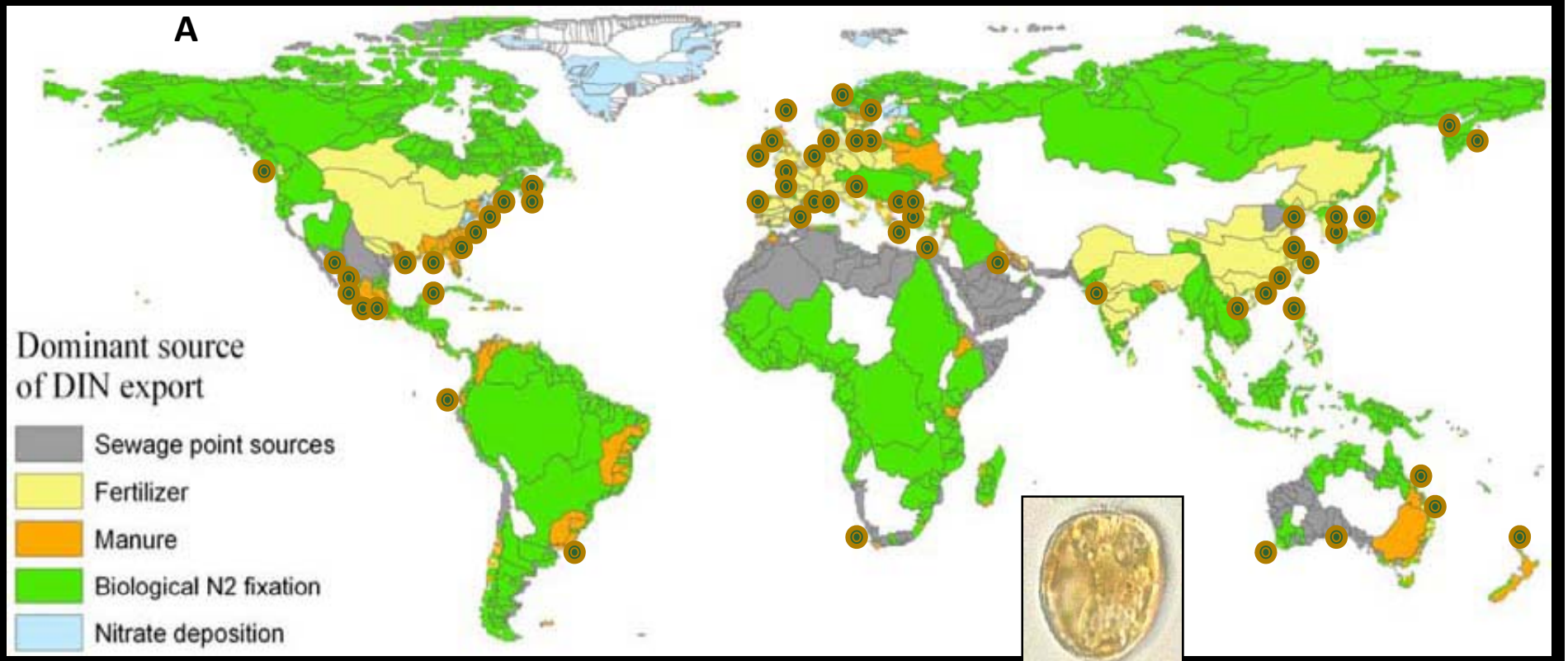
# Global distribution of blooms of the high biomass producer *Prorocentrum minimum* appear to generally track zones of high DIN export



Base map:
Seitzinger and Kroeze 1998

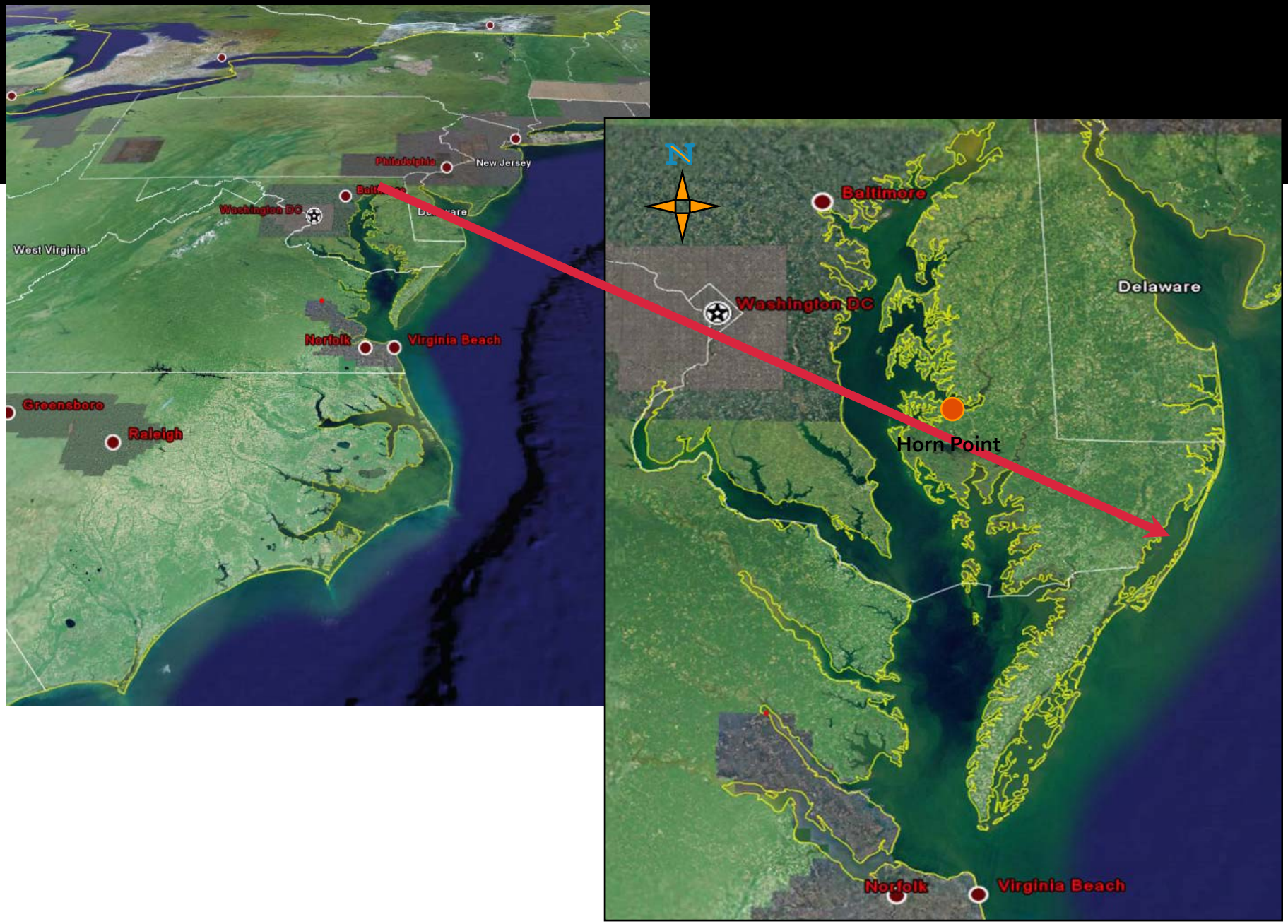
From:
Glibert and Burkholder 2006
Based on P. minimum maps fro
Heil, Glibert and Fan 2005

