Nitrogen Processes in Large Rivers

Sponsored by: WOTS and SWWRP

Using Stable Isotopes to Link Hydrology to Nitrogen Biogeochemistry Over Multiple Space and Timescales

Dr. Herb Fredrickson and Dr. Elly Best

Environmental Laboratory

U.S. Army Engineer R&D Center

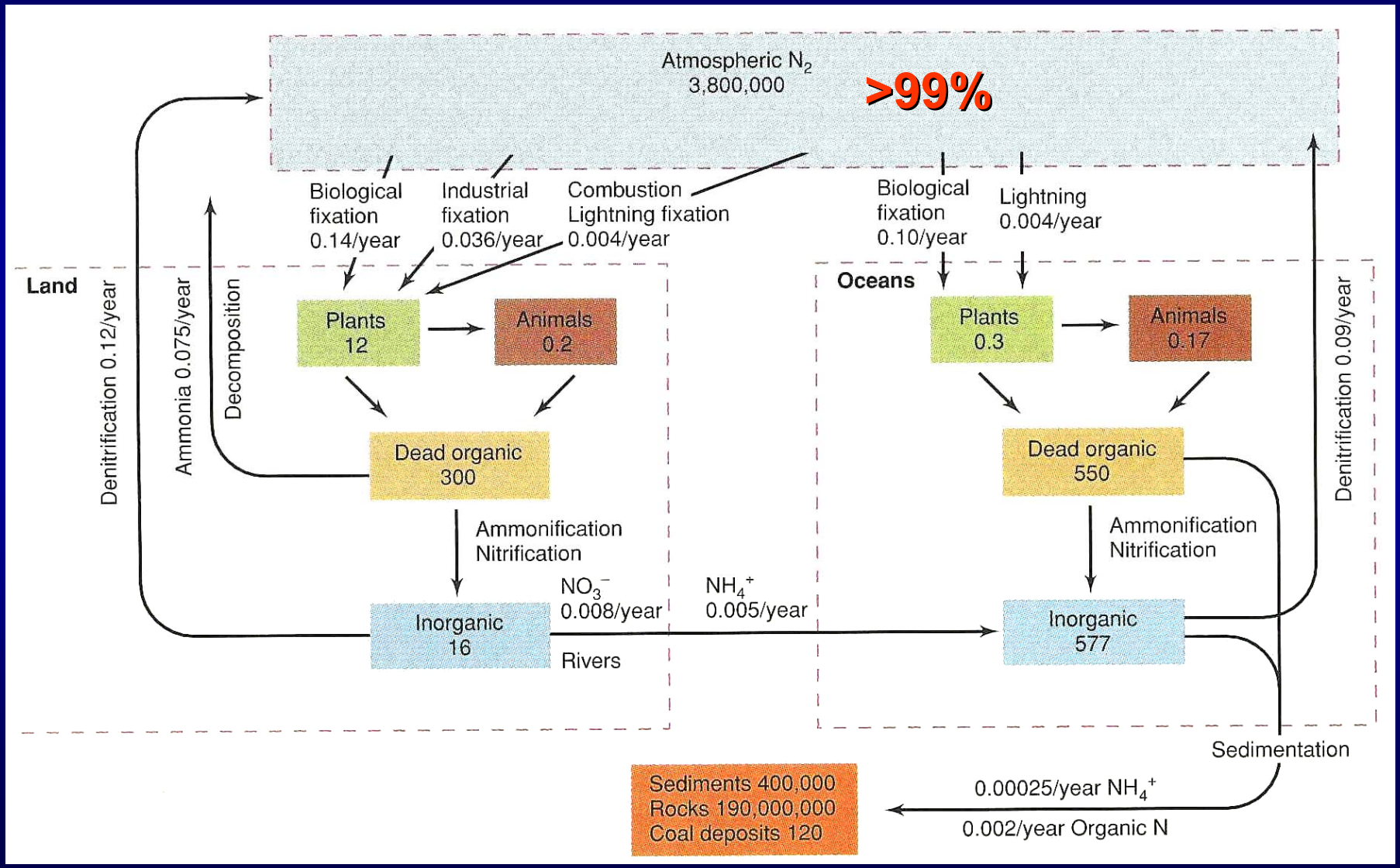
Vicksburg, Mississippi

Hotel Monteleone

214 Rue Royale, New Orleans, LA 70130-2201

23-24 August, 2005

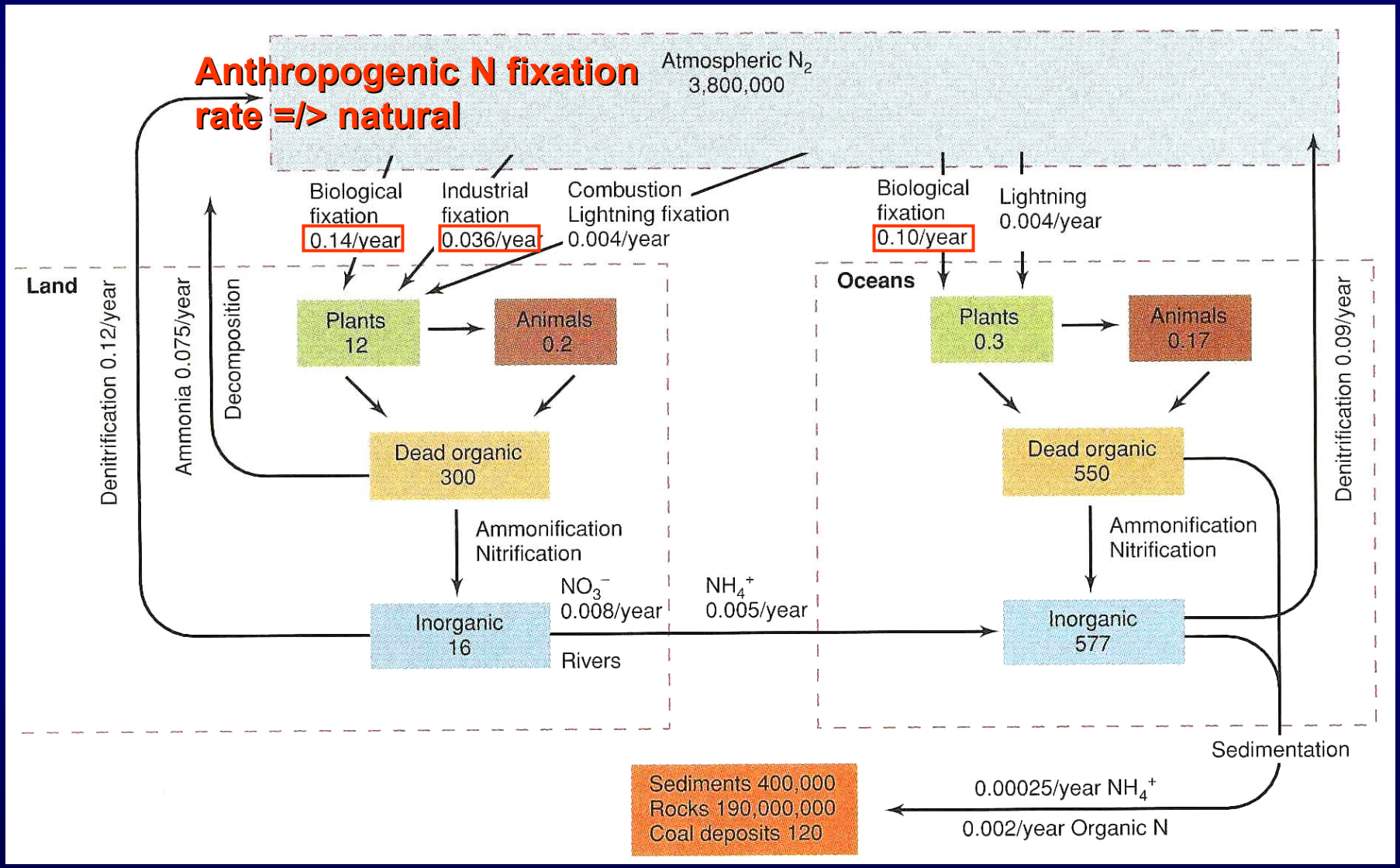
Global Nitrogen Budget



Multiply all numbers by 10^{15} to get grams

After Brock 1997

Global Nitrogen Budget



Multiply all numbers by 10^{15} to get grams

