ECOTOXICOLOGY

Lecture 7

Nutrients

(nitrogen)


Chao Lake

Tai Lake

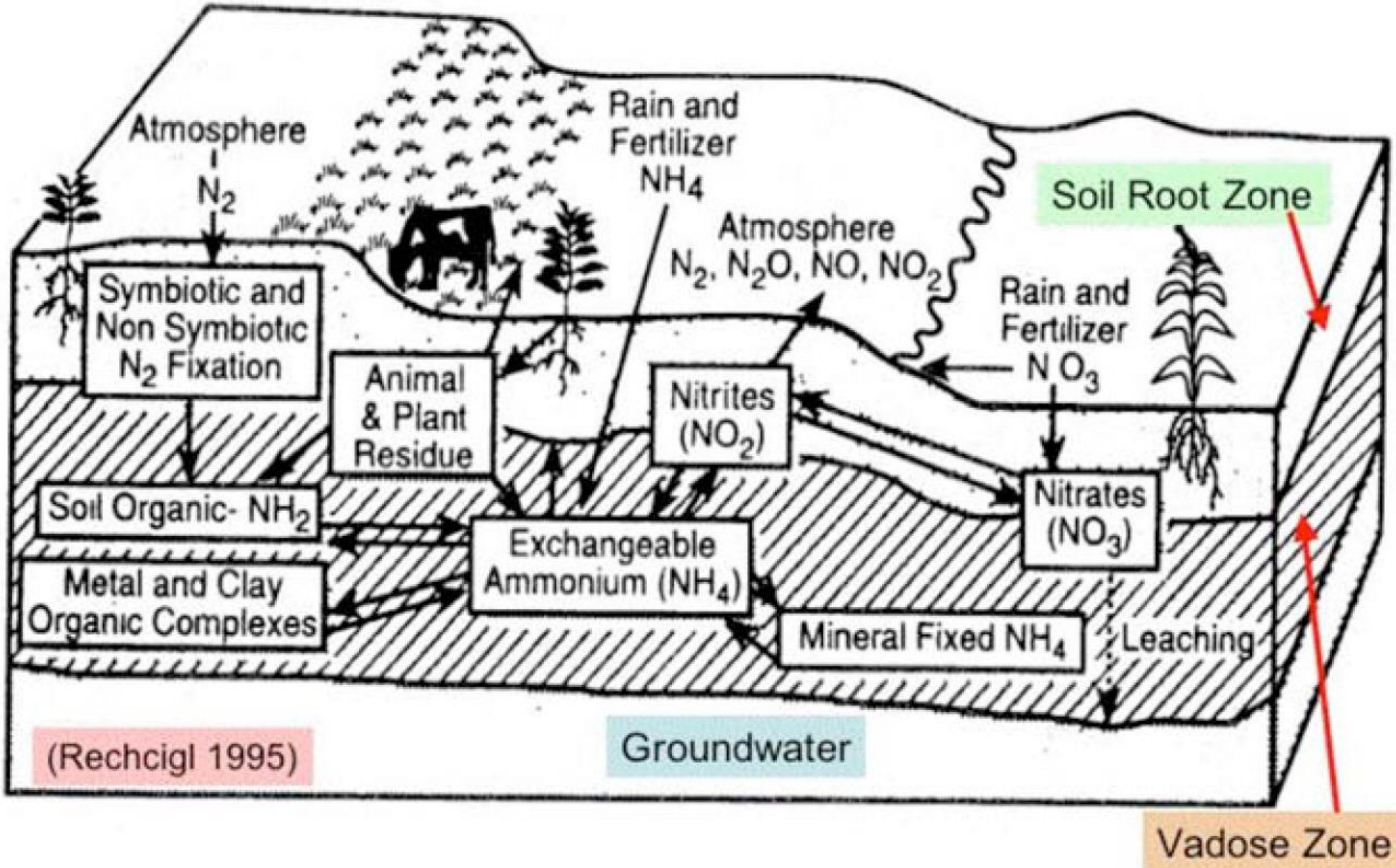
Three Basic Concerns About Anthropogenic Inputs of N

高铁血红蛋白症

- Infant Methemoglobinemia due to contamination wells
- Increased deposition of NOx (oxidized nitrogen species) that is associated with acid rain and decline of forests at higher altitudes
- Ecological effects
  - Acute & chronic toxicity
  - Hypoxia, especially in the Gulf of Mexico

缺氧

Nitrogen Biogeochemical Cycle



Nitrogen Transformations

1 = Assimilation of inorganic N

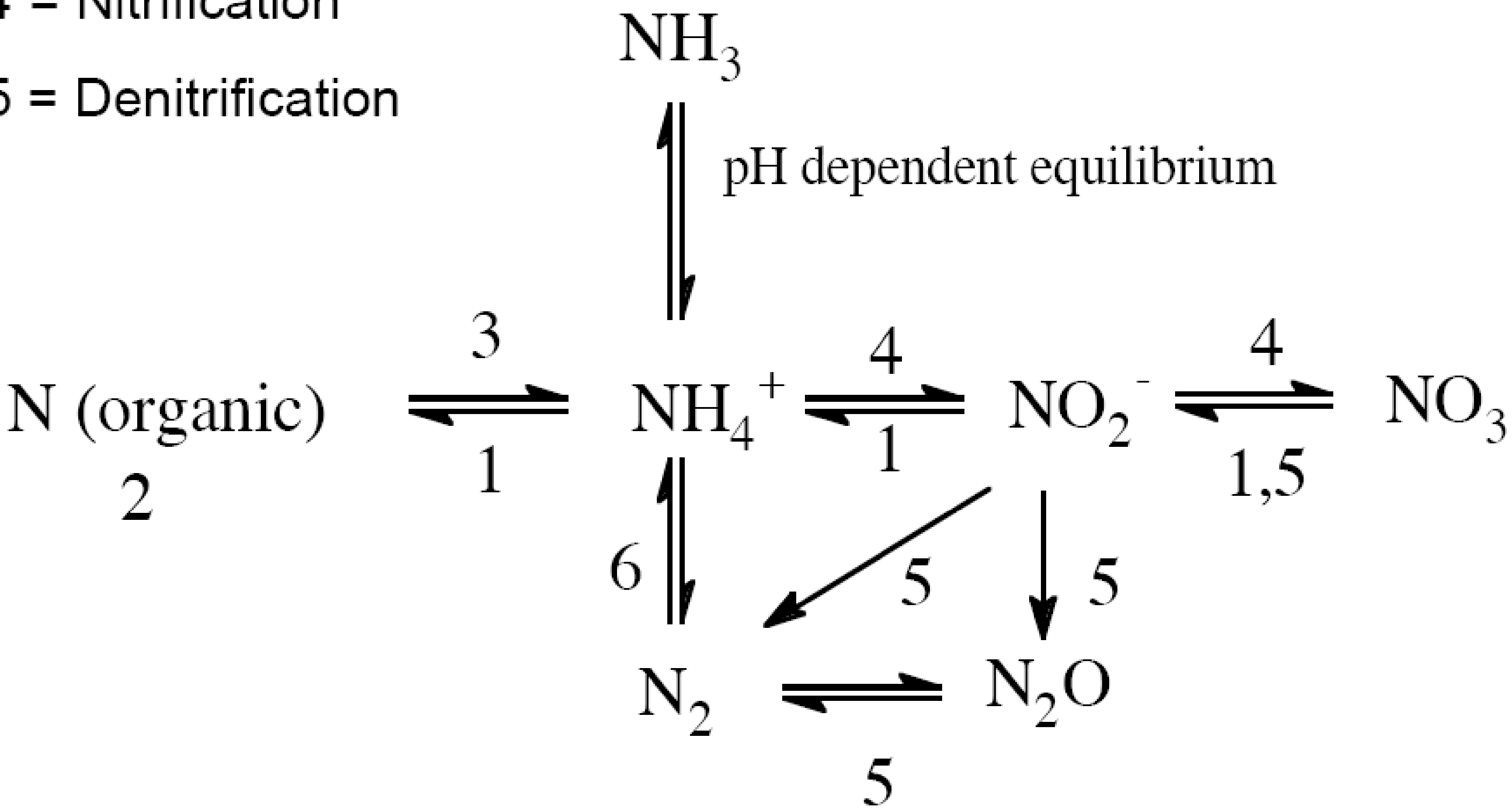
2 = Heterotrophic conversion of N among organisms

异养的

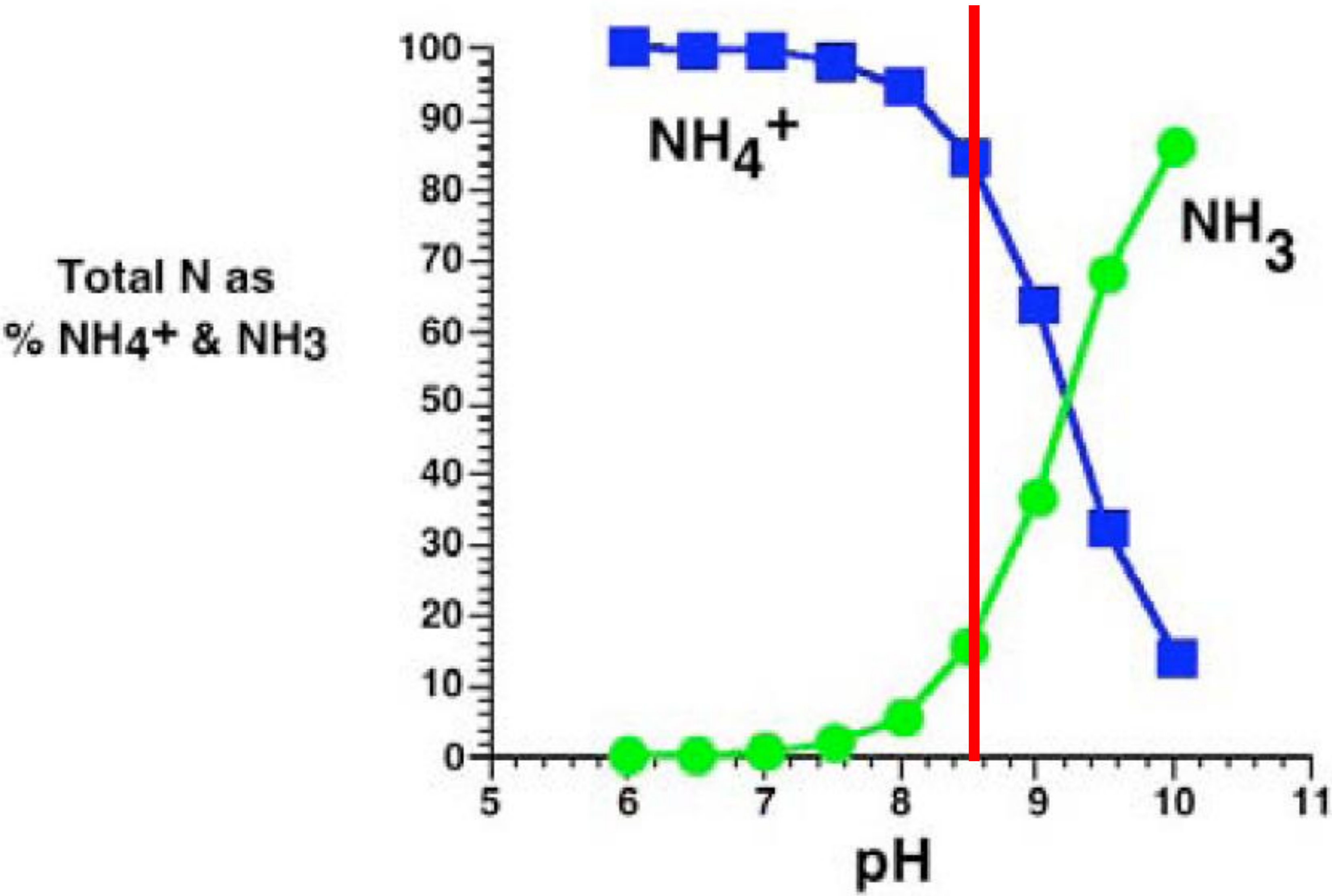
3 = Mineralization (ammonification)