# *Prorocentrum minimum* tracks fertilizer and manure export globally

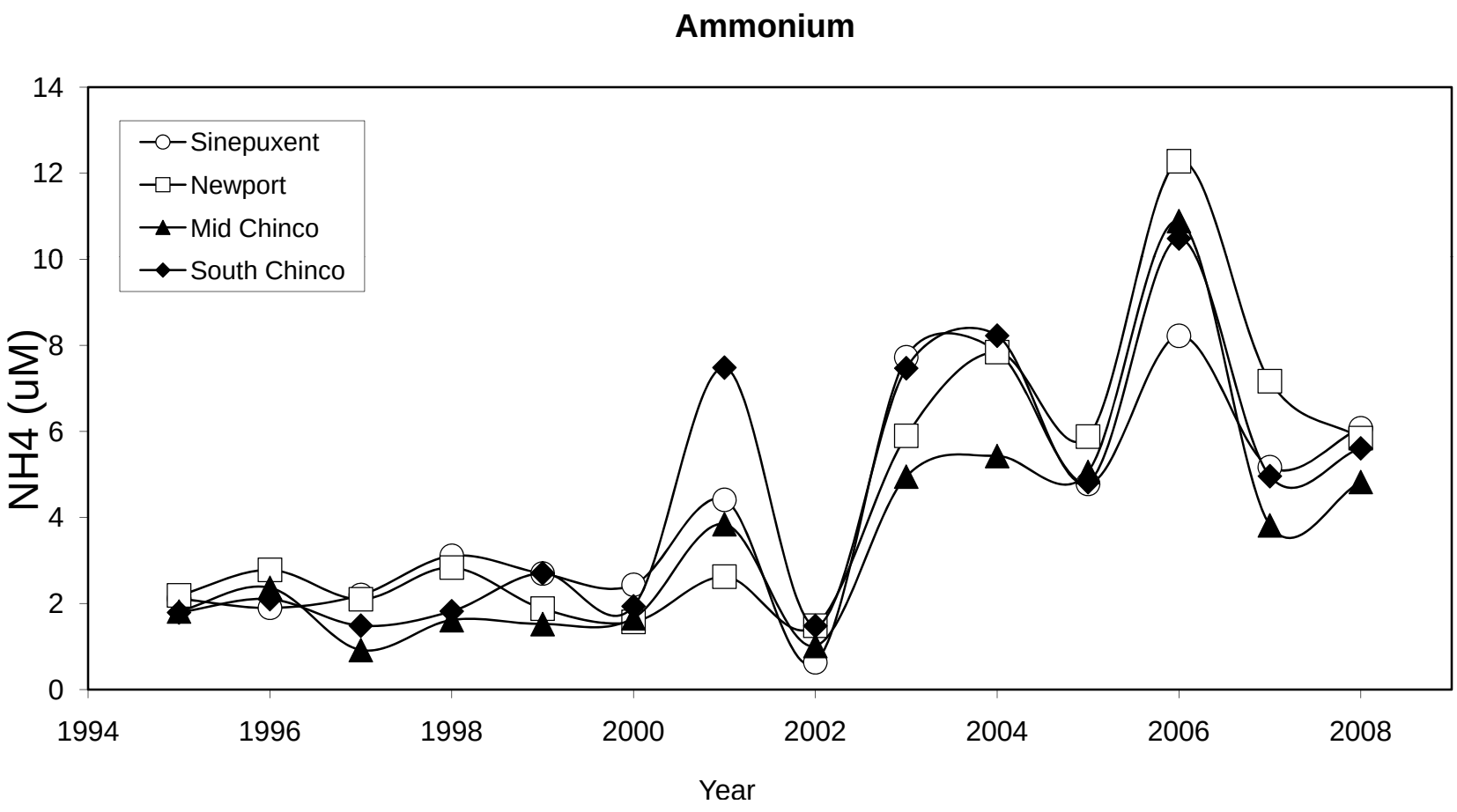


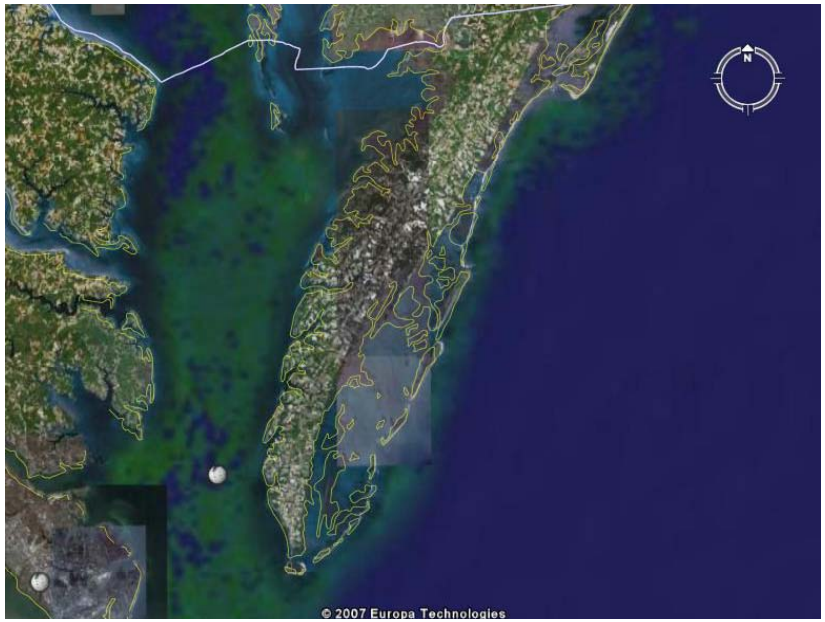
Global NEWS model from Dumont et al. 2005

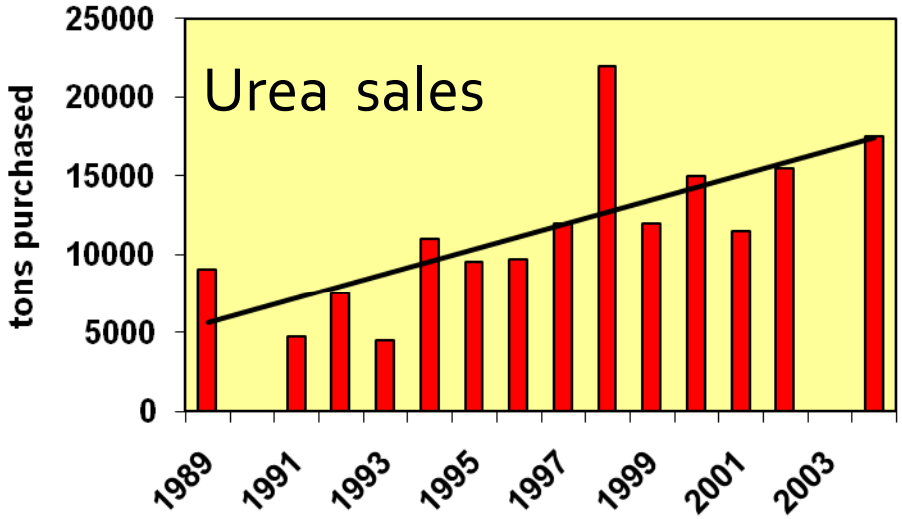
Glibert et al. 2008

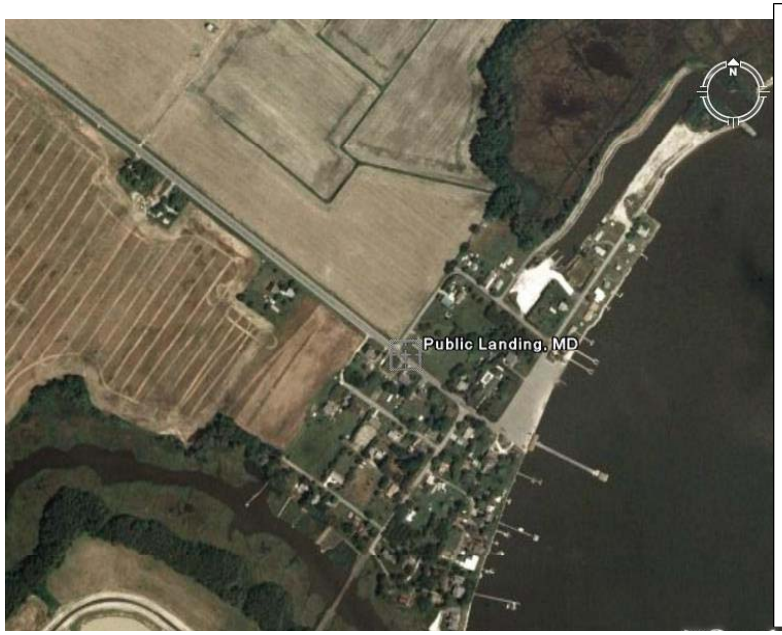

Philadelphia
New Jersey
Washington DC
West Virginia
Norfolk
Virginia Beach
Greensboro
Raleigh
N
Baltimore
Washington DC
Delaware
Horn Point
Norfolk
Virginia Beach

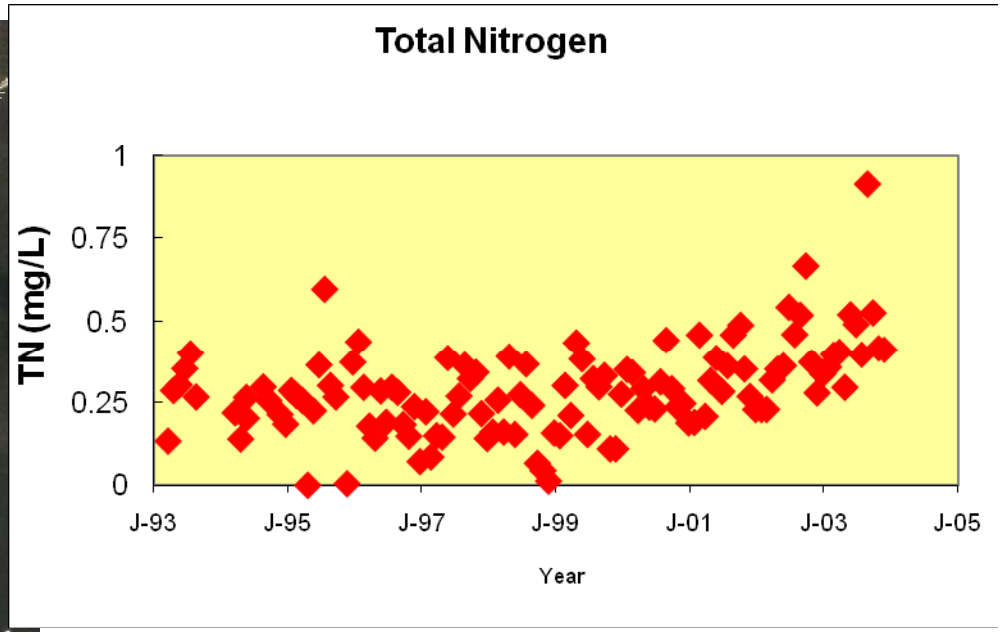
# Annual ammonium concentrations have increased in recent years




© 2007 Europa Technologies

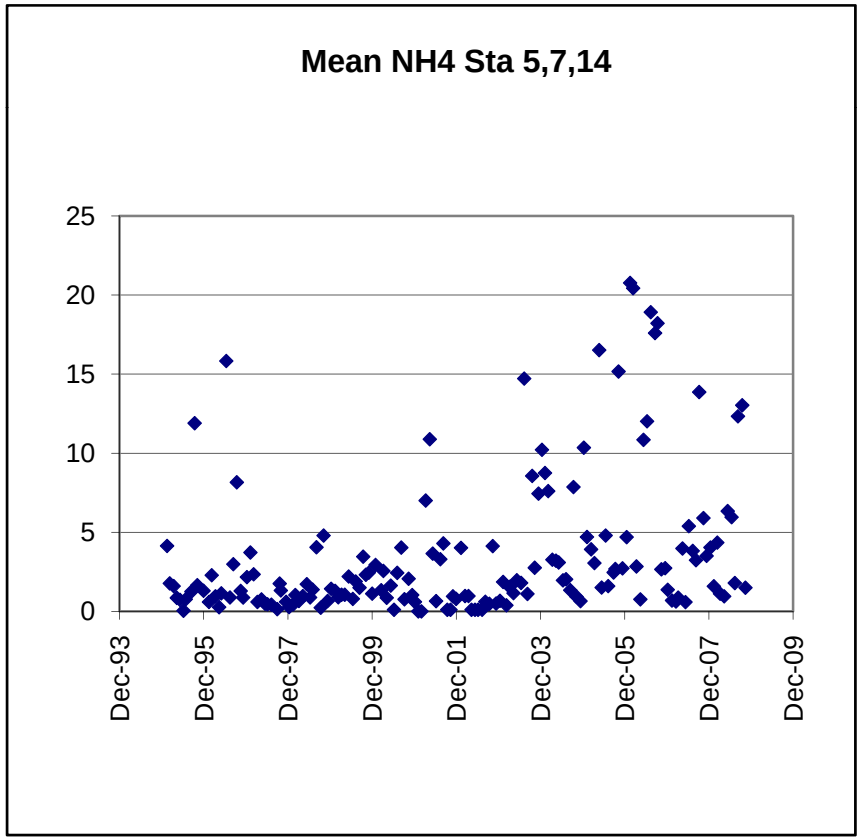

Urea sales
tons purchased
25000
20000
15000
10000
5000
0
1989
1991
1993
1995
1997
1999
2001
2003