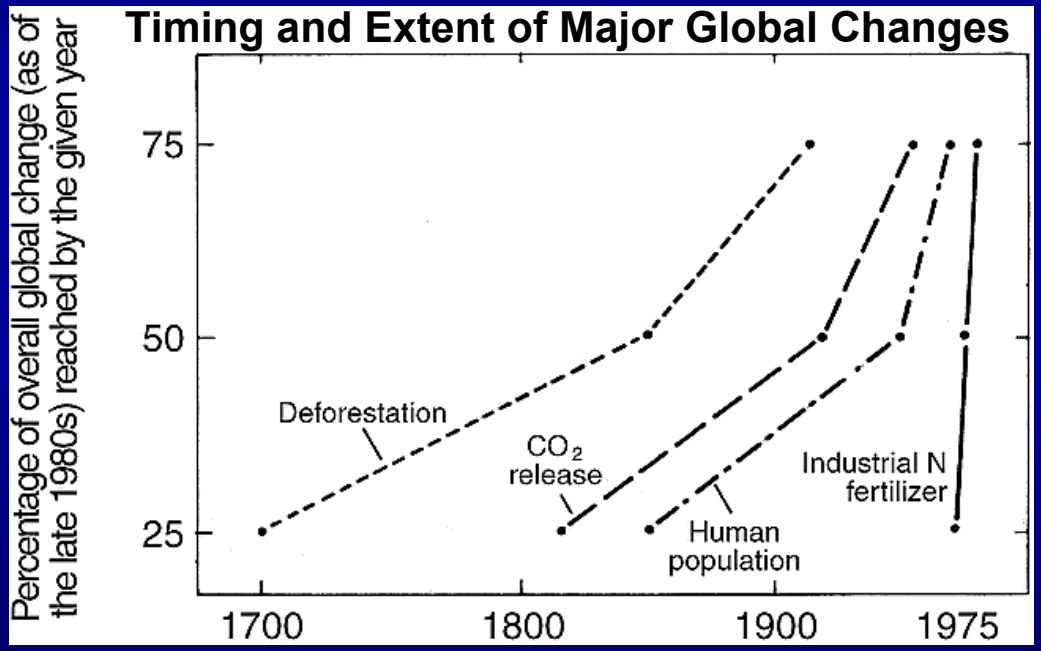
After Brock 1997

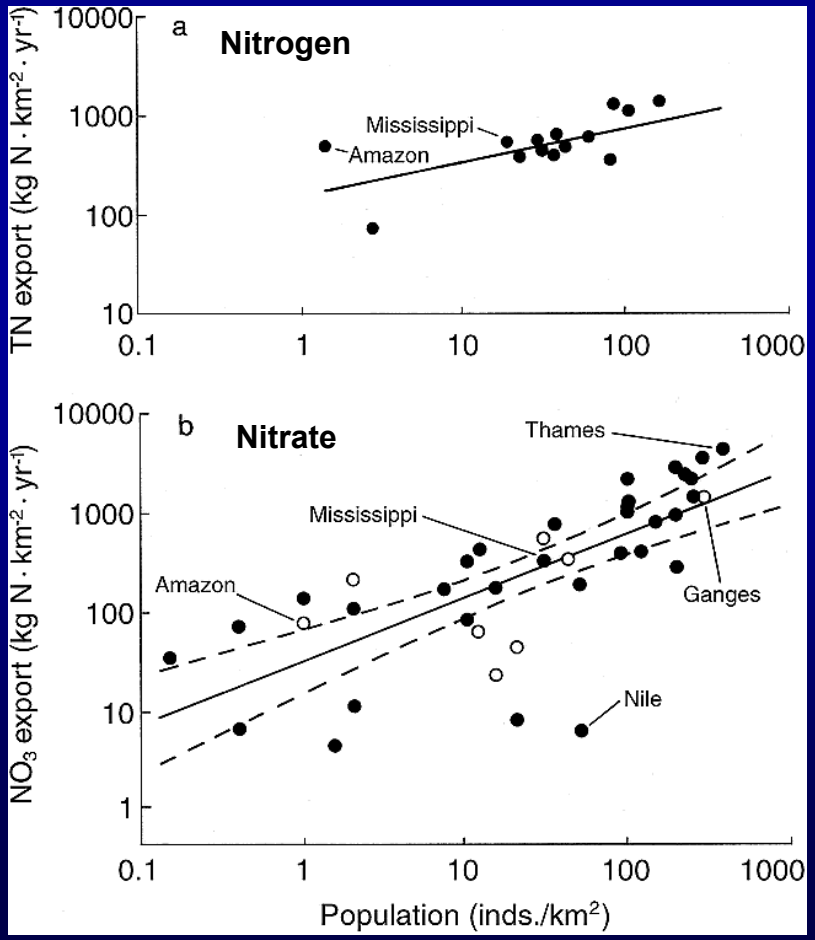
Unbalancing the Nitrogen Budget

HUMAN ALTERATION OF THE GLOBAL NITROGEN CYCLE: SOURCES AND CONSEQUENCES

Peter M. Vitousek, John D. Aber, Robert W. Howarth, Gene E. Likens, Pamela A. Matson, David W. Schindler, William H. Schlesinger, and David G. Tilman

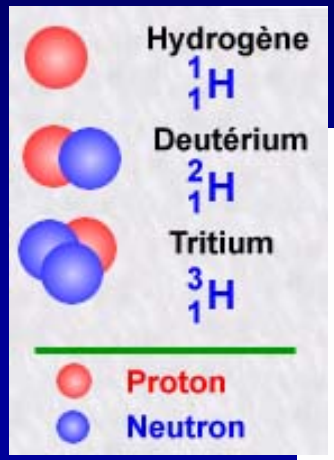
Ecological Applications: Vol. 7, No. 3, pp. 737–750.



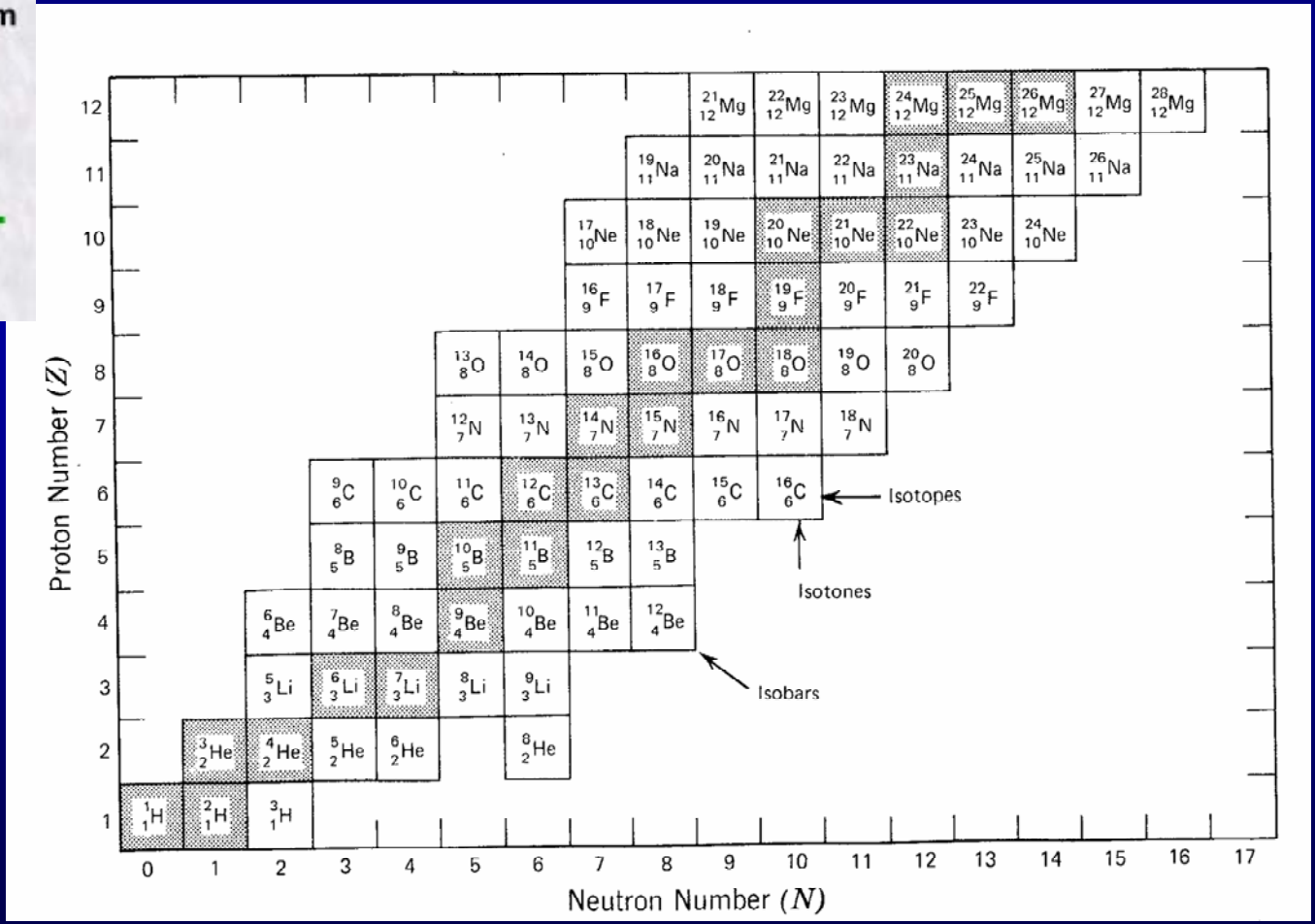


Export of total nitrogen (a) and nitrate (b) from river systems, as a function of human population density in the watershed. Note logarithmic scale