4 = Nitrification

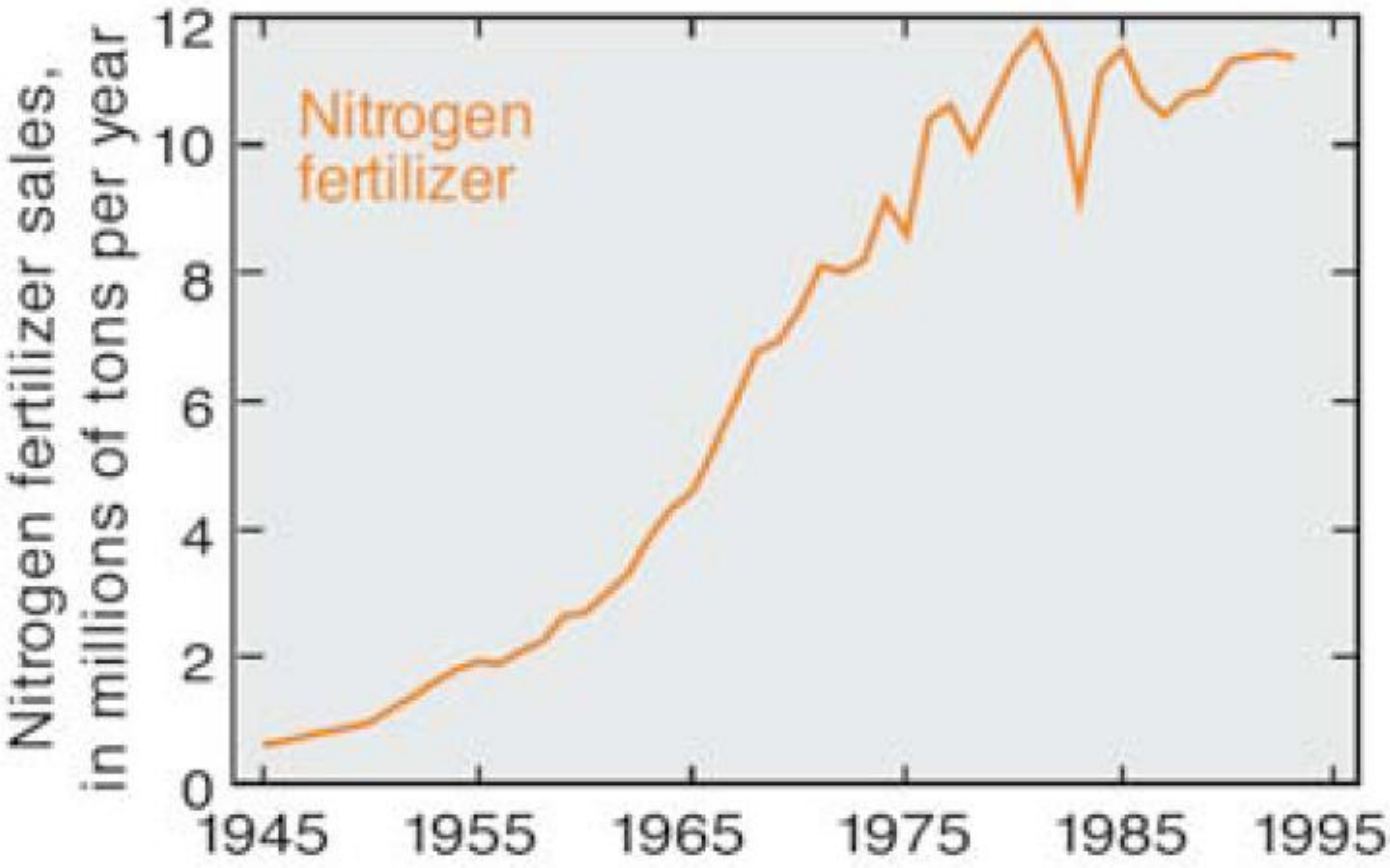
5 = Denitrification



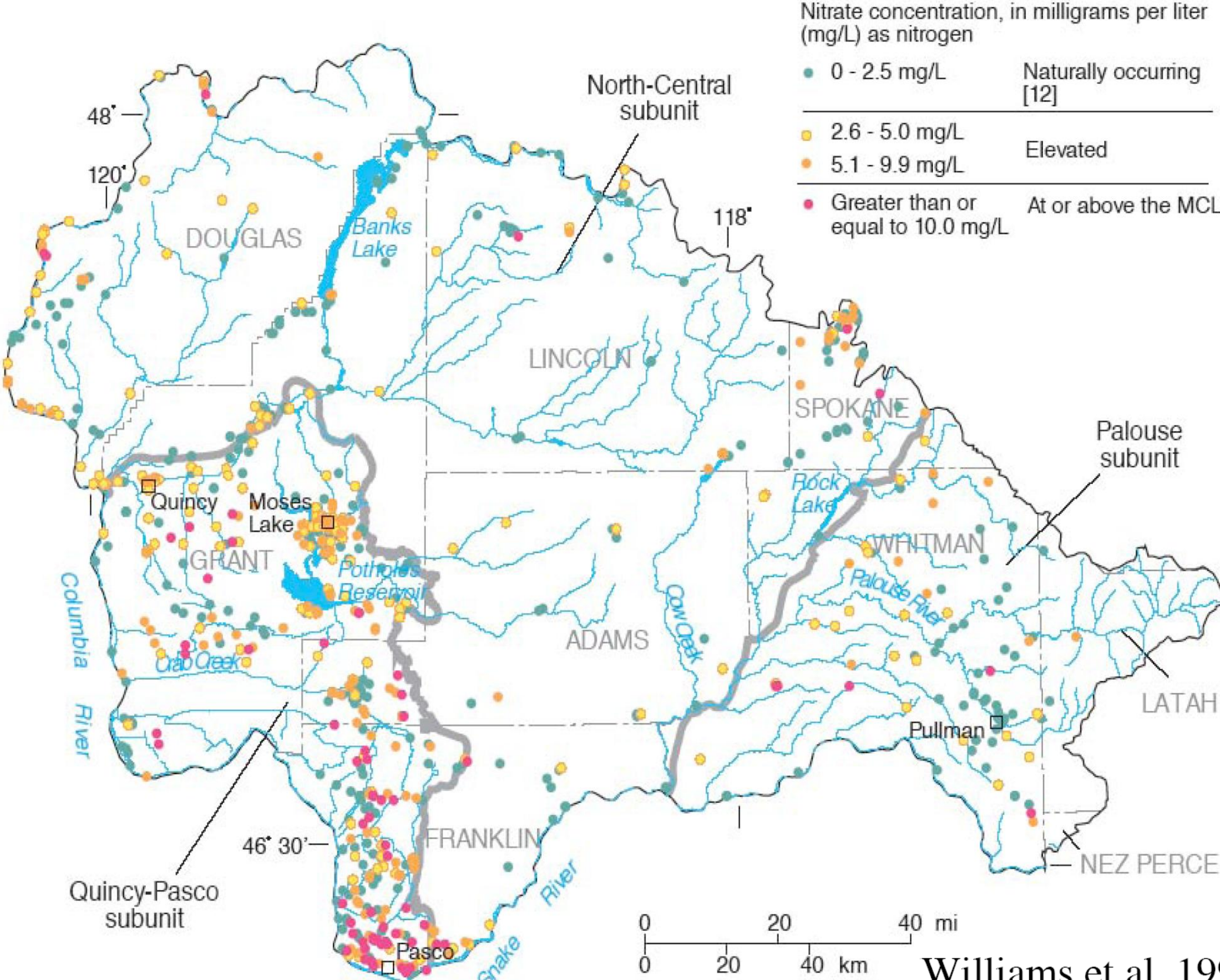
pH Dependence of Ammonia Speciation



Historical Trends in Nitrogen Fertilizer Use

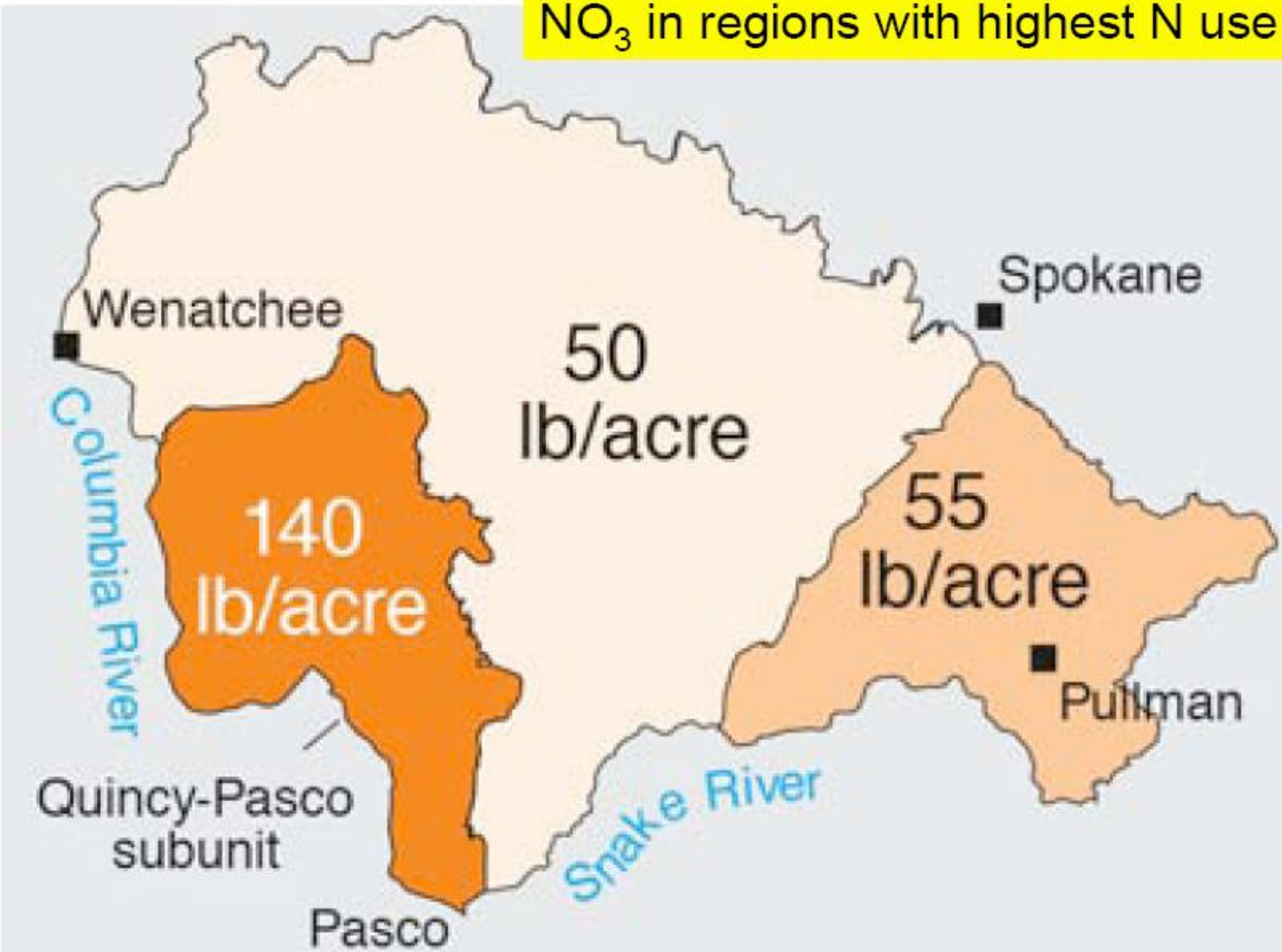


Williams et al. (1998) USGS Cir. 1144

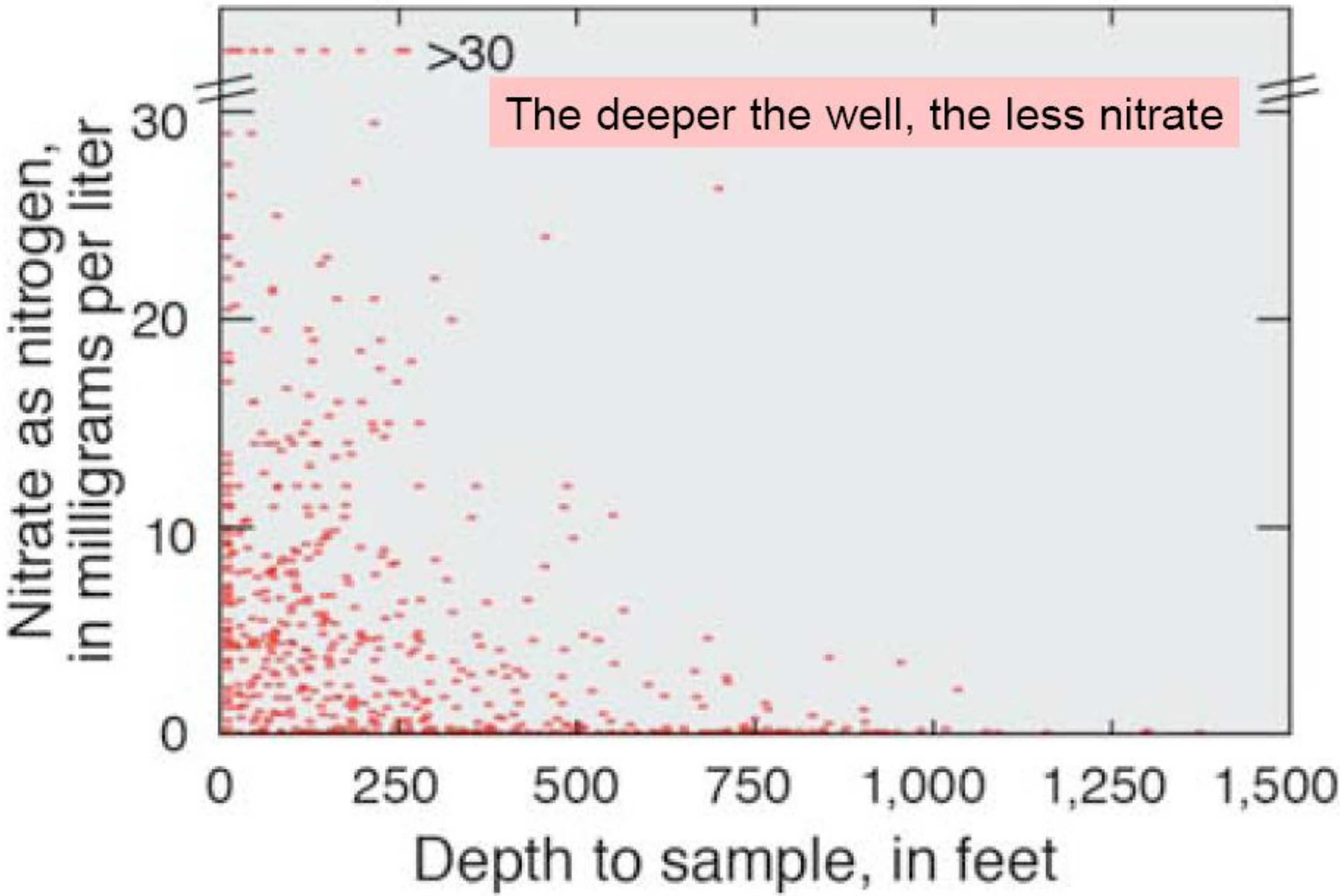


Williams et al. 1998)

Greater percentage of wells >10 ppm NO_3 in regions with highest N use



Williams et al. (1998) USGS Cir. 1144



Williams et al. (1998) USGS Cir. 1144

Nitrates Are Not the Problem!

- **Nitrites**, not nitrate, interact with hemoglobin to oxidize it's iron atom, making it incapable of carrying oxygen

亚硝酸盐 血红蛋白

$$Hb\text{-}Fe^{+2} + NO_2 \text{ --------> } metHb\text{-}Fe^{+3} + NO_3$$

- Low concentrations (0.5-3.0%) of met-Hb normal 血红蛋白
  - Levels up to 10% can occur without signs
  - Above 10%-cyanosis 苍白病
  - Above 25%--hypotension, rapid pulse, etc. 血压过低
  - Above 50%--lethal

Where Do the Nitrites Come From?

- Nitrates not reduced to nitrite in blood
- Nitrite comes from nitrate via reduction in salivary glands and from nitrate-reducing bacteria in stomach
  唾液腺