Public Landing, MD

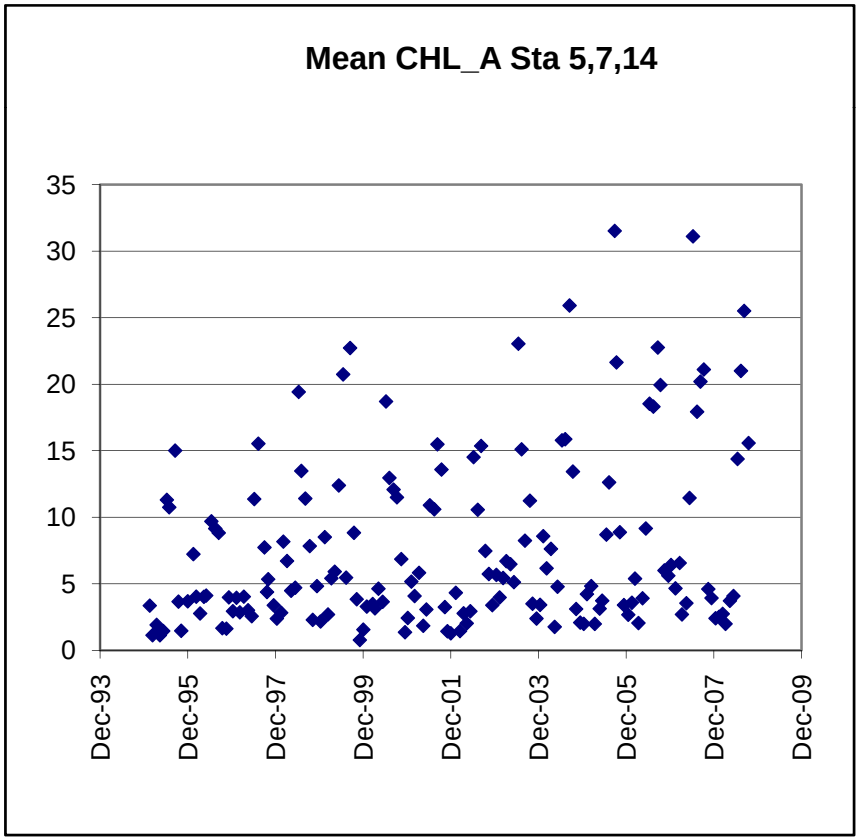

Total Nitrogen
TN (mg/L)
1
0.75
0.5
0.25
0
J-93
J-95
J-97
J-99
J-01
J-03
J-05
Year