Introduction to Stable Isotopes



Partial Chart of Nuclides



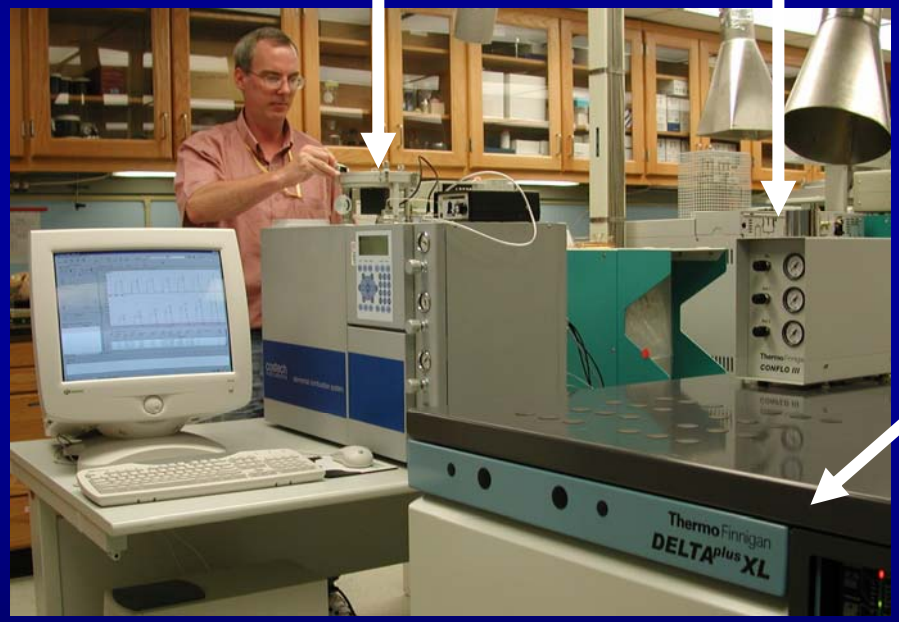
Stable nuclides are shaded; Unstable nuclides (radioactive) are not shaded.

Introduction to Stable Isotopes

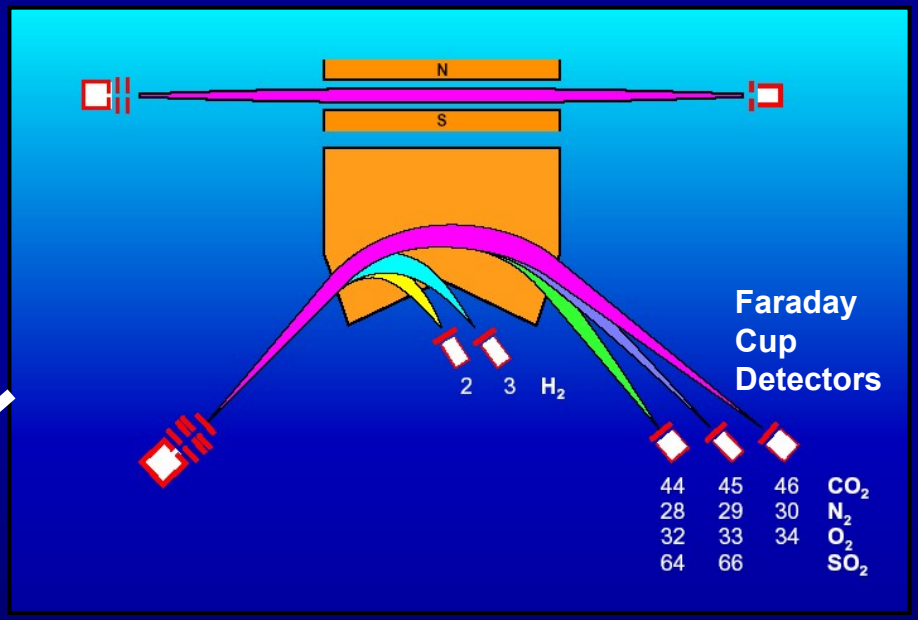
Precise Measurements of Light Stable Isotopes

Elemental Analyzer

Open split interface



Magnetic Sector Mass Spectrometer



$$\delta\,^{15}N\,(‰) = \left[\frac{(^{15}N/^{14}N)_{sample} - (^{15}N/^{14}N)_{standard}}{(^{15}N/^{14}N)_{standard}} \right] * 1000$$

Precision (in our hands):

$\delta^{13}C = X \pm 0.2$

$\delta^{15}N = X \pm 0.4$

$\delta^{34}S = X \pm 0.5$

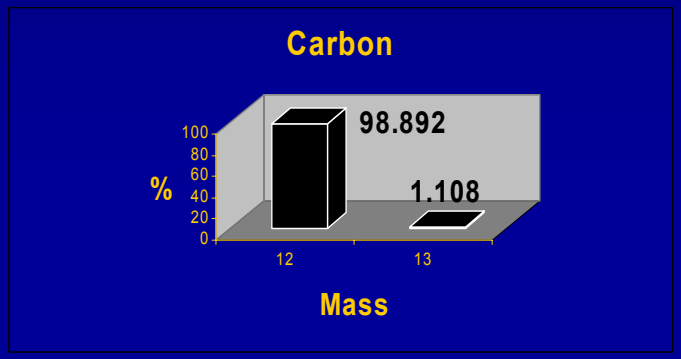
Introduction to Stable Isotopes

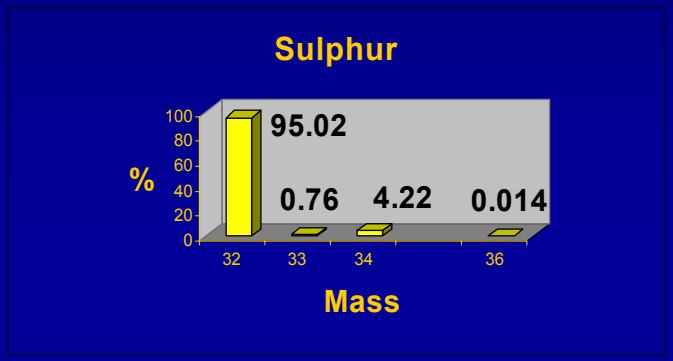
Two General Types of Use

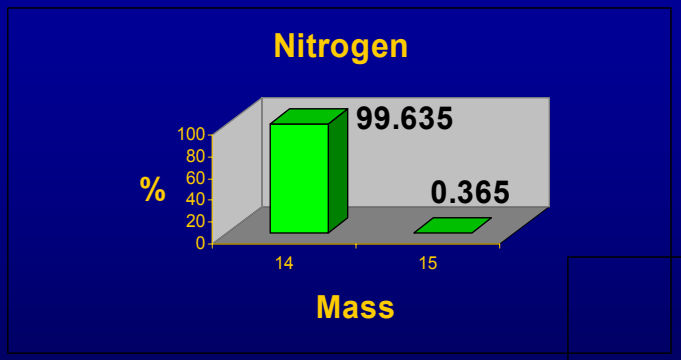
1. **Natural abundances of light stable isotopes**
   - **Know ratios of potential sources**
   - **Know causes/extents of isotopic discrimination**
2. **Spike into system a heavy isotope of the element in the appropriate chemical species.**