  - Nitrate is absorbed from intestine, some passes through salivary glands where ~5% is converted to nitrite
    肠
- Endogenous production of nitrate/nitrite
  内生的

Why Infants More at Risk than Adults?

- Infants less than 6 months most susceptible 易受影响的
- Infant stomach with lower acidity than adult
  - Allows nitrate-reducing bacteria to flourish

Exposure Assessment

- Most exposure in diet
- Previous NRC (NAS-National Research Council) report concluded that for 99% of U. S. population, about 97% of exposure comes from diet (just food)
- Endogenous nitrate production accounts for ~50% of total nitrate “load”

Uptake of Nitrite

- Nitrite seems to be absorbed through intestine more slowly than nitrate
- However, GI disturbance may cause nitrite to more easily pass through intestine as a result of epithelial erosion and hemorrhage ("leaky intestine")

胃肠

上皮的

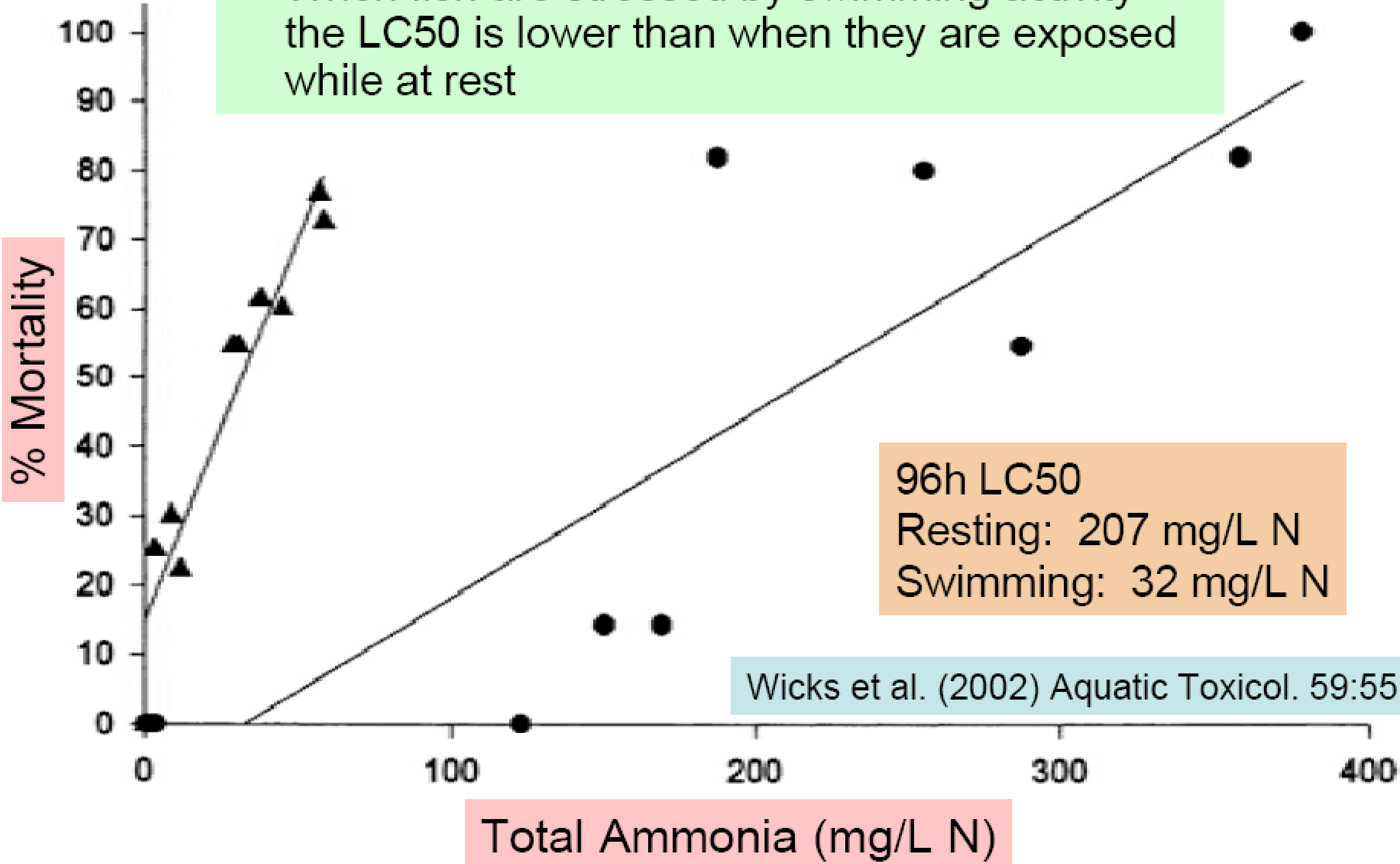
出血

Risk Characterization (NAS '95)

- Standard based on epidemiological studies published by Walton in 1951
  - NOAEL is considered to be 10 mg NO_3-N/L
  - Thus, there is no safety factor in the MCL
  - The standard for NO_2-N is 1 mg/L
- As of 1995, found no studies of nitrate-induced MHB since EPA '90 report