# Maryland Coastal Bays 1994-2008

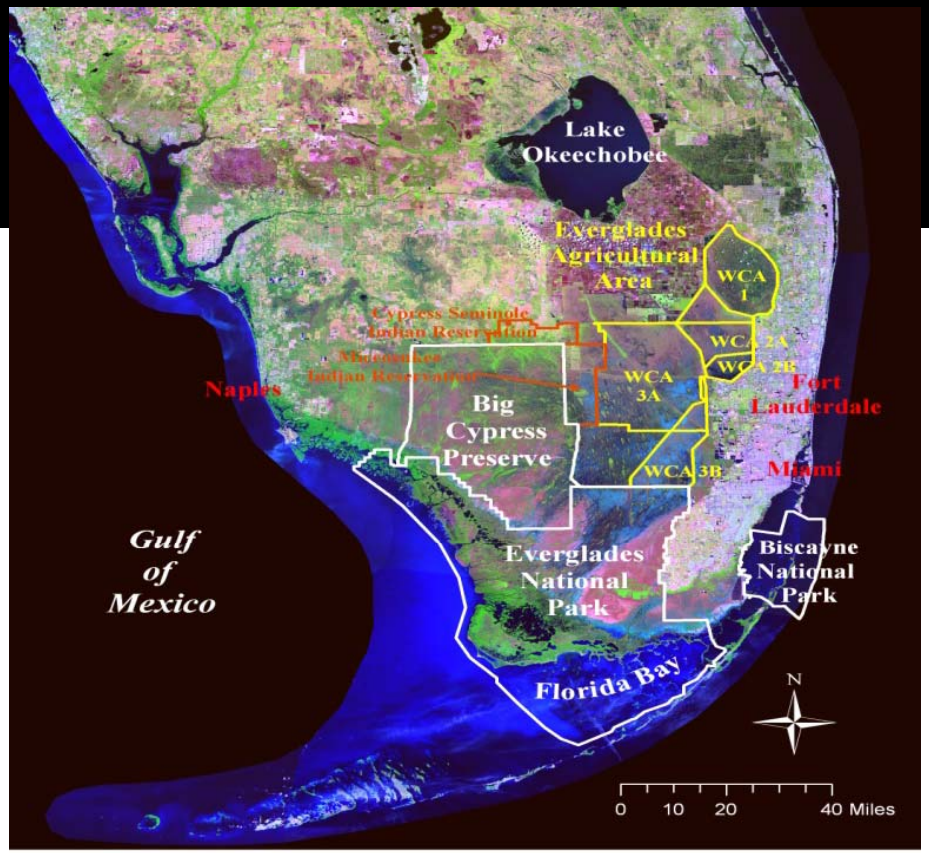
## AMMONIUM TRENDS

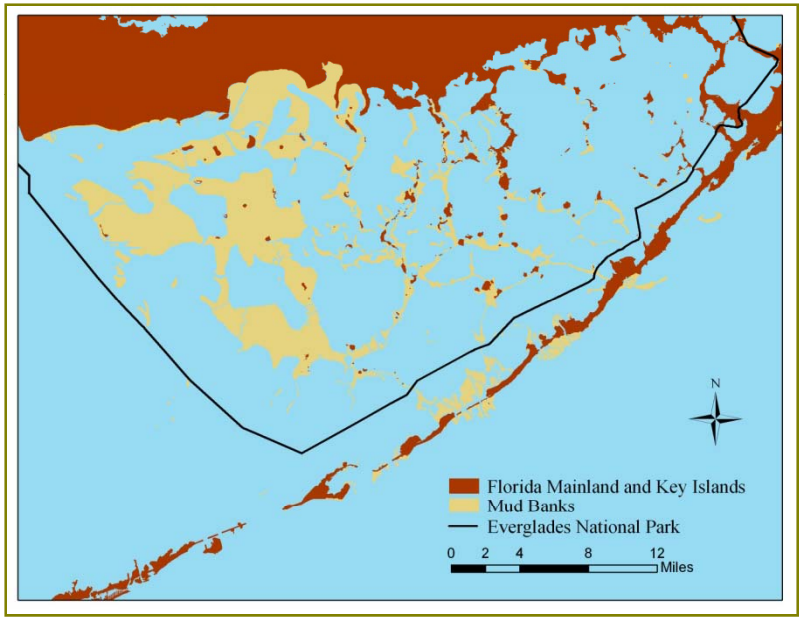



## CHLOROPHYLL TRENDS



# Florida Bay



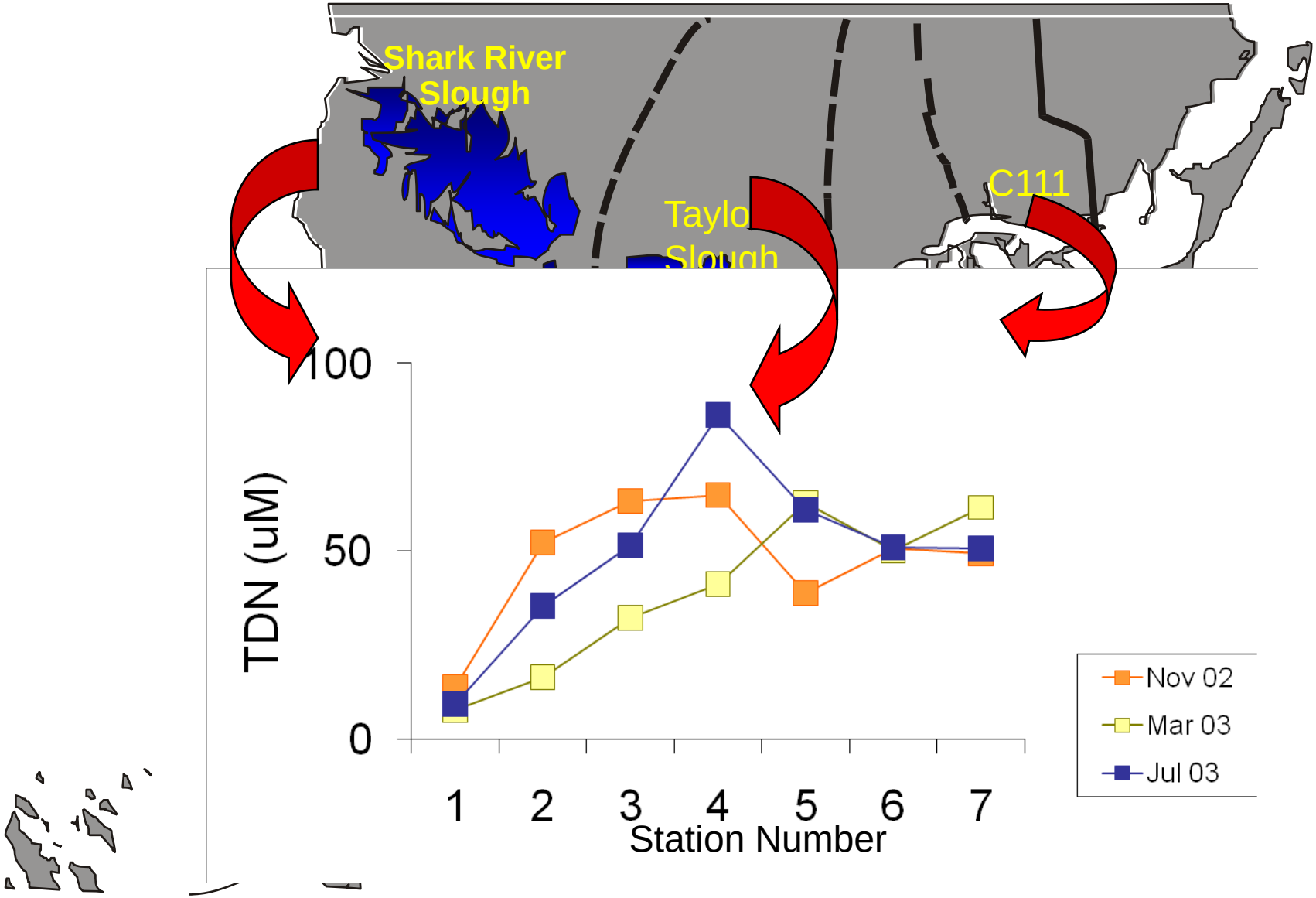



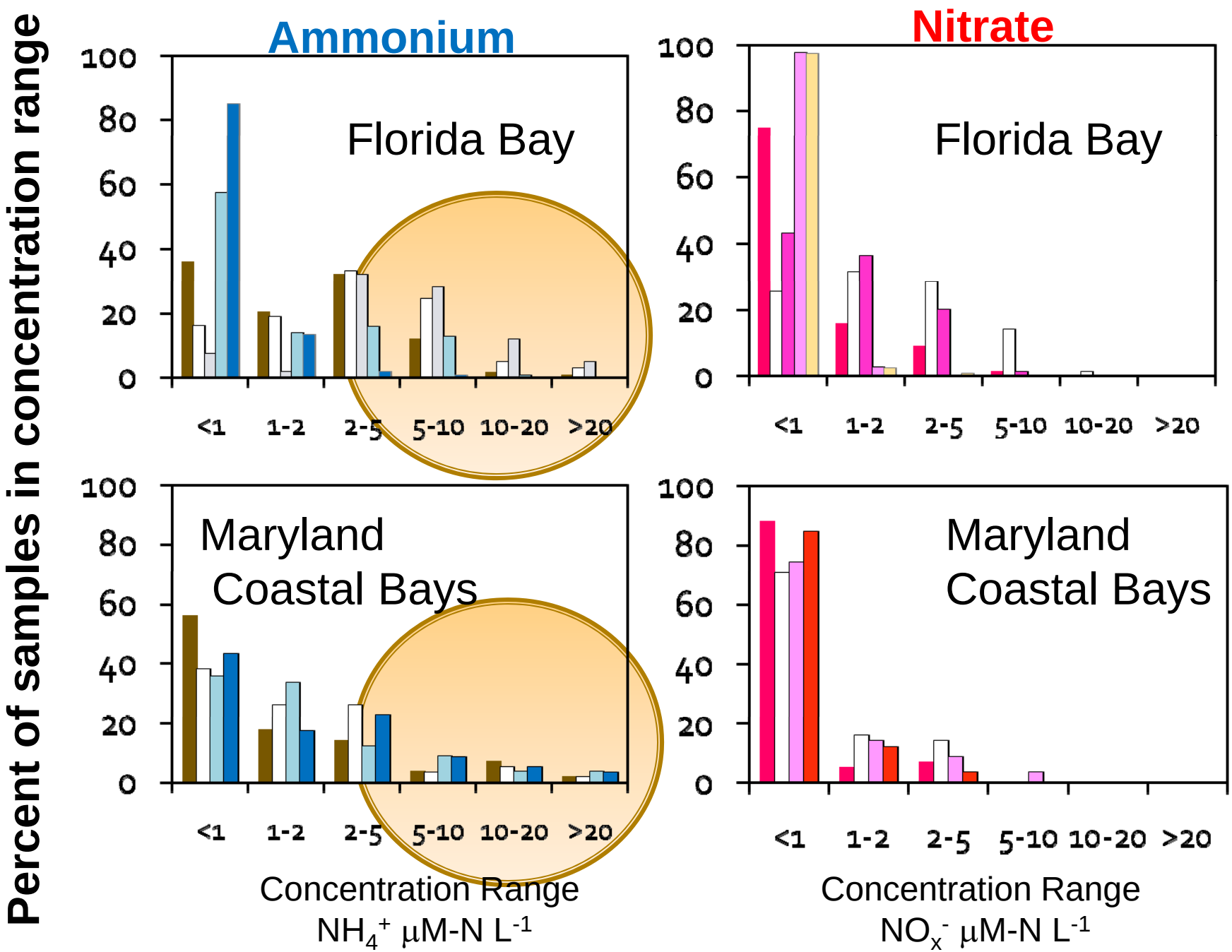

These lagoons have
limited river input,
long residence time
limited oceanic exchange

Challenge: Understanding how alteration in landscape affects the delivery and stoichiometry of nutrients to coastal waters and the resulting incidences of HABs

In Florida, the amounts, forms, and the ratios of nutrients are expected to change with changes in flow through the Everglades

# Florida Bay has a strong nitrogen to phosphorus gradient from west to east




Ammonium
Nitrate
Florida Bay
Florida Bay
Maryland
Coastal Bays
Maryland
Coastal Bays
Percent of samples in concentration range
100
80
60
40
20
0
<1
1-2
2-5
5-10
10-20
>20
Concentration Range
$NH_4^+$ µM-N $L^{-1}$
Concentration Range
$NO_x^-$ µM-N $L^{-1}$

# The common response to ammonium enrichment (when P is sufficient) in both systems is blooms

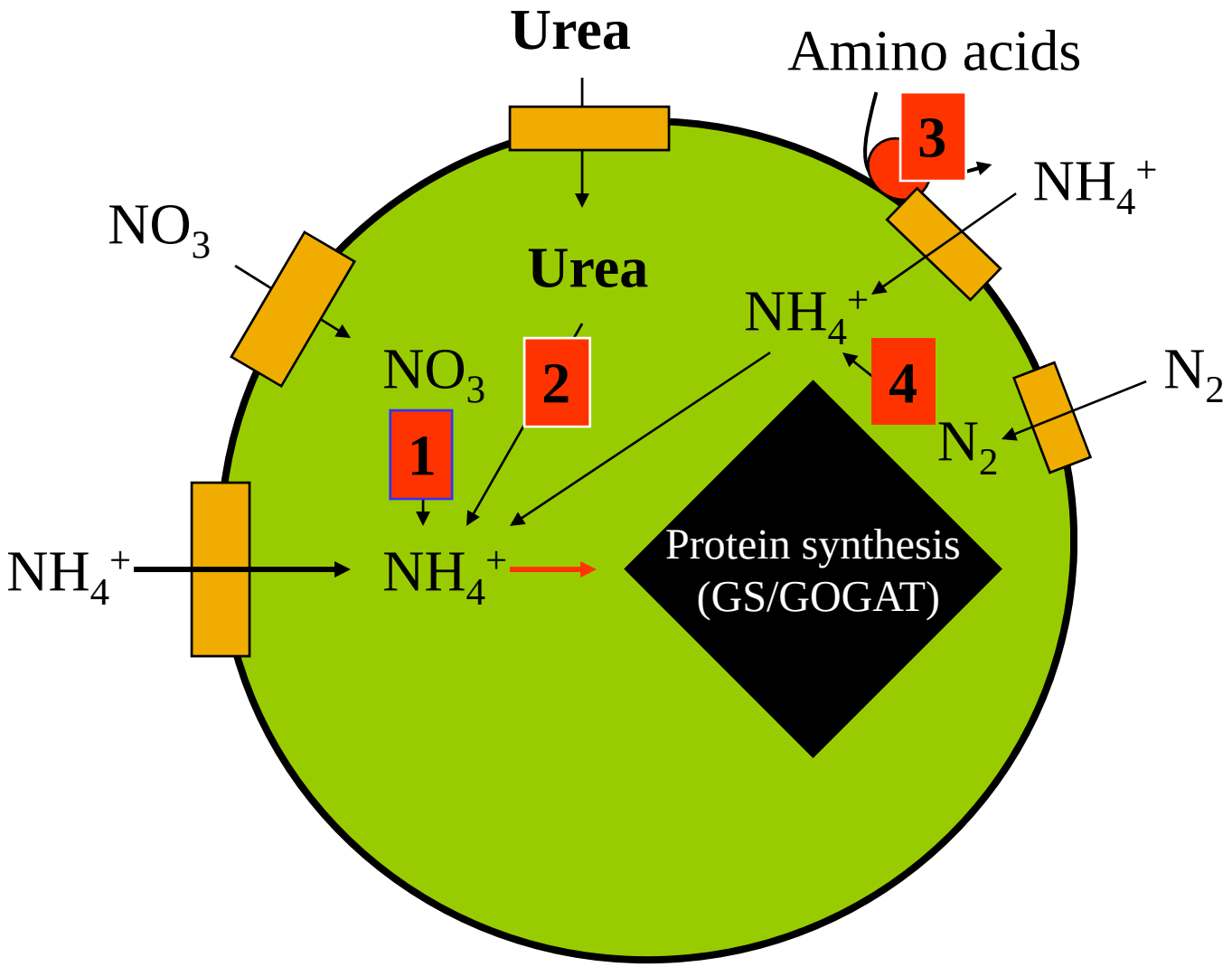
- Often dominated by picoplankton (<3 mm)
- Often mono-specific

*Synechococcus* in Florida Bay

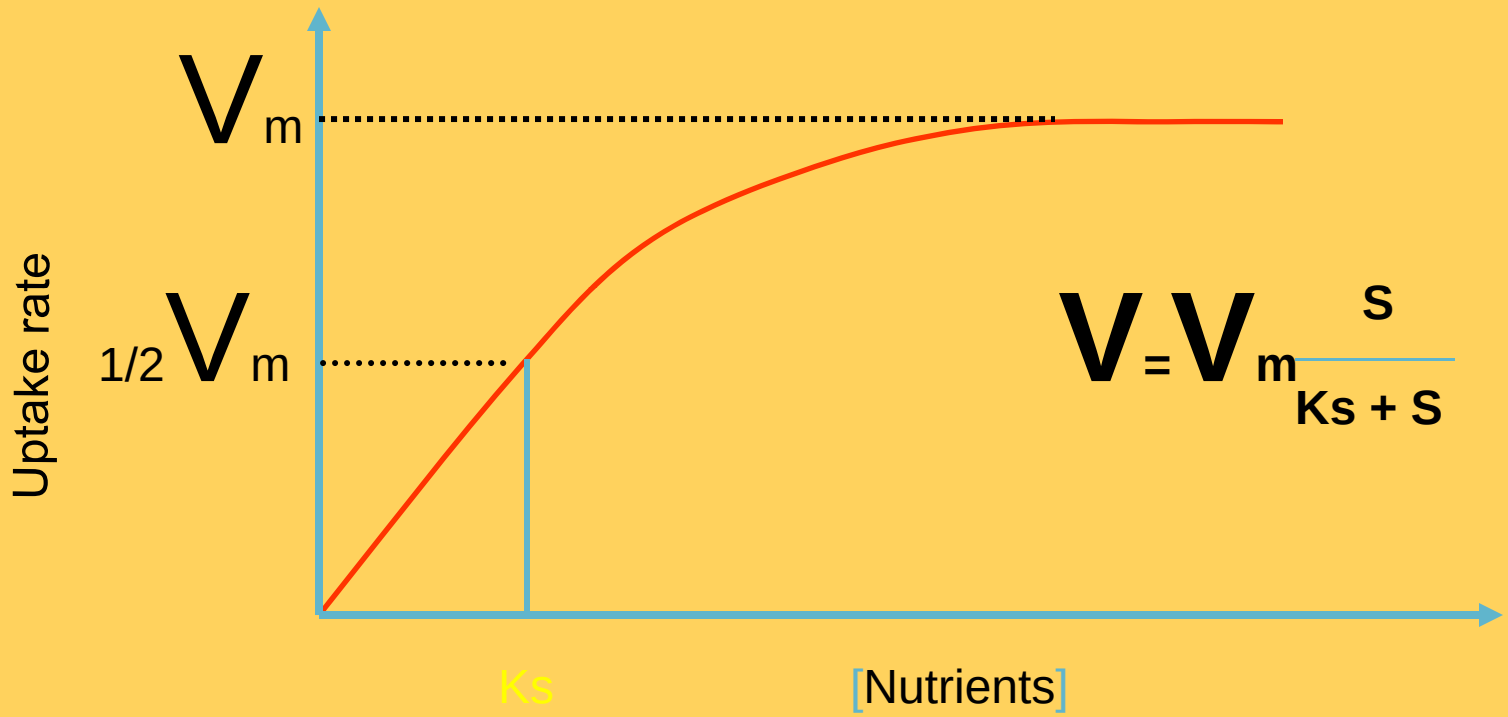
*Aurecococcus* in Maryland

# N Assimilation

Note that all nitrogen forms are converted to $NH_4$ before assimilation. Ammonium plays a key regulatory role in the cells