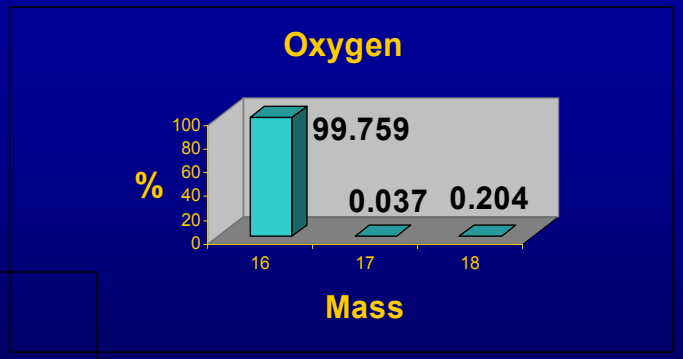
Introduction to Stable Isotopes

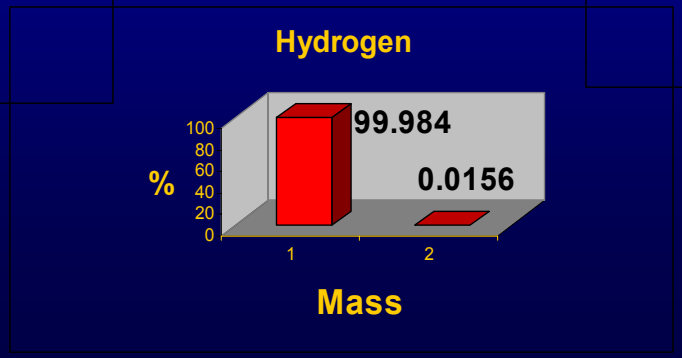
Natural Abundances of Light Stable Isotopes







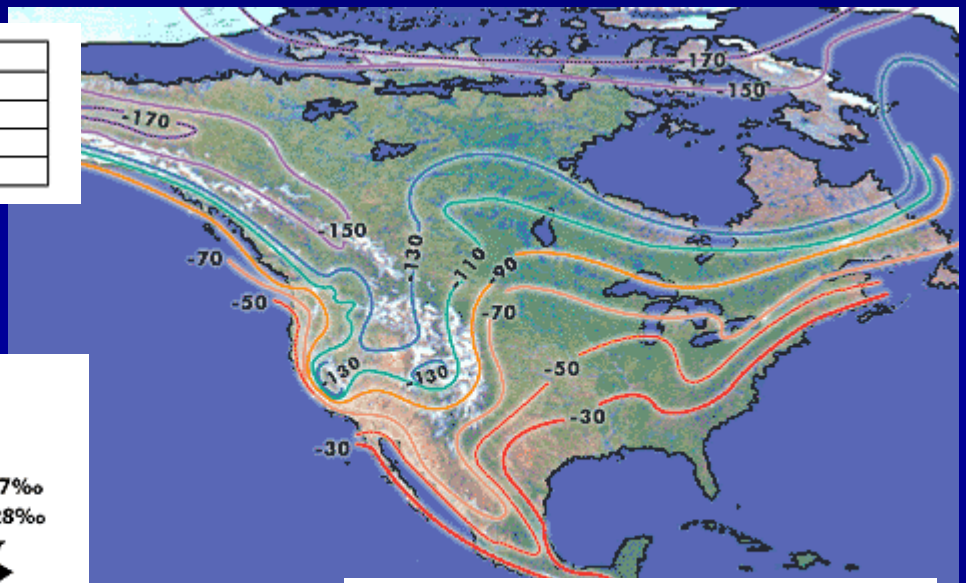




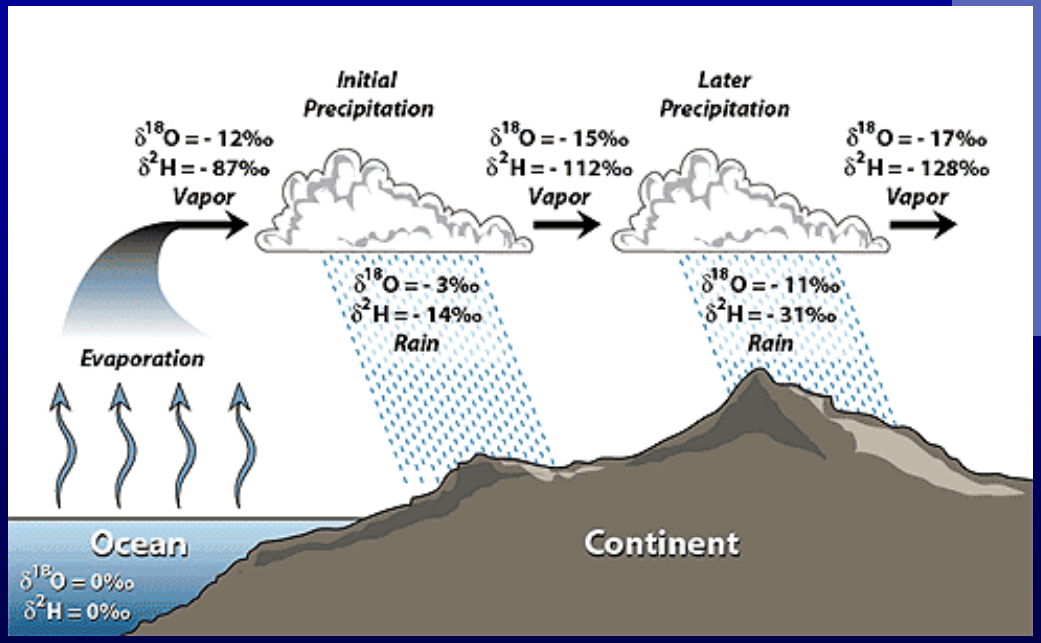
Use of O and H Stable Isotopes in Hydrology

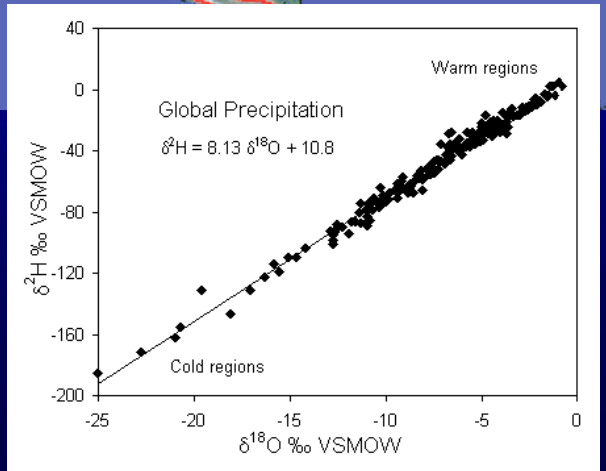
Natural Abundances of Light Stable Isotopes

	$^{1}H_2{}^{16}O$	$^{2}H_2{}^{16}O$	$^{1}H_2{}^{18}O$
density @ 20°C	.997	1.1051	1.1106
boiling point	100.0	101.42	100.14
vapor pressure @100°C	760	721.60	?
temperatory density max	3.98	11.24	4.30