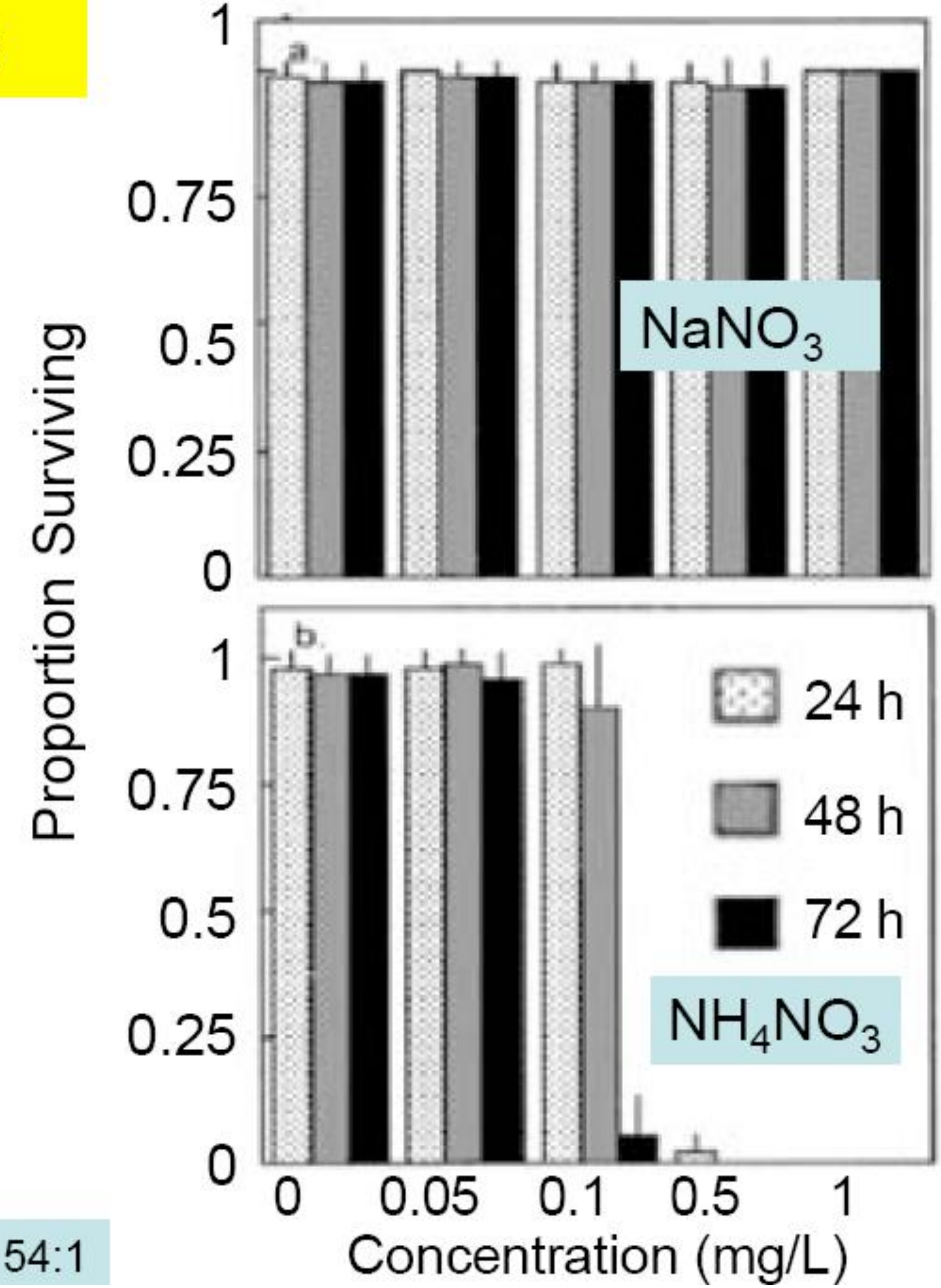
Ecotoxicity

- Ammonia is highly toxic to fish
- When fish are stressed by swimming activity the LC50 is lower than when they are exposed while at rest



Frogs and Nitrates

- Frogs are not sensitive to nitrates at concentrations up to 1000 mg/L
- However, frogs are sensitive to ammonia concentrations as low as 1 mg/L

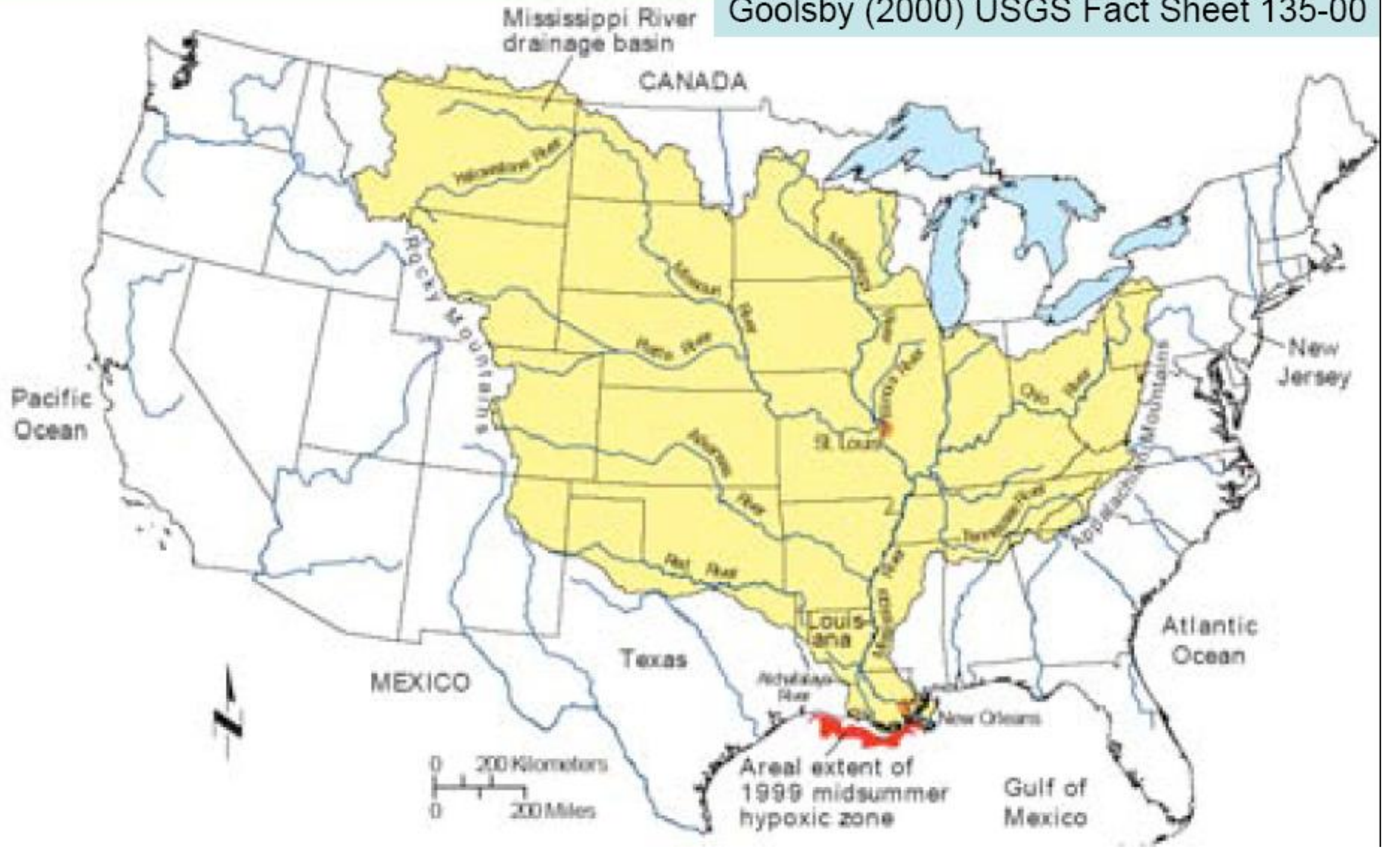


Johansson et al. (2001) Aquatic Toxicol. 54:1

Hypoxic Zone in the Gulf of Mexico

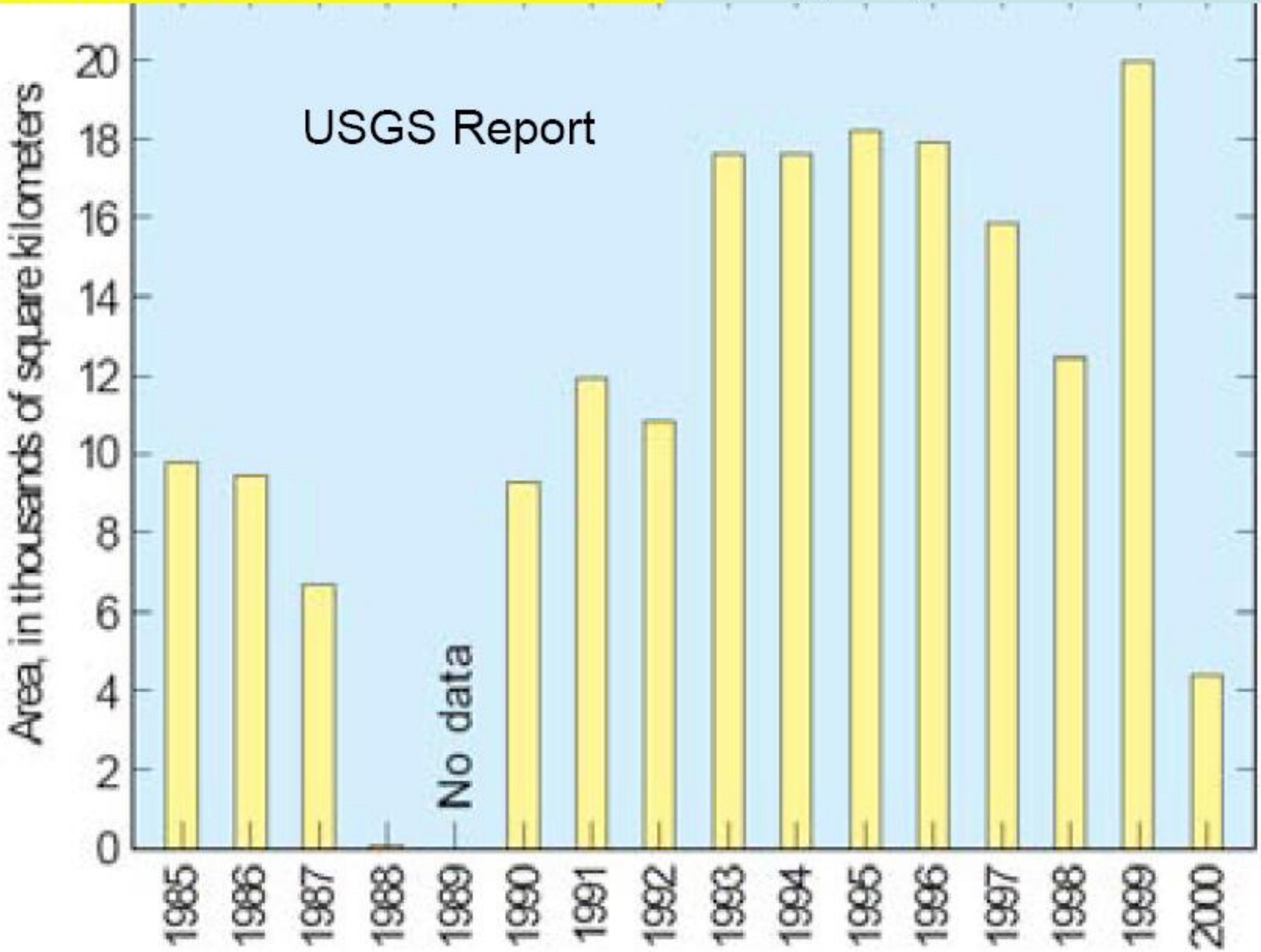
Yearly occurrence but the size “dramatically” increased during the last decade.
Increased nitrate loading from up river use of fertilizers belied to be a causal factor