# Nutrient uptake rate can be described as a saturating hyperbola

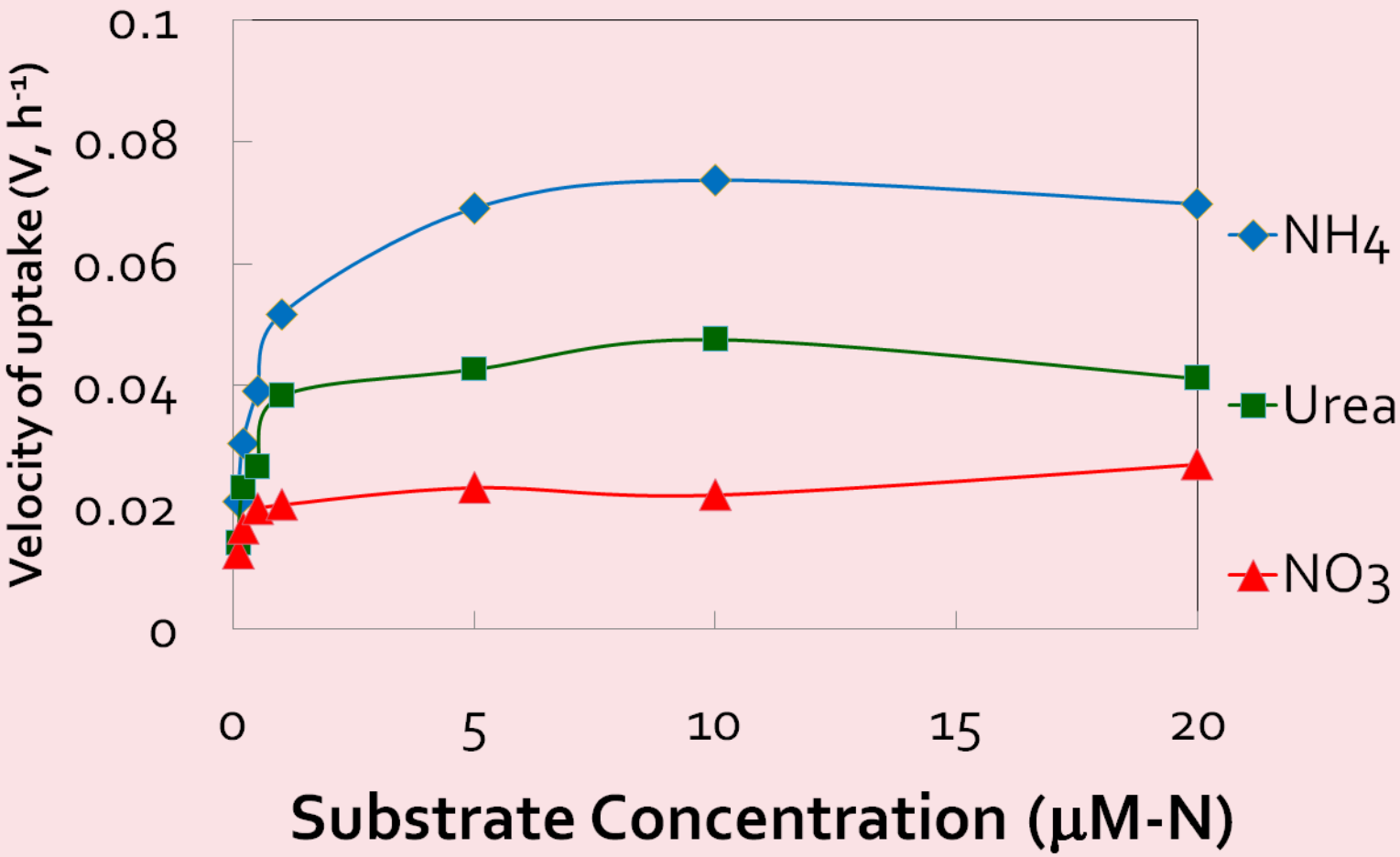



$$V = V_m \frac{S}{Ks + S}$$

Half saturation constant

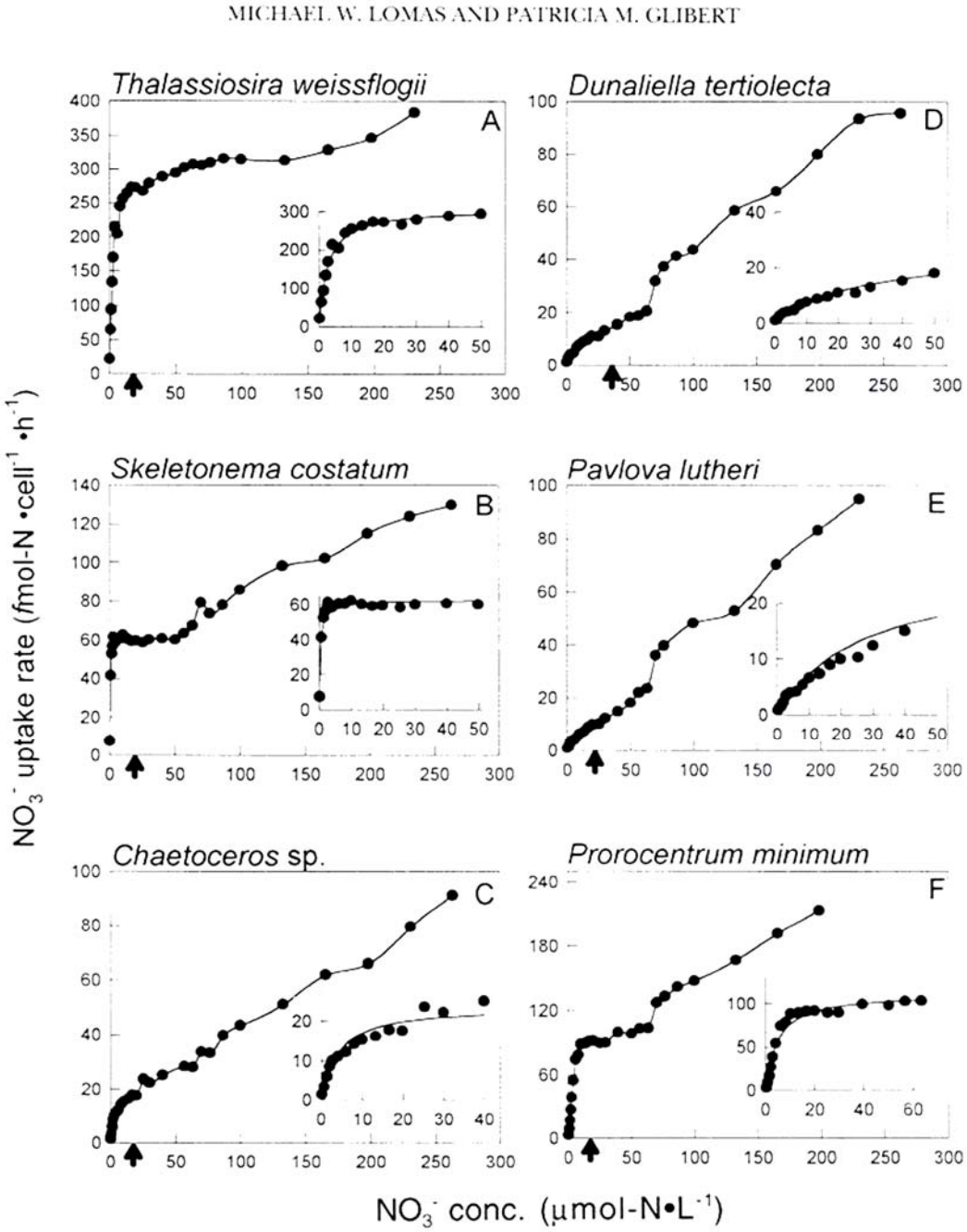
indicating affinity for a particular substrate

# Typically very high efficiency for $NH_4^+$ and urea uptake is observed – compared to $NO_3^-$



Nitrate uptake often doesn't follow the rules: Nitrate uptake rate often shows a linear (nonsaturable) relationship with concentration:

Many cells have a huge capacity for "processing" nitrate



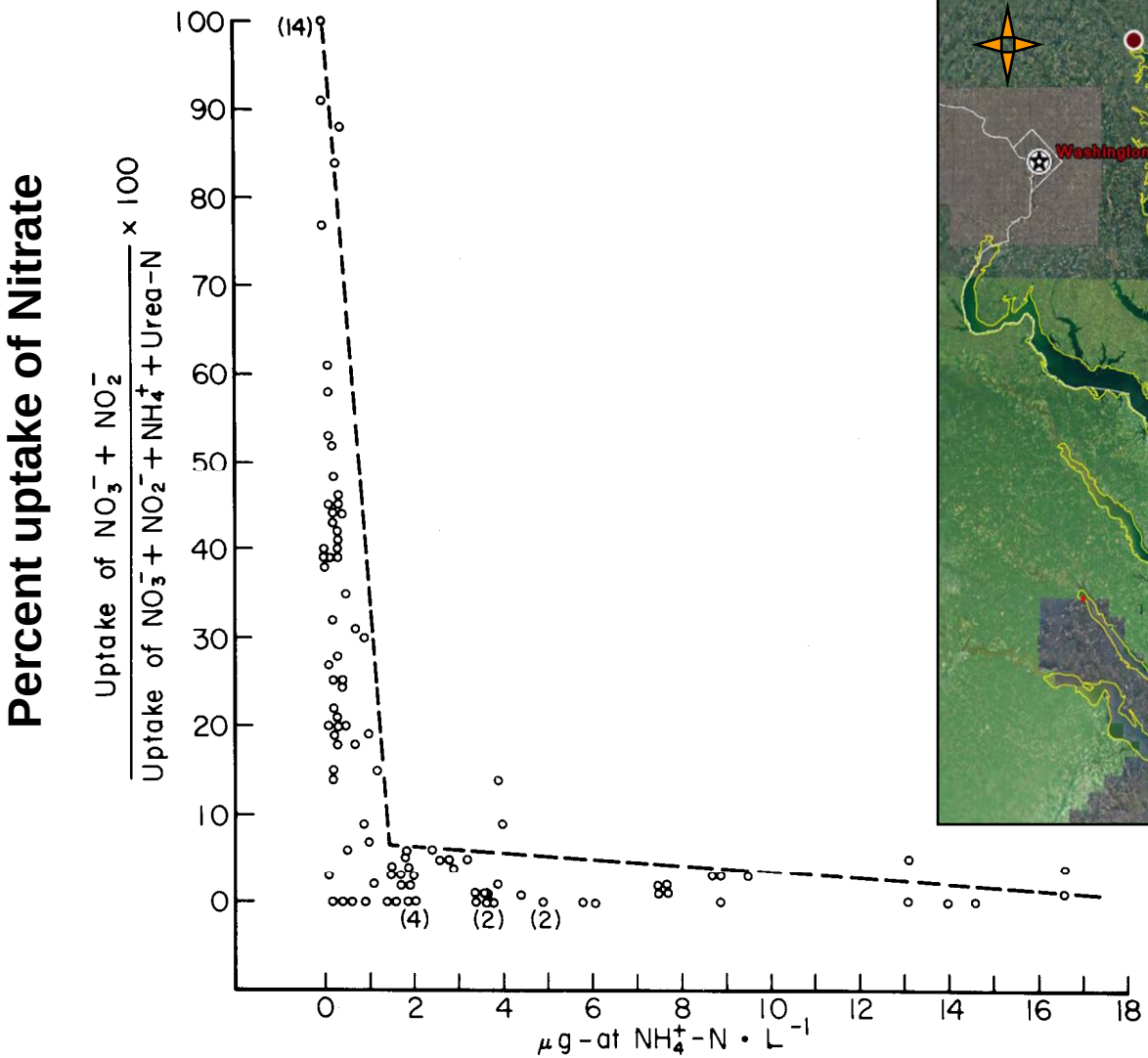
*In general*, the presence of ammonium is thought to:

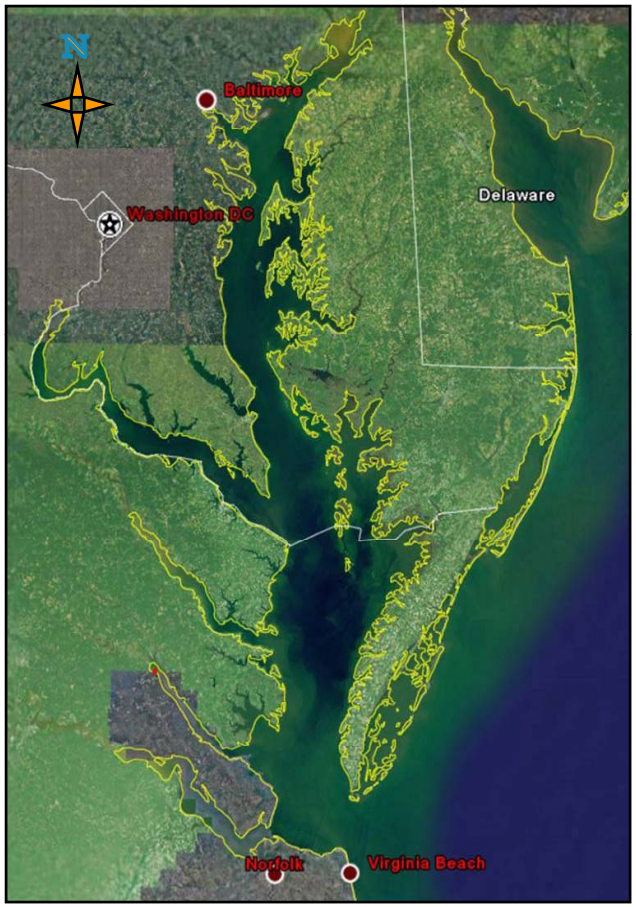
- suppress the synthesis of nitrate reductase, the cellular enzyme that converts nitrate to ammonium

- hasten the decay of existing nitrate reductase

- block the transport of nitrate across the cell membrane

Nitrate uptake as a fraction of total N uptake decreases with $NH_4$ concentration in Chesapeake Bay:



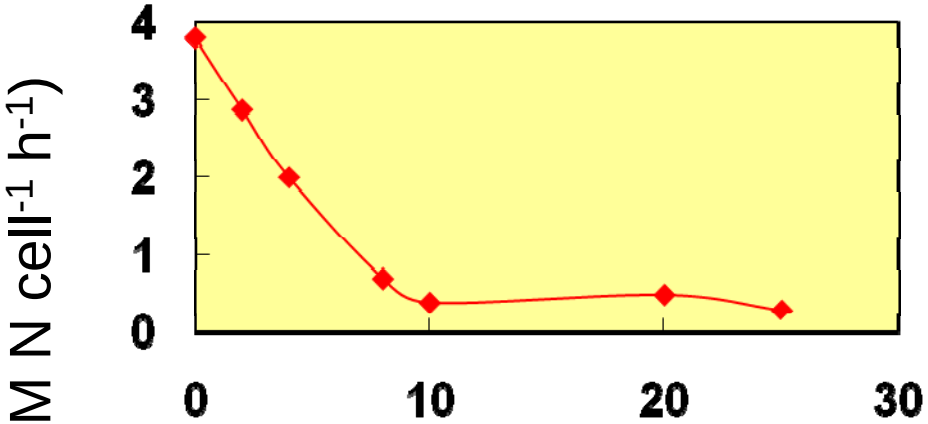




1977

McCarthy et al.

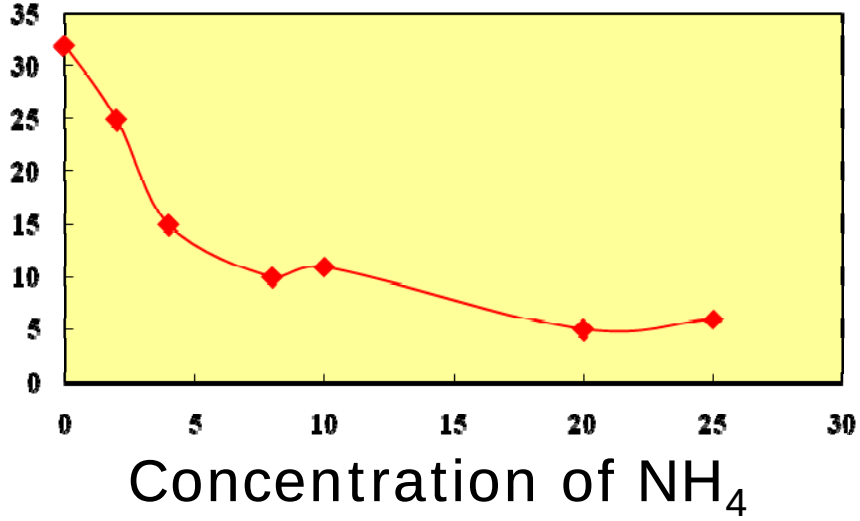
# Nitrate uptake inhibition by ammonium varies by species

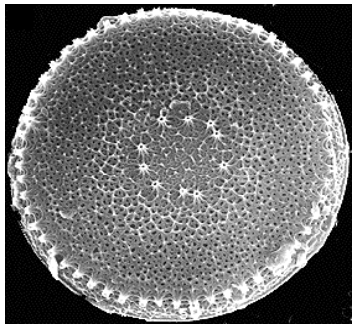
Chaetoceros sp.



©Embleton

Thalassiosira weisfloggii



©Kuylenstierna & karlson

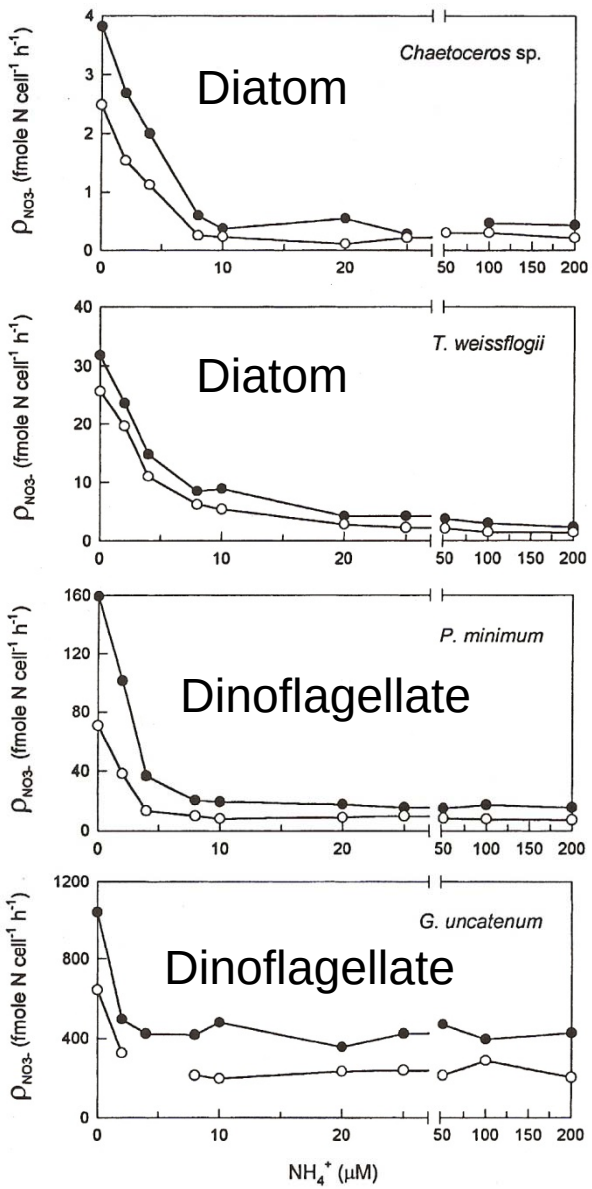
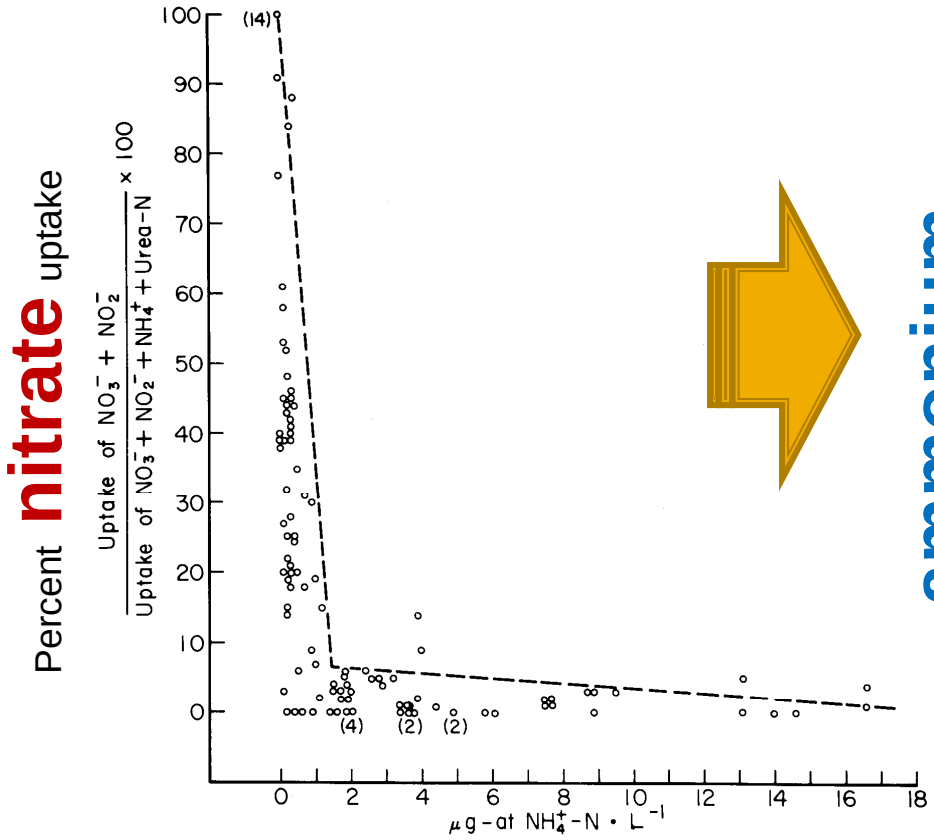