Rayleigh Distillation

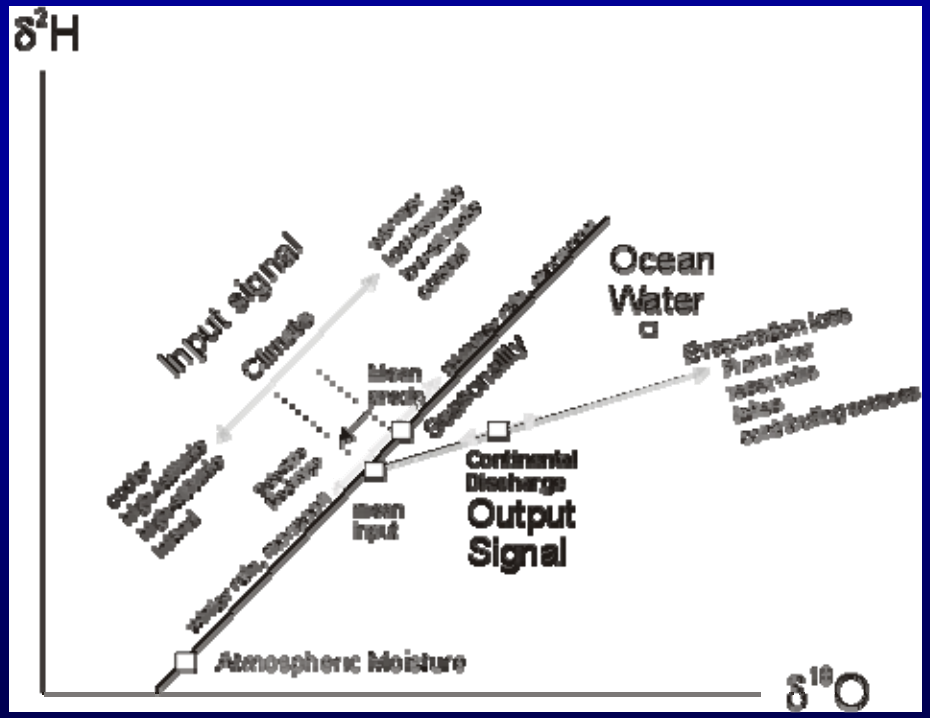


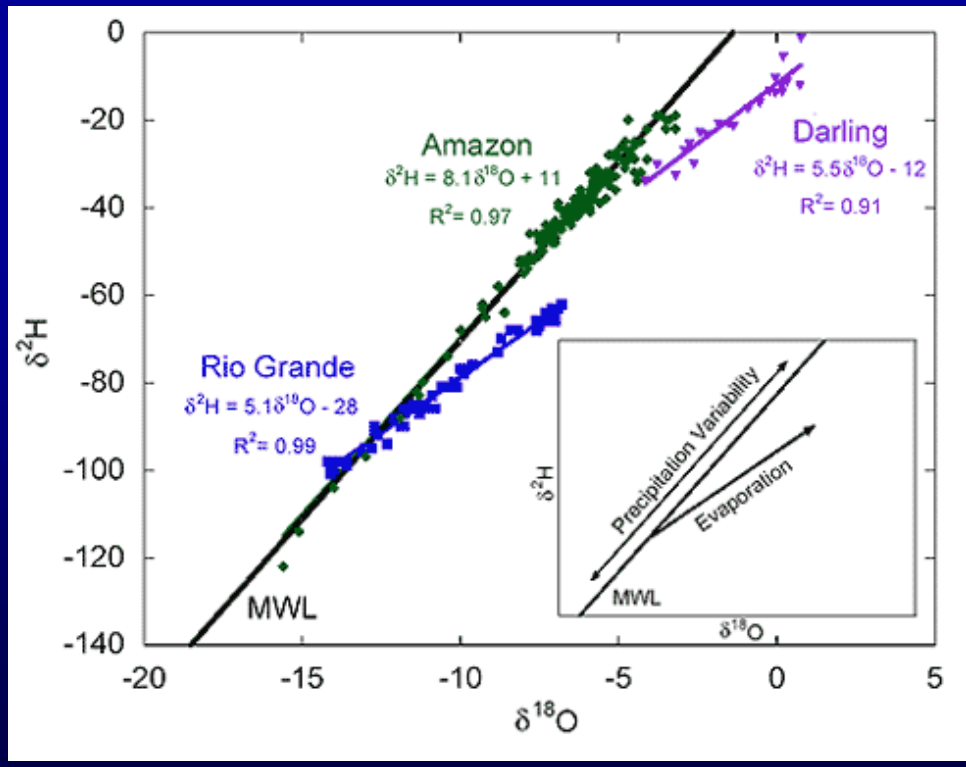


Use of O and H Stable Isotopes in Hydrology

Natural Abundances of Light Stable Isotopes

Primary forcings on isotope composition of hydrological inputs and outputs from large river basins.

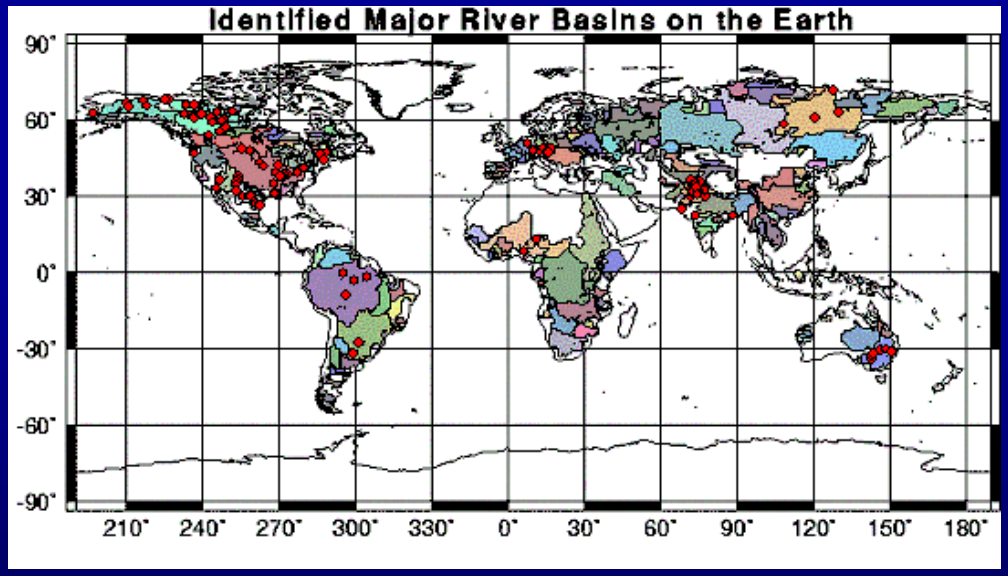




Basin Scale Hydrological Models

International Atomic Energy Agency

Isotopic Tracing of Hydrological Processes in Large River Basins, 2002-06



http://www.iaea.org/programmes/ripc/ih/rivers_hp/rivershome1.htm

IAEA Workshop on: Isotopic Tracers in Water Cycle Models, July 2003, Sapporo, Japan

1. Current models using isotopic data
   - ECHAM-4
   - GISS
   - AGCM
   - FORSGC AGCM
2. Global Energy & Water Studies
   - GAPP (USA)
   - MAGS (CA) WATFLOOD
   - GAME (Japan)

Basin Scale Hydrological Models

International Atomic Energy Agency

New York Times SCIENCE DESK | July 26, 2005, Tuesday, **With a Push From the U.N., Water Reveals Its Secrets** By WILLIAM J. BROAD (NYT) 1924 words; Late Edition - Final , Section F , Page 1 , Column 1

Thematic Plan for IAEA Technical Cooperation Activities in River Basin Management

Problem/Issue	Applicable Isotopic Parameter					
	δ^2H $\delta^{18}O$	$\delta^{15}N$	$\delta^{18}O$ NO_3	$\delta^{13}C$	$\delta^{34}S$	$\delta^{18}O$ SO_4
Pollutant transport & fate	††	††	†	††	†††	†
Water balance	†††			†		
Water allocation	†					
Wetland & floodplain management	†††	††	†	††	†	
Plant & animal ecology	†	†††	†	†††	†	
Sediment transport dynamics						
Irrigation-water management	†					
Period monitoring & baseline characterization	†††			†		
Hydrodynamic time-scales in river basins	†††			†		
Climate & environmental or landuse change	†††			†††		
Biogeochemical transport & fate	†	†††	††	†††	††	
Surface water - groundwater interaction	†††	††		††		
Coastal zone management	†††				†††	
Fish stock analysis from otoliths	††			††		

† = Possible application but limitations exist or potential not fully evaluated

†† = Probable application but development needed and applicability is case-study dependent

††† = Proven and demonstrated applicability

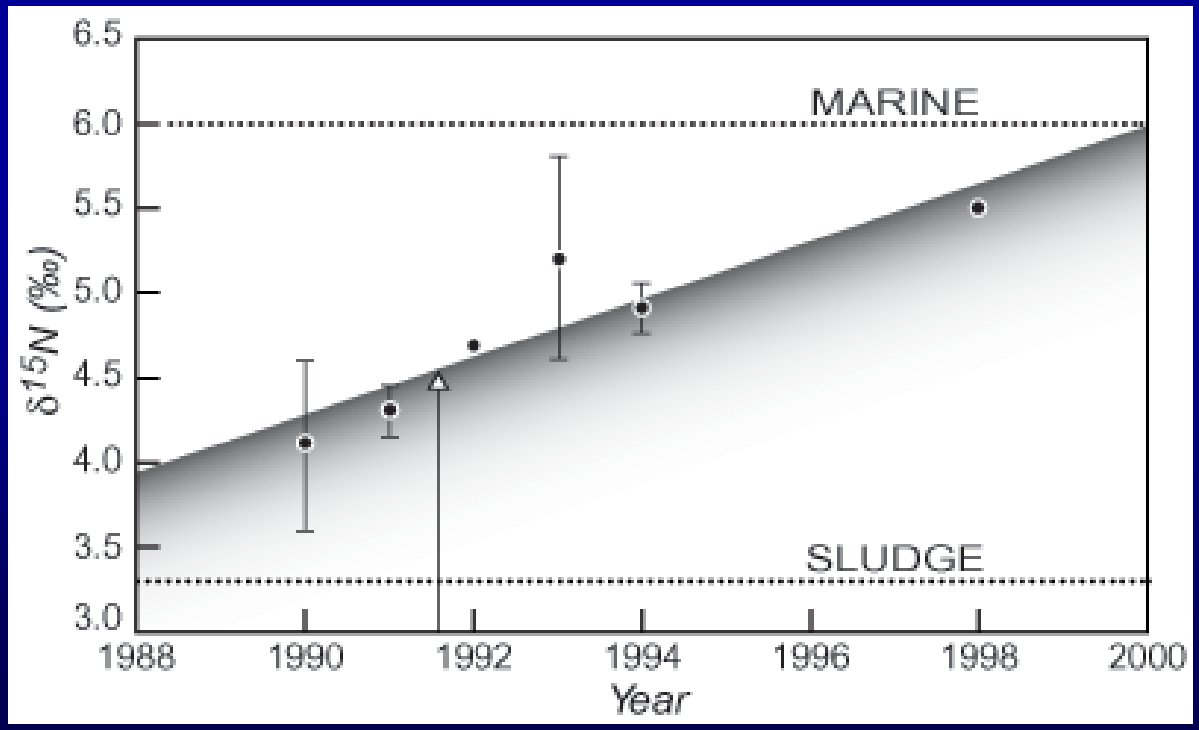
http://www-tc.iaea.org/tcweb/abouttc/strategy/thematic/pdf/summary/Summary_report_RBM.pdf