Goolsby (2000) USGS Fact Sheet 135-00



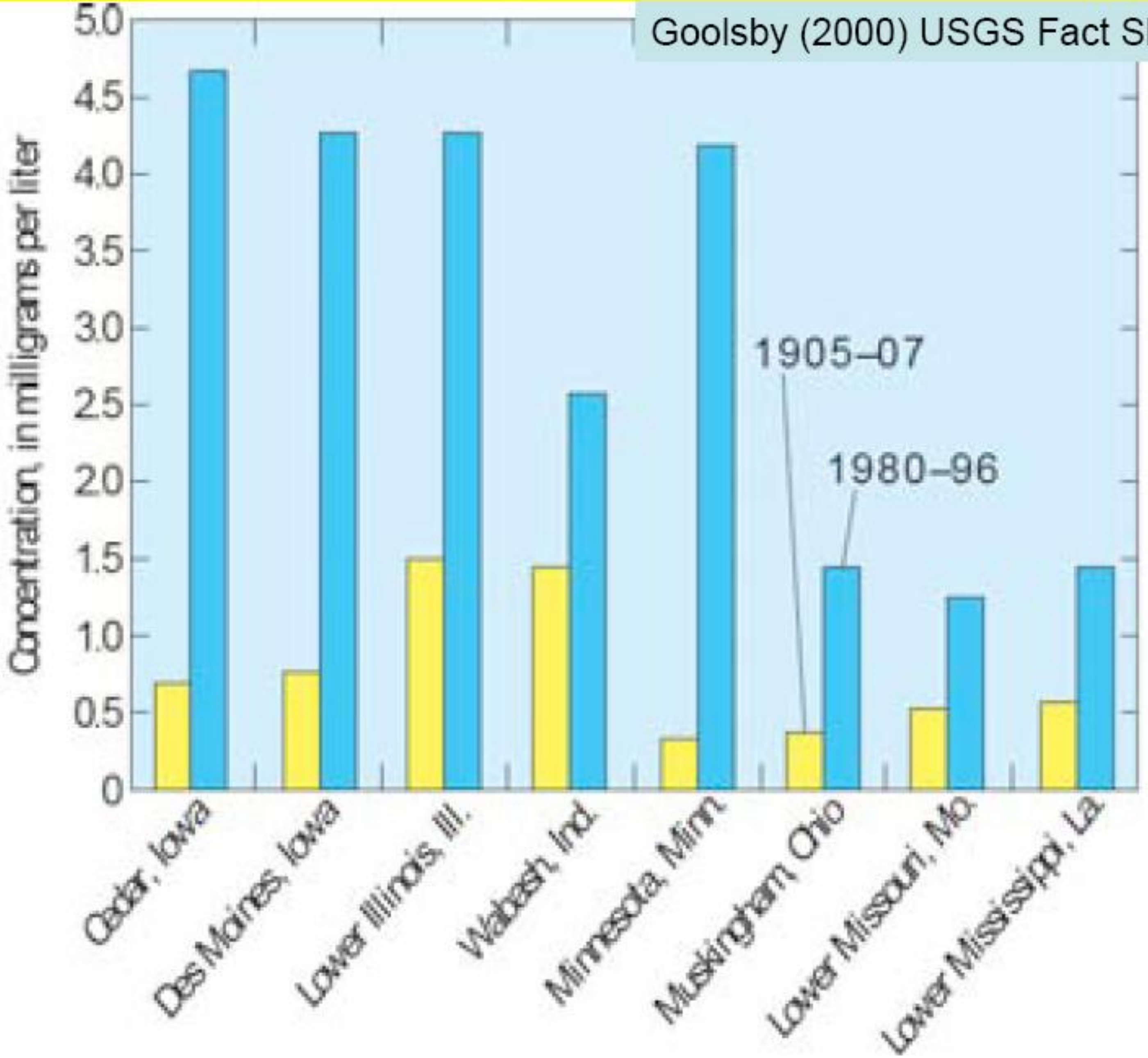
Increase in Size of Gulf of Mexico Hypoxic Zone Since Start of Monitoring in 1985

Goolsby (2000) USGS Fact Sheet 135-00



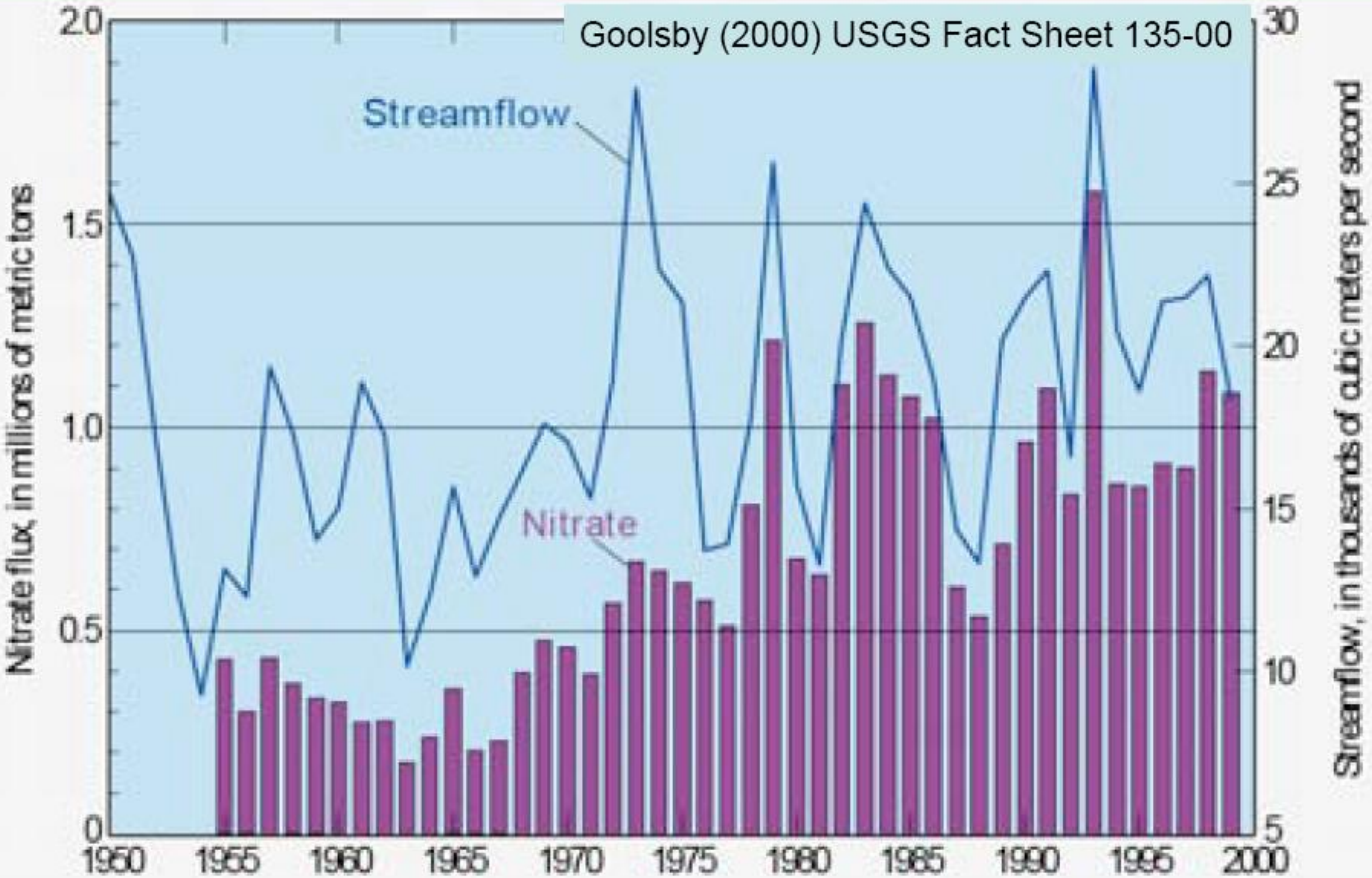
Historical Increase in Nitrate Concentration in Tributary Rivers

Goolsby (2000) USGS Fact Sheet 135-00



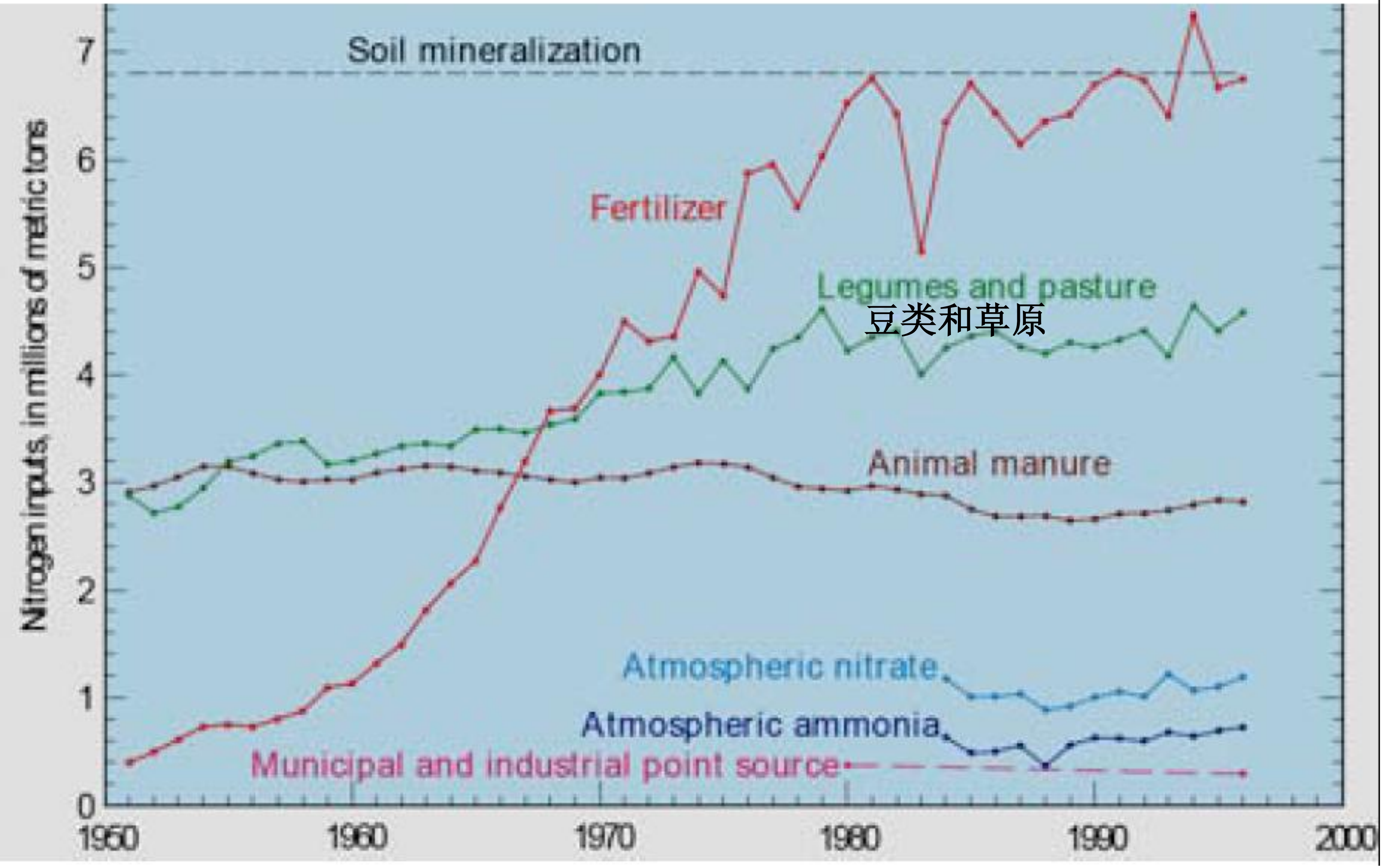
Increase in Nitrate Flux in the MS River

Note, however, that the increase in flux coincides with increase in streamflow; recall that the use of nitrogen fertilizers has stabilized over the last 20 years