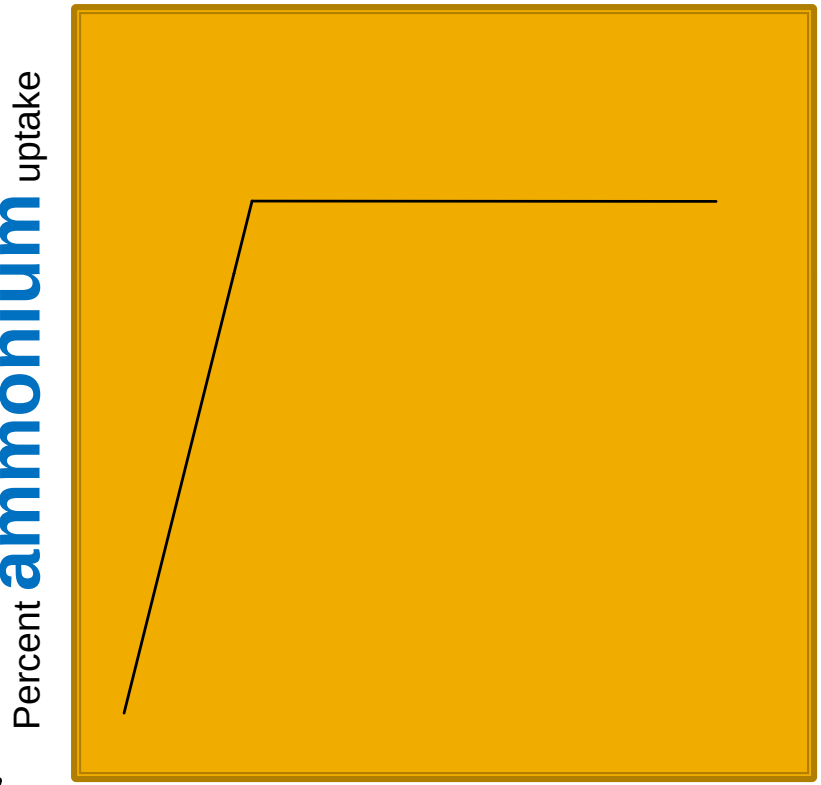

**Fig. 3** Representative patterns of $NO_3^-$ uptake as a function of added $NH_4^+$ for each species at 20 °C. Both non-TCA-extracted $NO_3^-$ uptake rates (●) and TCA-extracted $NO_3^-$ uptake rates (○) are shown

Uptake of nitrate by diatoms was less inhibited by ammonium than that of some flagellates

# *Viewing this curve another way....*

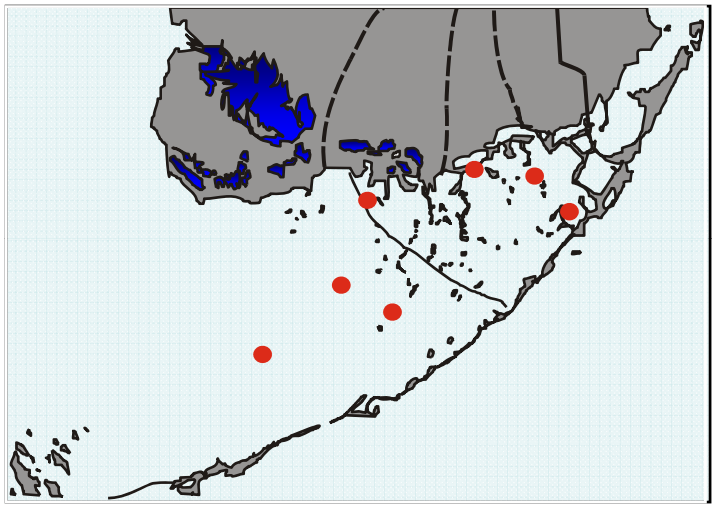
as the percent of nitrate uptake goes down,
the percent of ammonium uptake goes up