Elemental and Isotopic Surveys

Anthropogenic impacts on the Nitrogen Cycle

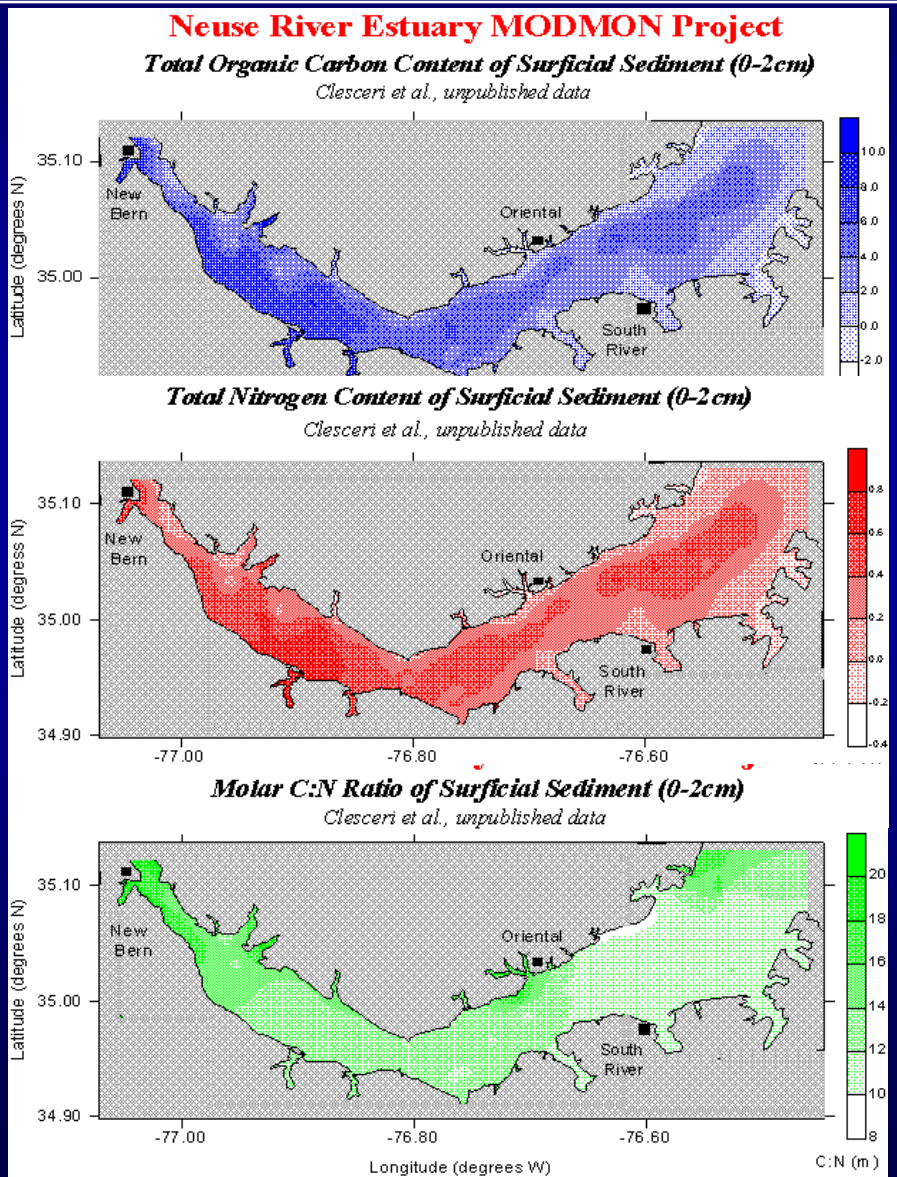
Fritz Haber's Process: N_2 gas + $3H_2 \rightleftharpoons 2NH_3$ gas = 92.4kJ $mole^{-1}$

Explosives and Fertilizer – N2 from atmosphere, $\delta^{15}N \sim 0$

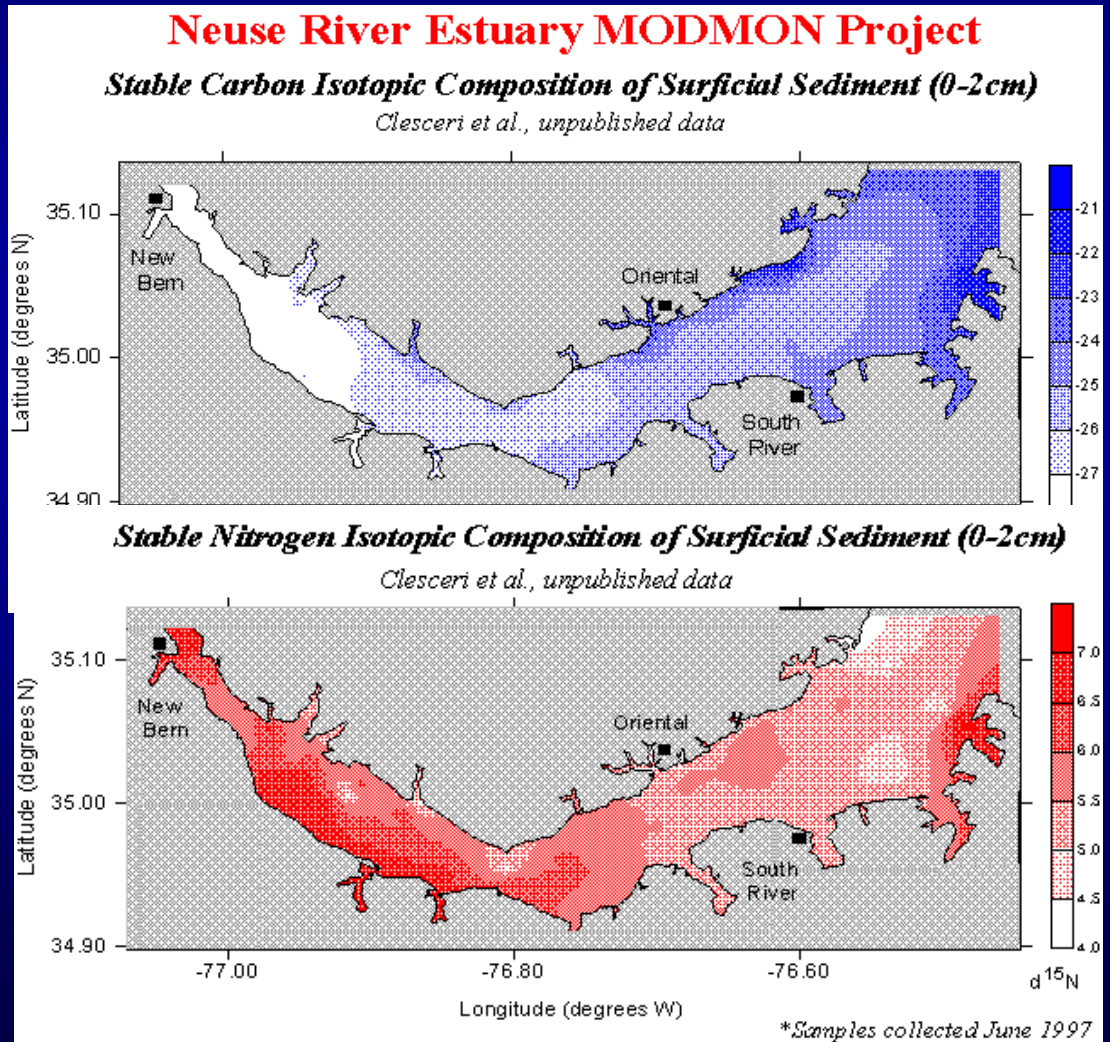


Change in annual average delta $\delta^{15}N$ over time for the northern harbor stations in Boston Harbor, Mass. http://www.whoi.edu/seagrant/education/focalpoints/isotope.html