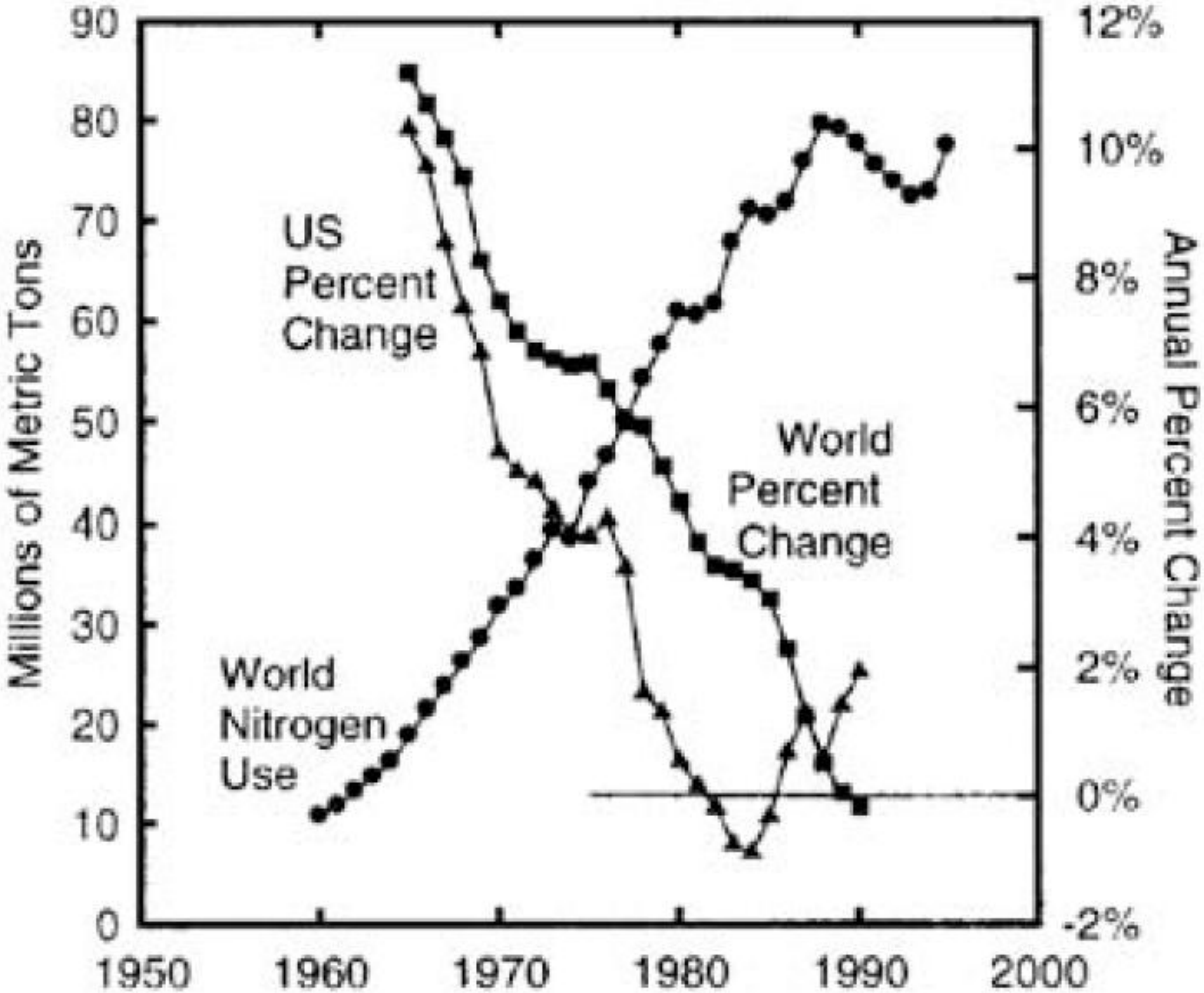


Input Sources for Nitrate in the Mississippi River Basin

Goolsby (2000) USGS Fact Sheet 135-00

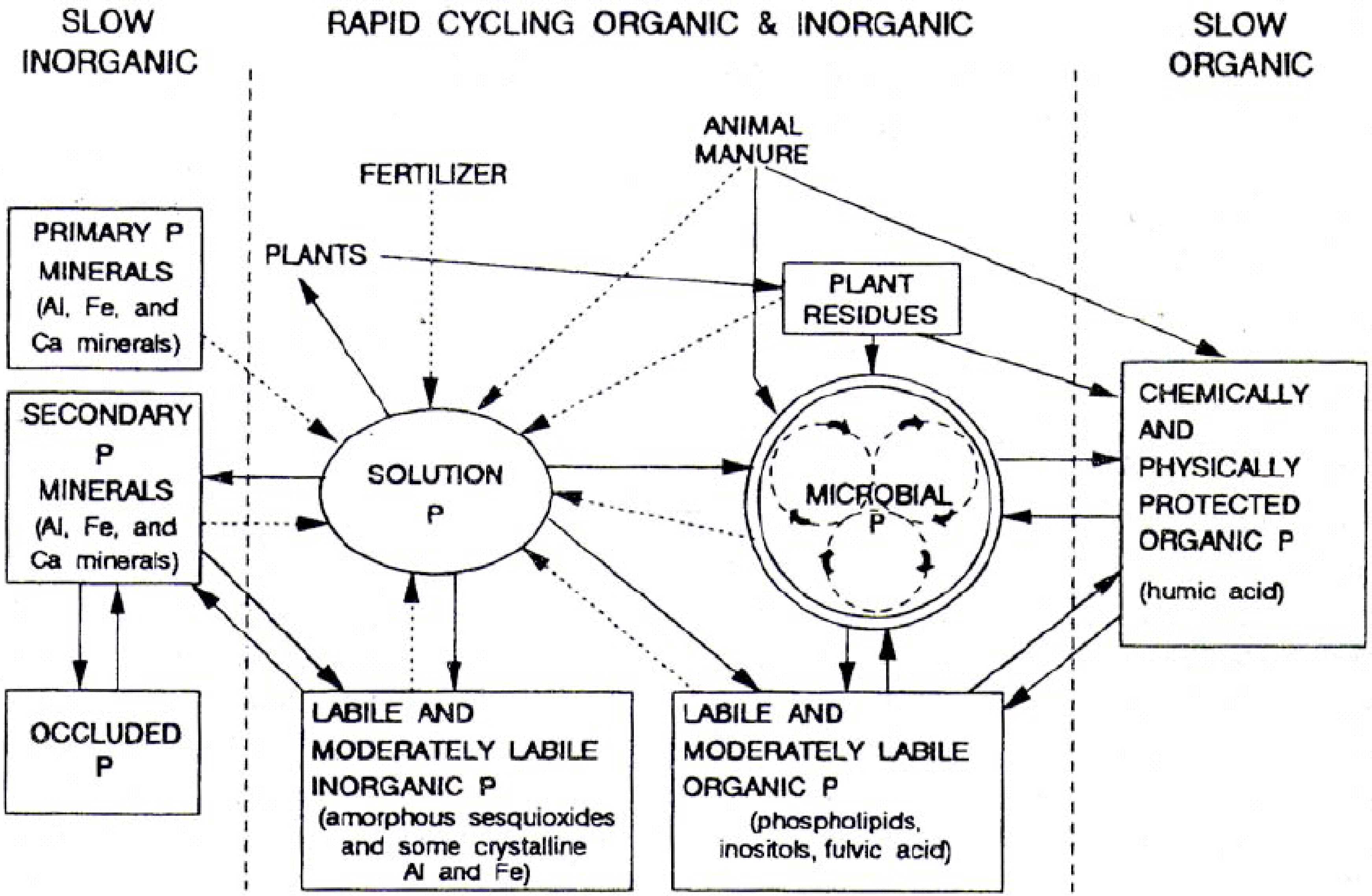


Future Trends Expected for N Use & Deposition

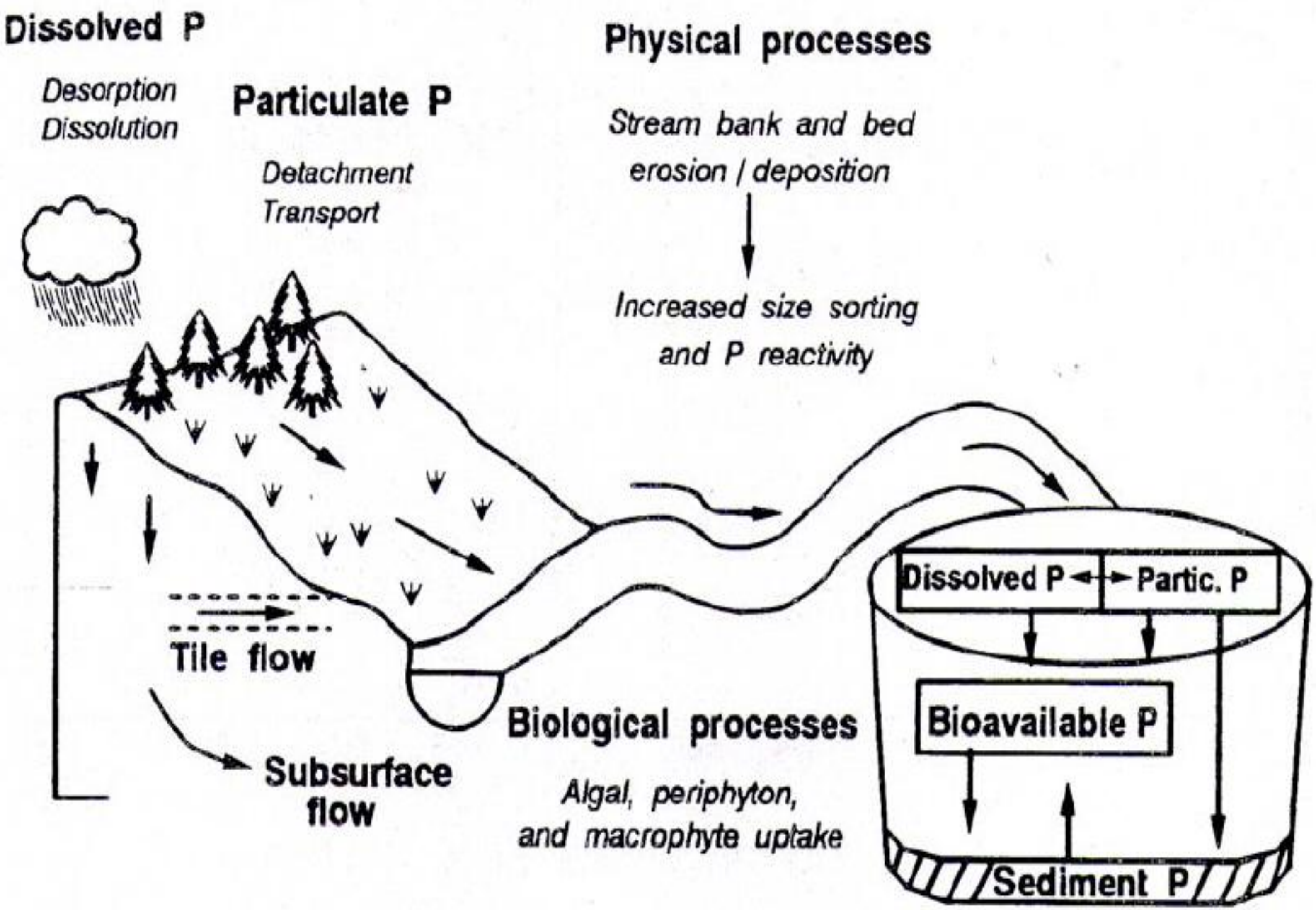


Frink et al. Proc. Natl. Acad. Sci. (1999) 96:1175

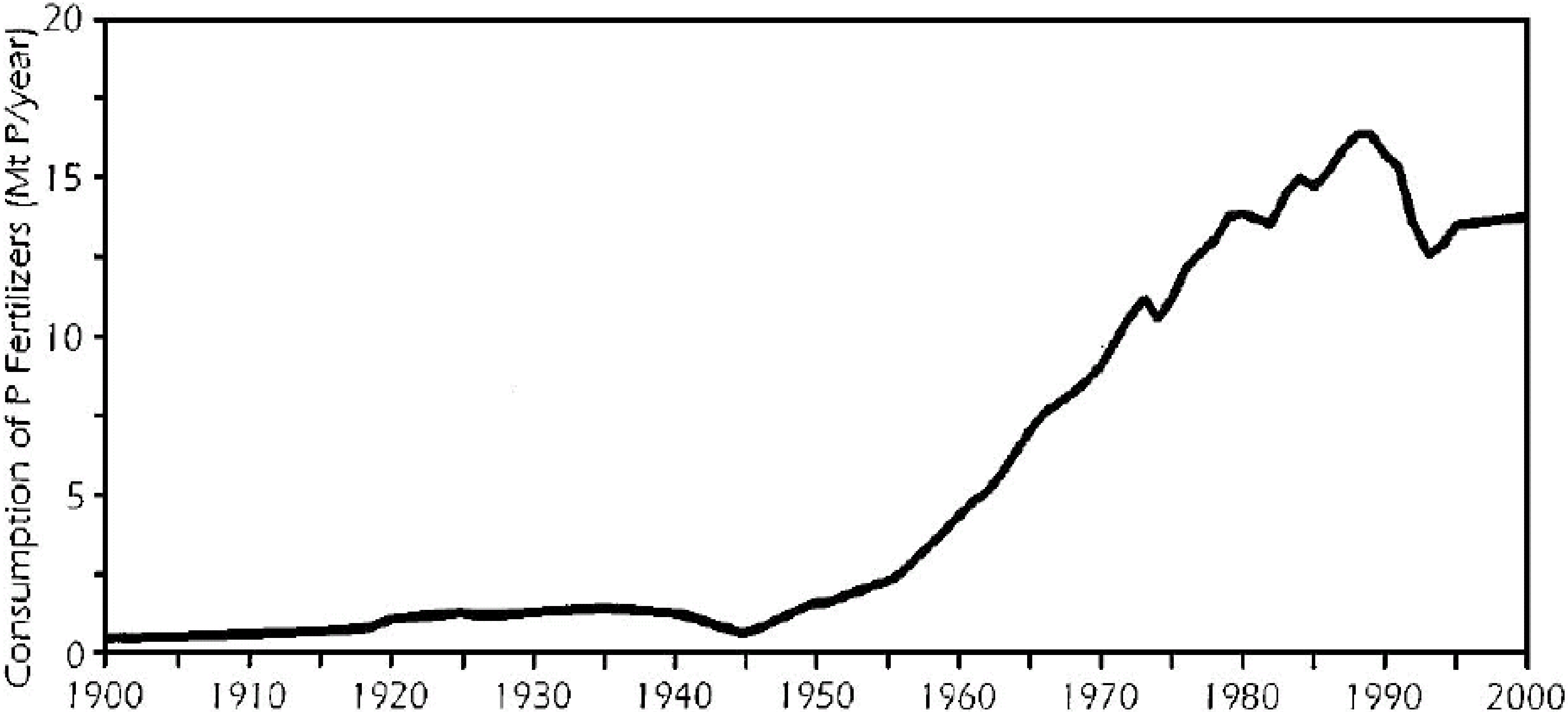
Phosphorus



(From Rechcigl 1995)


Dissolved P
Desorption
Dissolution
Particulate P
Detachment
Transport
Physical processes
Stream bank and bed
erosion / deposition
Increased size sorting
and P reactivity
Tile flow
Subsurface
flow
Biological processes
Algal, periphyton,
and macrophyte uptake
Dissolved P
Partic. P
Bioavailable P
Sediment P

Historical Trends in Use



Historical Trends in Global. Use of Phosphorus (Smil, V. 2000. Phosphorus in the environment: Natural flows and human interferences. Ann. Rev. Energy Environ. 25:53-88.)

Human intensification of the global phosphorus cycle (Smil 2000)

Fluxes	Natural (Mt P/yr)	Preindustrial (1800) (Mt P/yr)	Recent (2000) (Mt P/yr)
Natural fluxes intensified by human actions			
Erosion	>10	>15	>30
Wind	<2	<3	>3
Water	>8	>12	>27
River transport	>7	>9	>22
Particulate P	>6	>8	>20
Dissolved P	>1	<2	>2
Biomass combustion	<0.1	<0.2	<0.3
Anthropogenic fluxes			
Crop uptake	--	1	12
Animal wastes	--	>1	>15
Human wastes	--	0.5	3
Organic recycling	--	<0.5	>6
Inorganic fertilizers	--	--	15

Ecological Concerns

- **Although an essential nutrient, when phosphates run off into aquatic systems (via sediment erosion), overloading of concentrations leads to algal blooms**
- **a. P may be a limiting factor in algal growth**
- **b. Blooms lead to die-offs**

  1. Bacterial decomposition of algal cells leads to oxygen depletion

  2. Eutrophication results

Cases