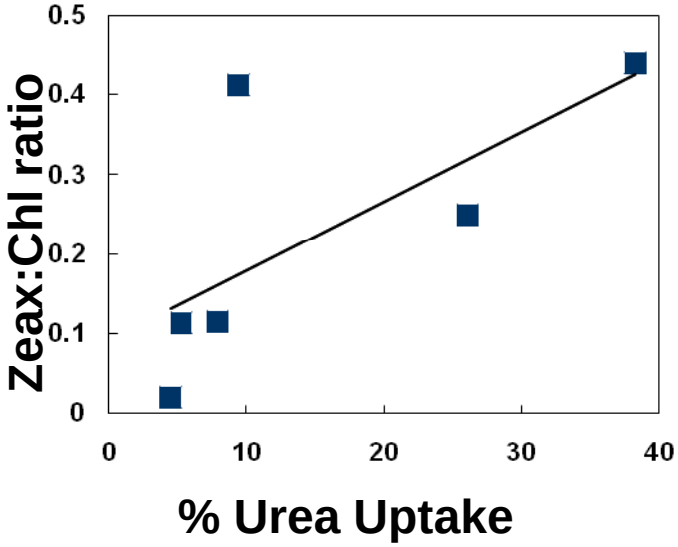


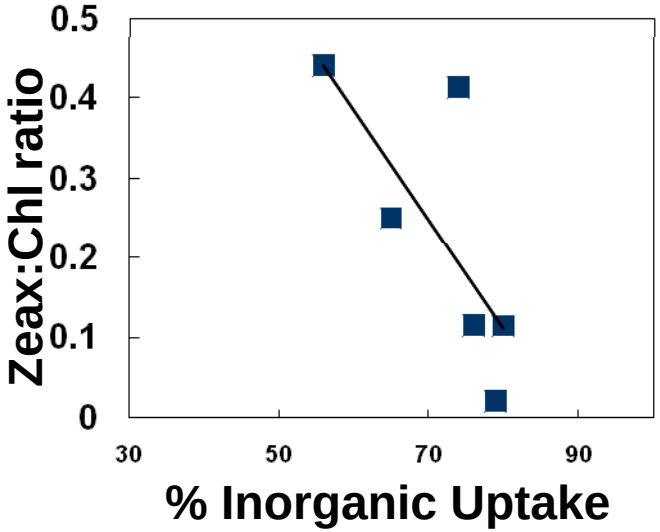



Cyanobacterial fraction

FLORIDA BAY

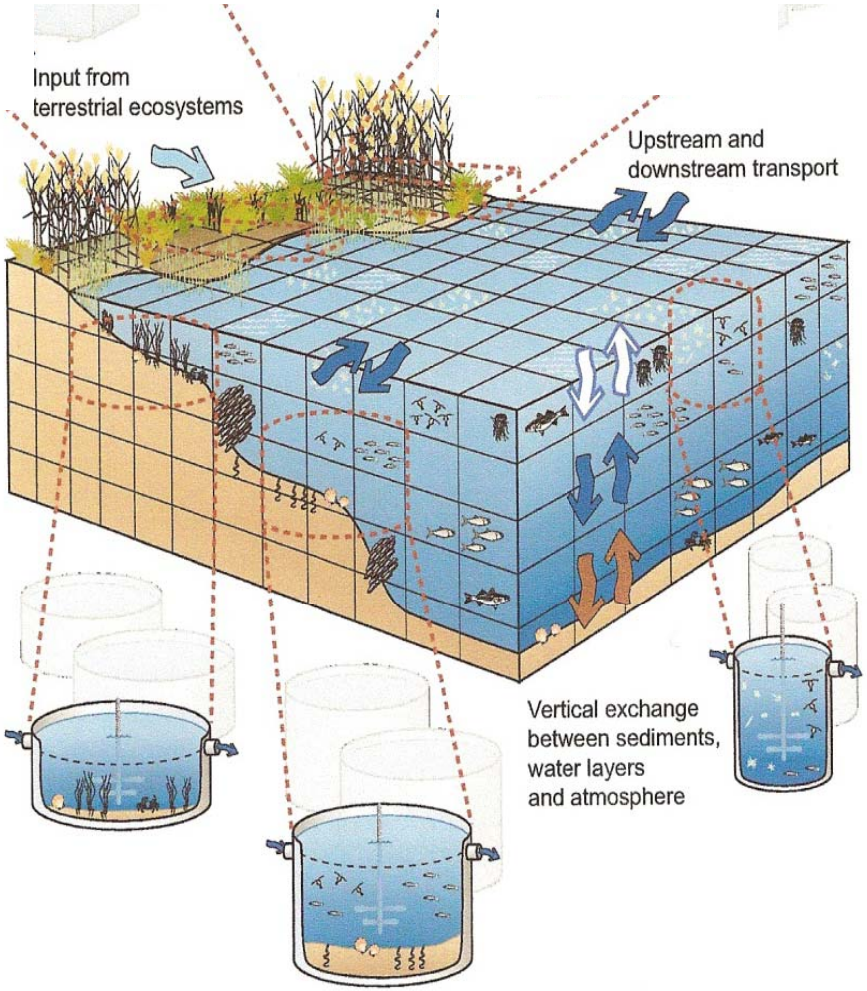


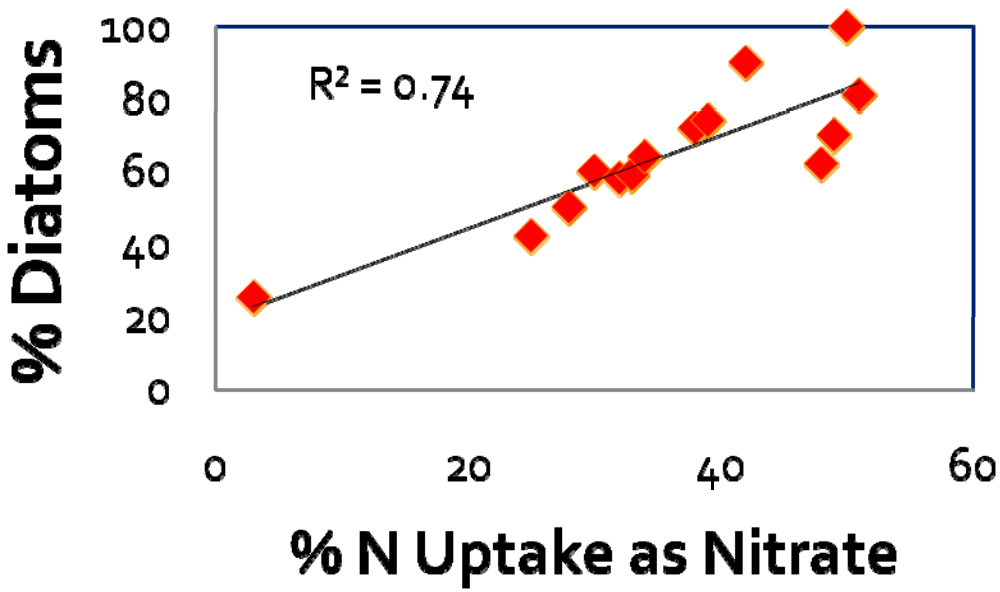


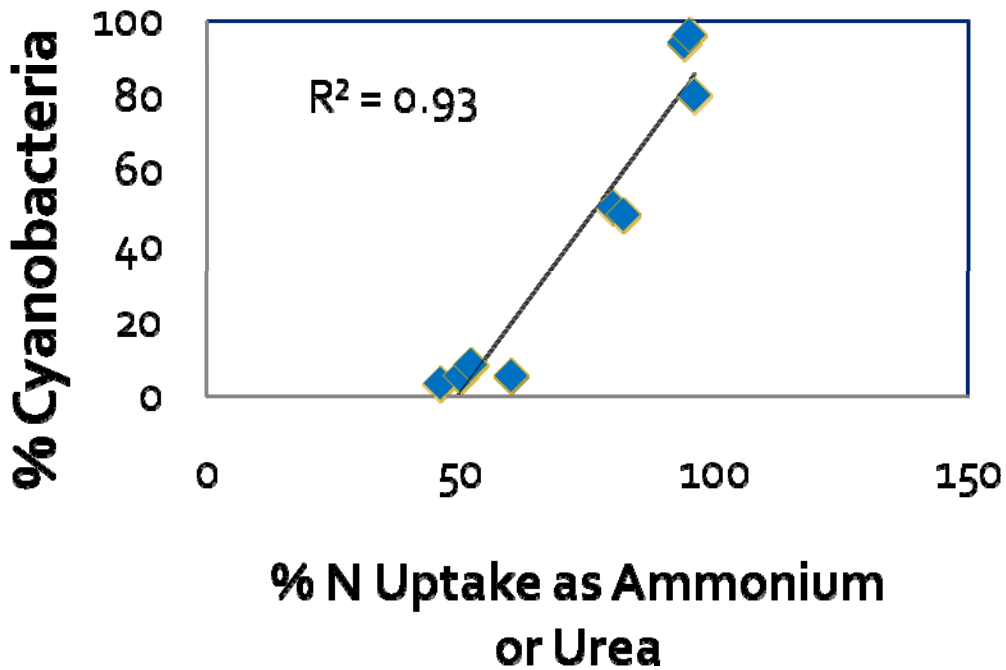

The cyanobacterial fraction of total chlorophyll is **positively** related to urea uptake and **negatively** related to inorganic N uptake

# Results from mesocosm studies show the same relationship with N form






Diatoms correlated with nitrate




Cyanobacteria correlated with ammonium and urea

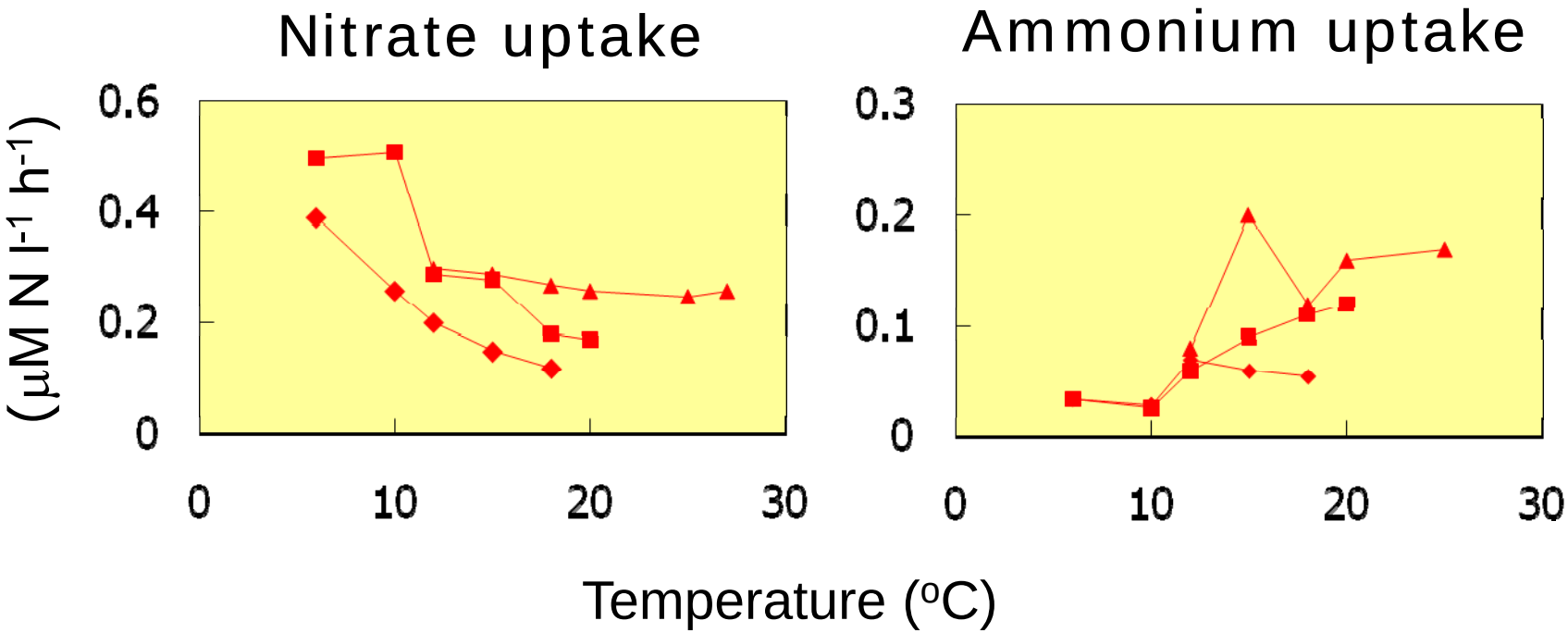
Glibert and Berg 2009

In sum, nitrogen quality in turn can drive the “quality” of the algae

***Diatoms*** tend to prefer nitrate

***Cyanobacteria*** and many ***flagellates*** tend to prefer ammonium, urea or dissolved organic nitrogen

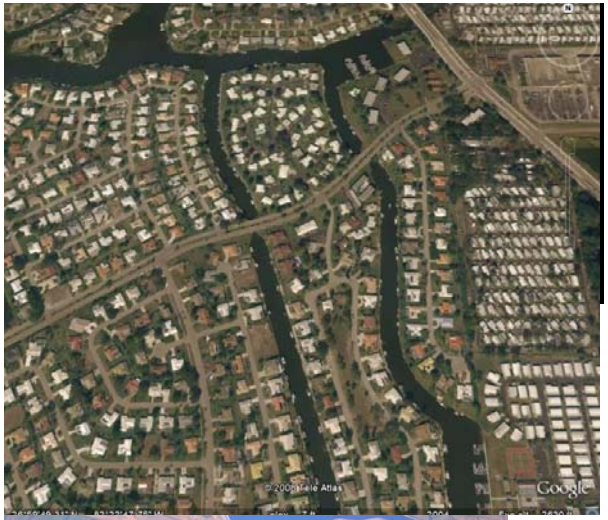
Every broad generalization must be qualified…preferences vary with temperature and other physical factors

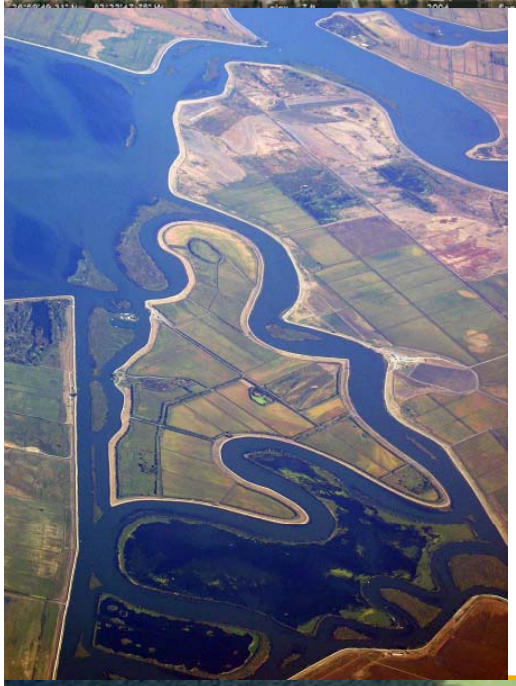


# Temperature Optima of Nitrate Enzymes

| ***Enzyme*** | *Skeletonema costatum* | *Chaetoceros sp.* | *Dunaliella teriolecta* | *Pavlova lutheri* | *Prorocentrum minimum* |
|---|---|---|---|---|---|
| Nitrate reductase | **12.2** | **17.5** | **27.3** | **30.1** | **19.9** |
| Nitrite reductase | **21.3** | **21.9** | **30.2** | **30.2** | **23.3** |

RUBISCO has a temperature optimum of 40°C





# Conclusions and Implications

Ammonium is increasing in waters worldwide due to fertilizer use, population increases and animal operations

In many estuaries, ammonium (and urea and DON) increases correlate with changes in algal composition and harmful algal blooms

Ammonium inhibition of nitrate uptake is common but species specific . Cyanobacteria and dinoflagellates  prefer ammonium and other "reduced" nitrogen forms; diatoms prefer "nitrate or "oxidized nitrogen forms

# Acknowledgements

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Ji Li, Horn Point Laboratory
Mike Lomas, Carrie Solomon, Horn Point Laboratory
*.....many other collaborators*

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Global Ecology and Oceanography of Harmful Algal Blooms