- c. In the 1950's and 1960's, many detergents had phosphates added "to boost cleaning power"

1. The most notable effect was the commencement of eutrophication of parts of Lake Eerie
2. Phosphates were banned and Lake Eerie recovered

Tracing source of nitrate using $\delta^{15}N$ and $\delta^{18}O$

Summarized by L. Yu

Application of $\delta^{15}N_{(NO3)}$

- The $\delta^{15}N$ of nitrate has been used in numerous studies to determine source of nitrogen in groundwater and surface water affected by agricultural land use.
- Successful reason: the potential contamination source such as fertilizer(-1-2‰) and animal waste(+8 +16‰) has distinct isotopic signatures of N.

Exner M.E. et al., 1994. *Appl. Geochem.*;
Kreitler C.W. et al., 1975. *Ground water*;
Mariotti A. et al.,1988. *Geochim. Cosmochim. Acta*;
Amberger A. et al., 1987.*Geochim. Cosmochim. Acta.*

Limitation of single isotopic technology

- NH_3 volatilization can lead to significant and variable enrichment of ^{15}N in the residual NH_4 source material and NO_3^- subsequently produced. (Wassenaar L.I.,1995 *Appl.Geochem.*)

Addition of $\delta^{18}O_{(NO3)}$ to determine the source

- $\delta^{18}O_{(NO3)}$ has useful in **separating atmospheric and microbial sources of nitrate in undisturbed watersheds**
- Nitrate produced by microbial nitrification in laboratory cultures derives two oxygen from water molecules and one oxygen from atmospheric O_2

The equation of microbial nitrification:

$$\delta^{18}O_{(NO3)} = 2/3\ \delta^{18}O_{(H2O)} + 1/3\ \delta^{18}O\ (O_2)$$

Burns and Kendall., 2002. *Water Resour. Res*.; Durka W., 1994.*Nature*;
Liu C.Q. 2006. *Environ. Sci. Technol*.; Tye A.M. 2007. *Geochim. Cosmochim. Acta*

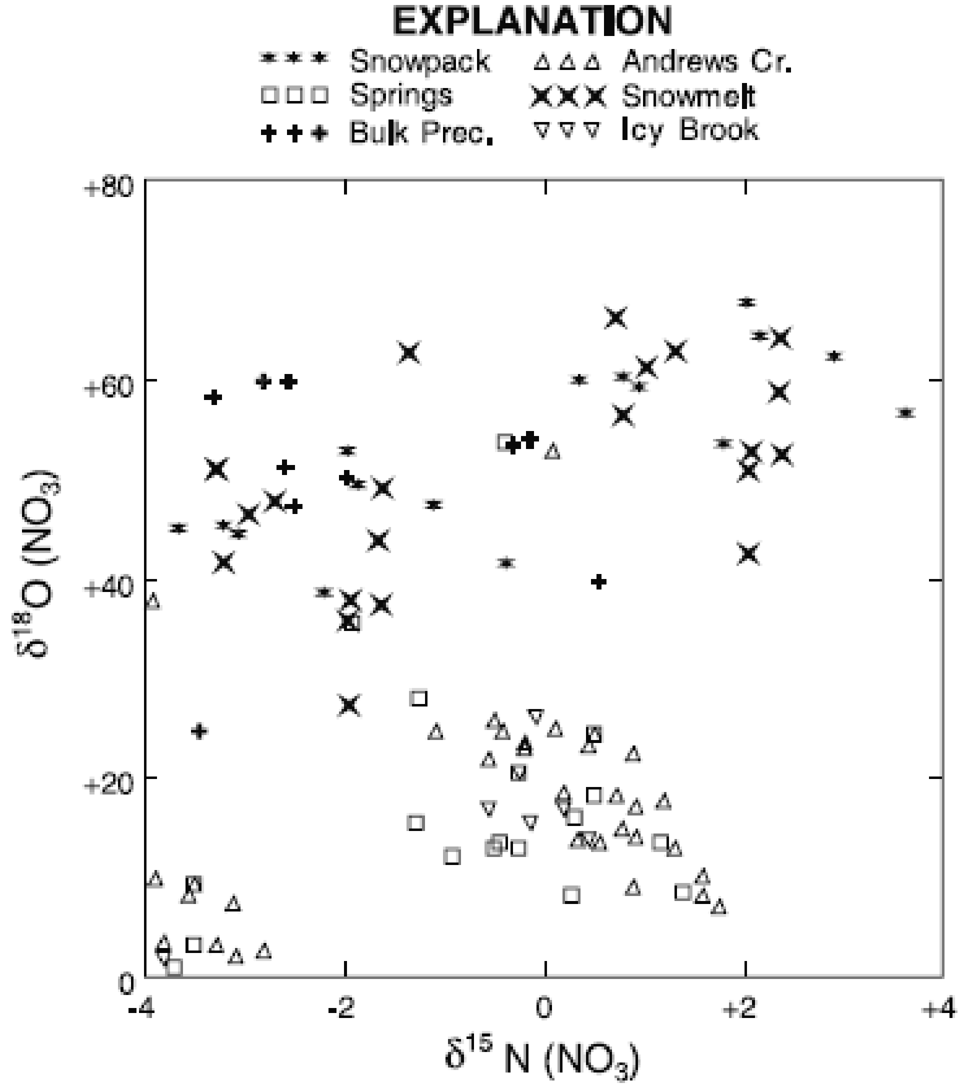
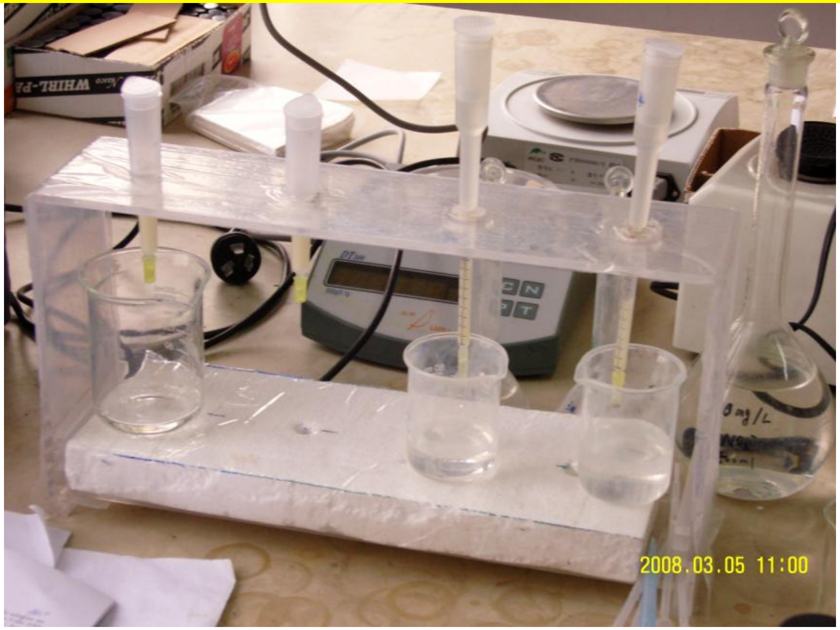


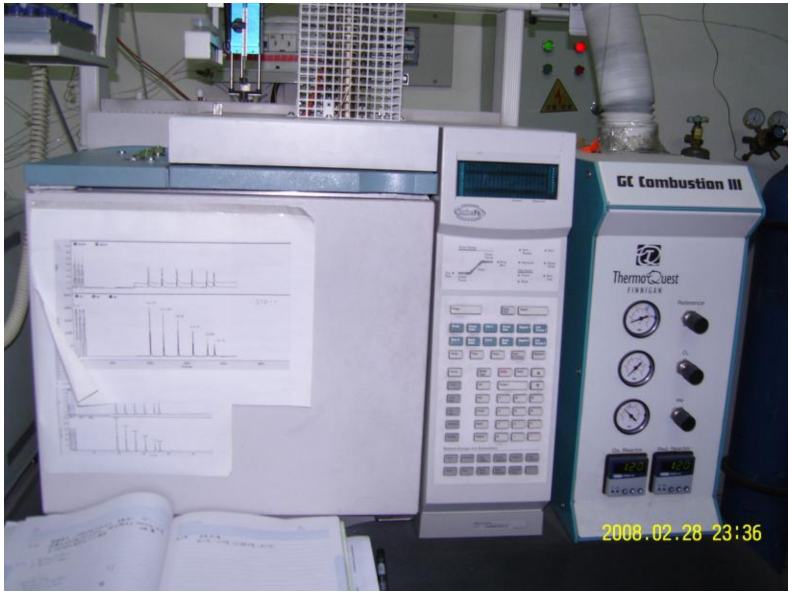
Figure 2. The $\delta^{18}O_{(NO3)}$ (‰) versus $\delta^{15}N_{(NO3)}$ (‰) in all samples, 1995–1997.

Values of $\delta^{18}O$ (NO_3) in atmospheric deposition(snowpack, snowmelt, and bul precipitation) were distinct from values i water from streams and talus springs. The $\delta^{15}N_{(NO3)}$ vales were not distinct between the different water types.

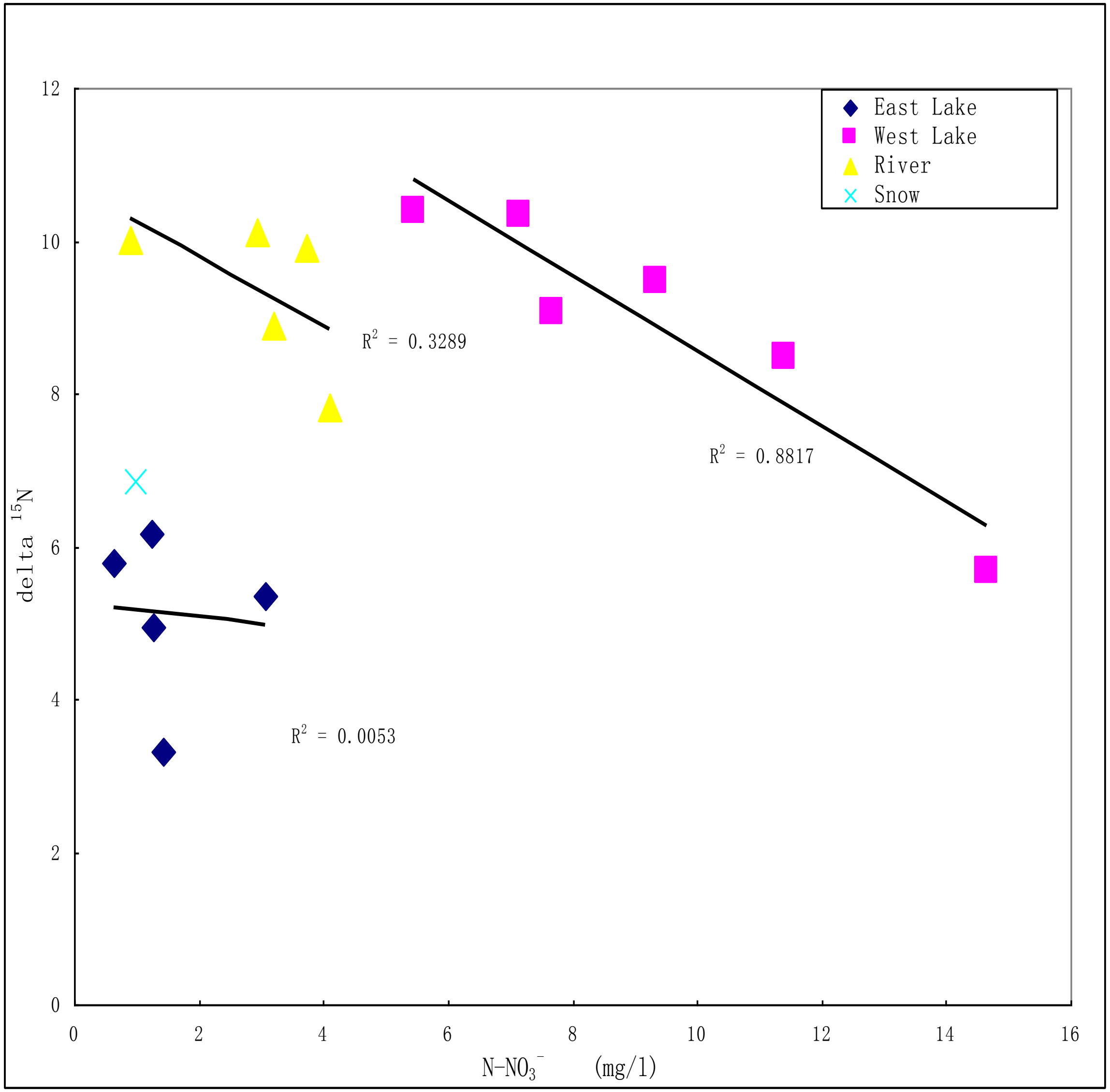
Campell D.H. 2002 *Water Resour. Res.*

Preparing sample and stable isotope analysis on EA-MS





Cross-plot of the $\delta^{15}N$ versus the $N\text{-}NO_3^-$ concentration

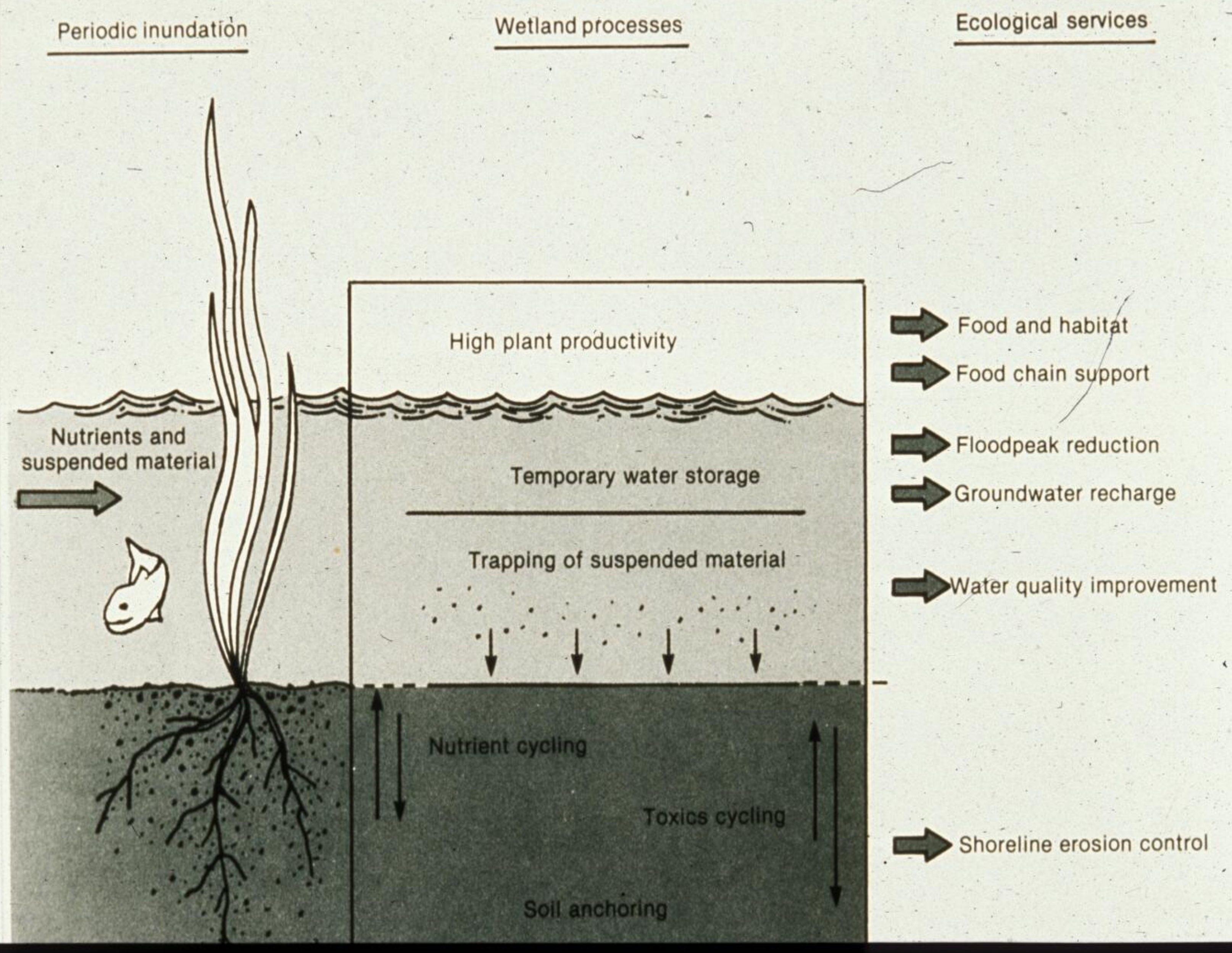


- There was no correlation between $\delta^{15}N$ and $N\text{-}NO_3^-$ in River and East Lake, but there was a negative correlation(r^2=0.9917) in West Lake.
- It might indicate that mixing was the major cause controlling the transportation of nitrate in River and East Lake in winter.
- And there might be denitrification happened in west Lake.

Ecosystem Services of Wetlands

1. Sponge effect - decrease flood peak and increase flow during drought
2. Groundwater cleansing – wetlands metabolize water → increase water quality (biological filters)

Figure 4.—Relationship Between Wetland Processes and Values



Lacustrine wetlands in Pine Barrens, southern NJ

Photo by R. Grippo

Coastal mangrove swamp, Belize, Central America

Photo of R. Grippo and Penn State student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2007.09.14 14:59

Thank you for your contributions!