Elemental and Isotopic Surveys

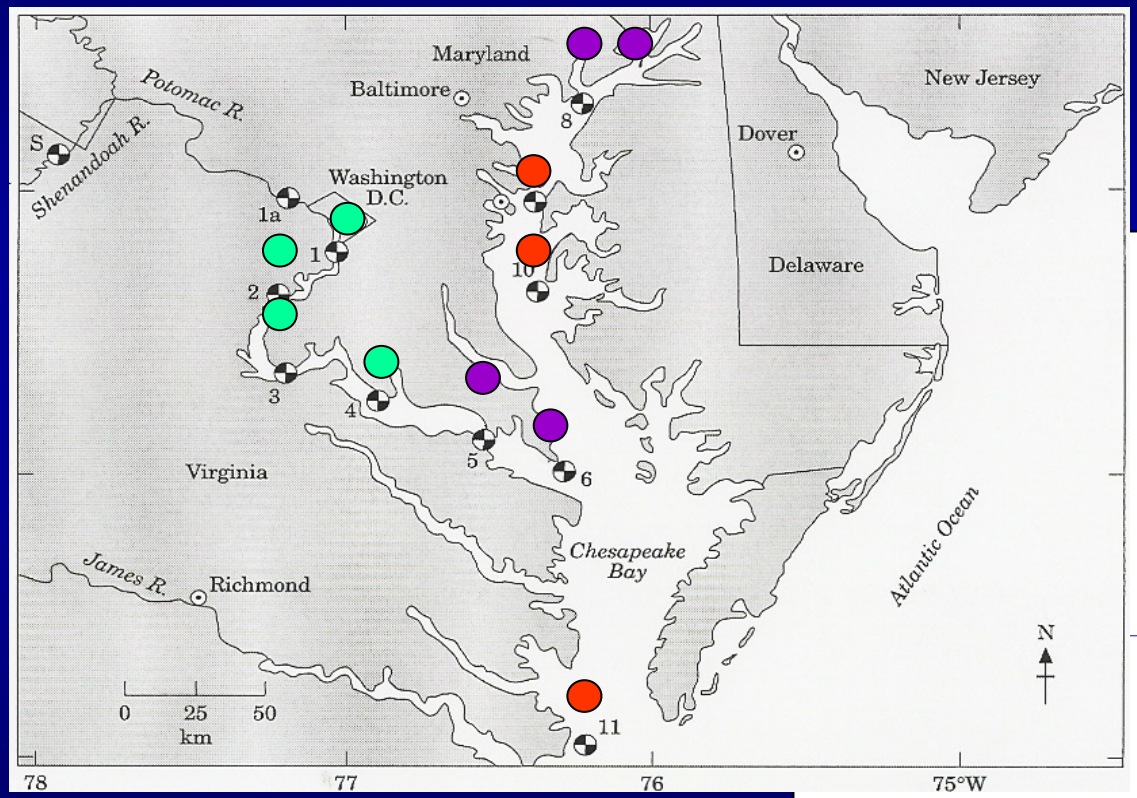


Elemental and Isotopic Surveys



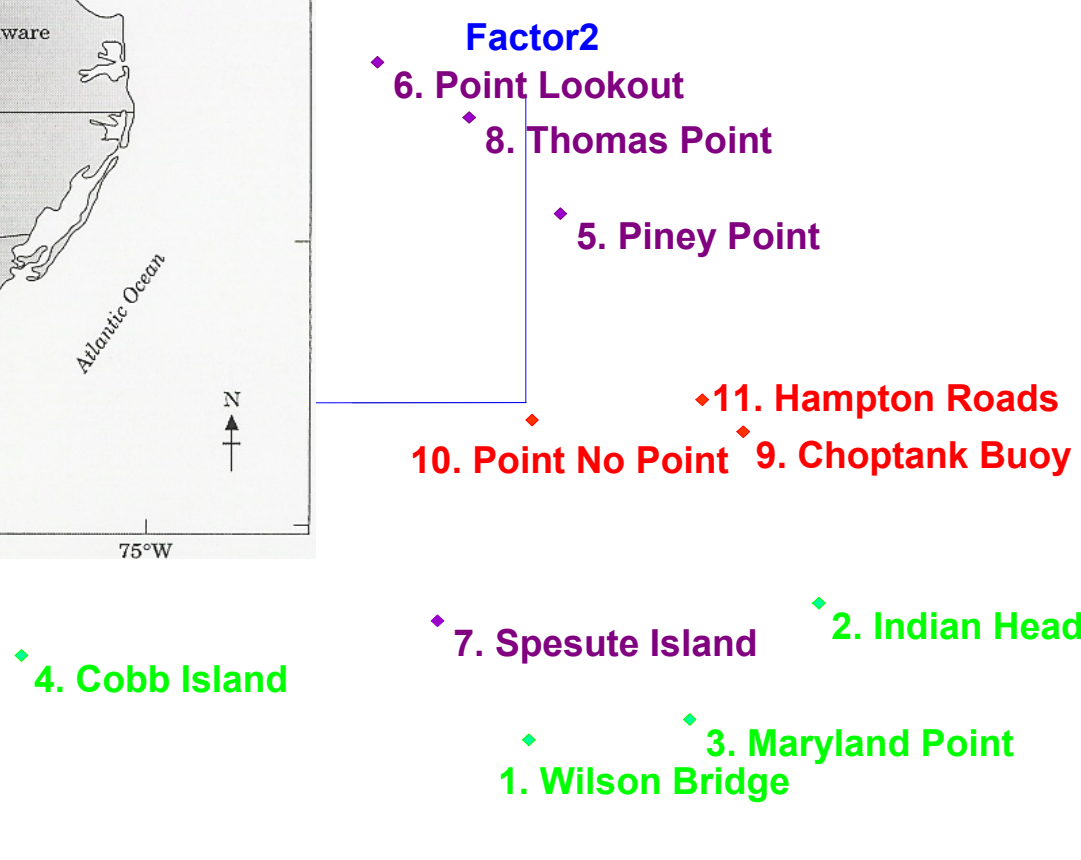
Elemental and Isotopic Surveys

Multivariate Characterization of Sediment



Characteristics:

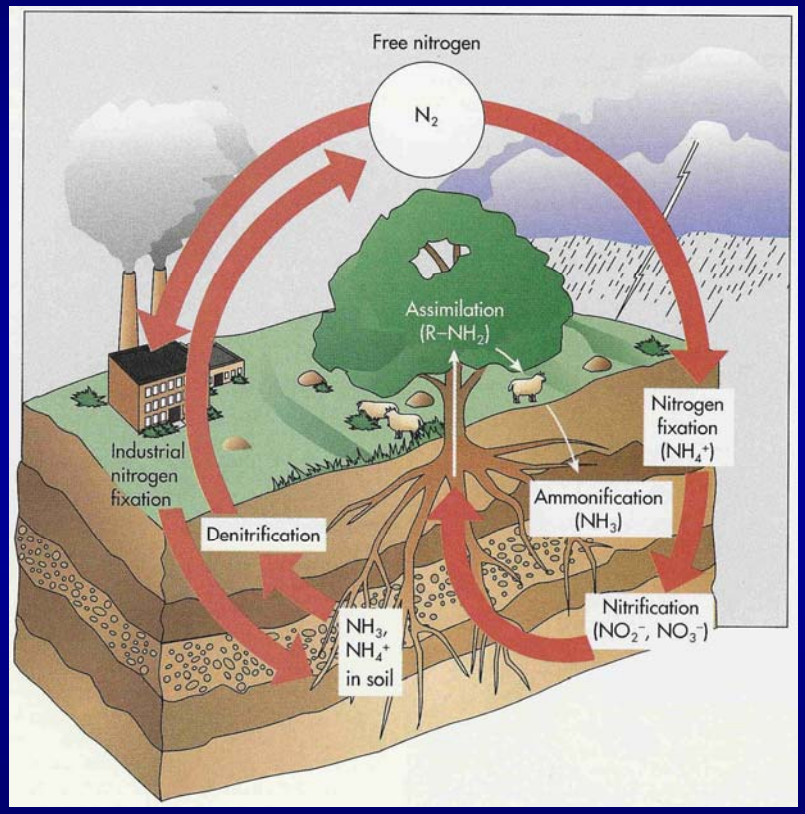
TN, TC, TS, ^{15}N, ^{13}C, ^{34}S



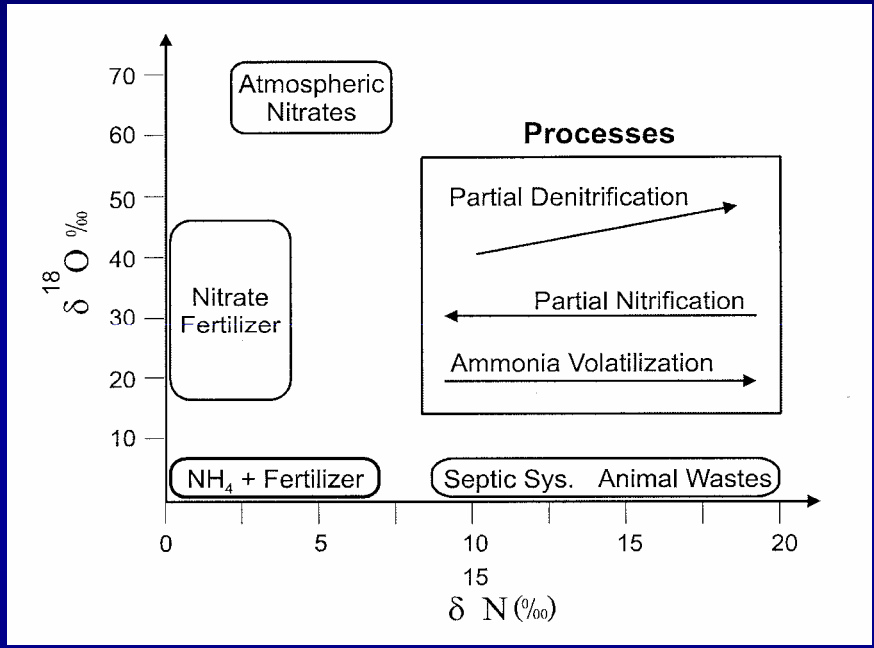
Our analysis of data of Sigleo and Macko, 2002 Estuarine, Coastal & Shelf Sci.

Nitrogen Source Tracking

Anthropogenic Impacts on N Cycle



Discrimination of Potential Sources



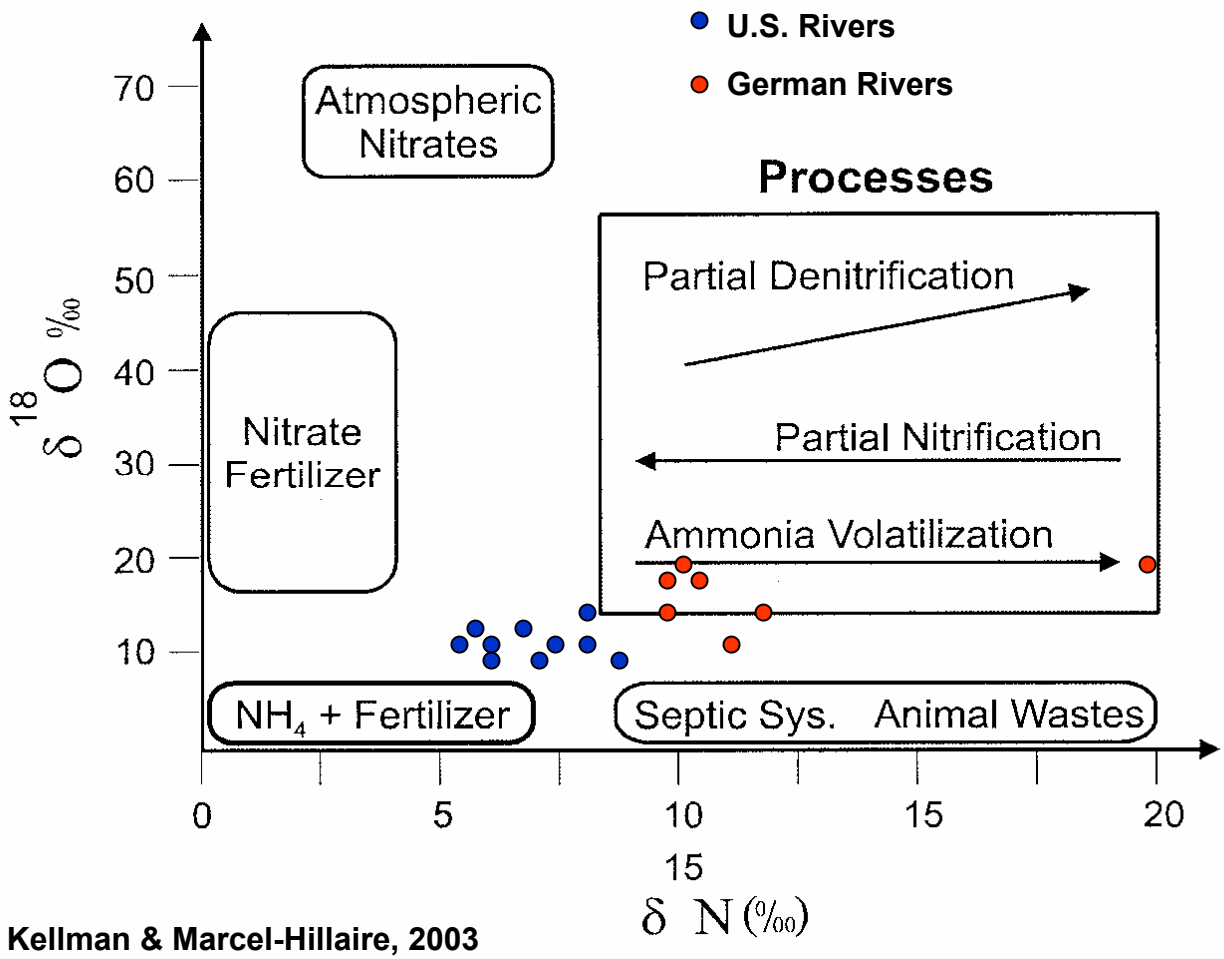
Nitrogen Source	Mean $^{15}\delta N$	SD
Swine manure	13.82	7.03
Swine Slurry	29.68	9.98
Poultry manure	10.98	4.44
Dairy cattle manure	12.19	2.69
Beef cattle manure	17.14	ND
Sewage Plant Sludge	11.42	7.21
Sewage Plant Effluent	11.61	2.71

Curt et al, 2004 – Water, Air, Soil Pollution 151

Sources must be discernable.

Microbial Nitrogen Source Tracking

$\delta^{15}N$ and $\delta^{18}O$ ratios of Nitrate in Major Rivers

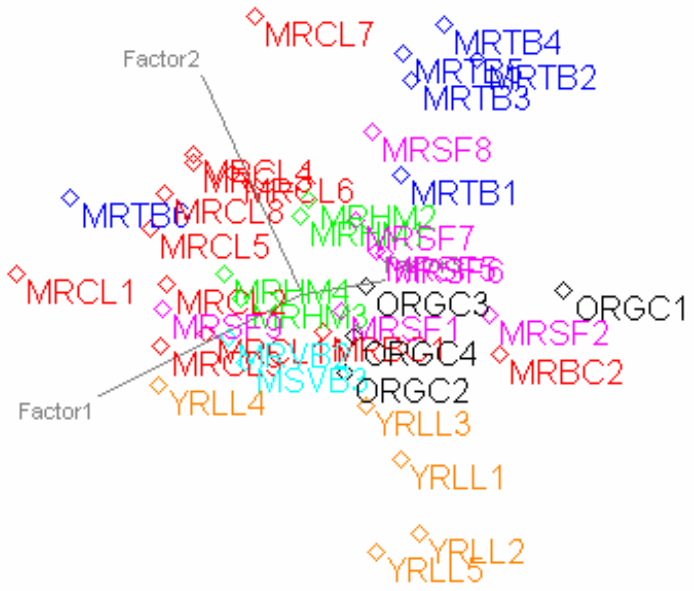


Kellman & Marcel-Hillaire, 2003

Microbial Nitrogen Source Tracking

PCA of MS River water using mg/L NO_3, $\delta^{15}NO_3$, $N\delta^{18}O_3$

MR @ Clinton, IA	MRCL
Missouri River @ Hermann, MO	MRHM
MR @ Thebes, IL	MRTB
Ohio River @ Grand Chain, IL	ORGC
Yazoo River @ Long Lake, MS	YRLL
MR @ St Francisville, LA	MRSF
MR @ at Vicksburg, MS	MRVB
MR @ Belle Chasse, LA	MRBC



msn15

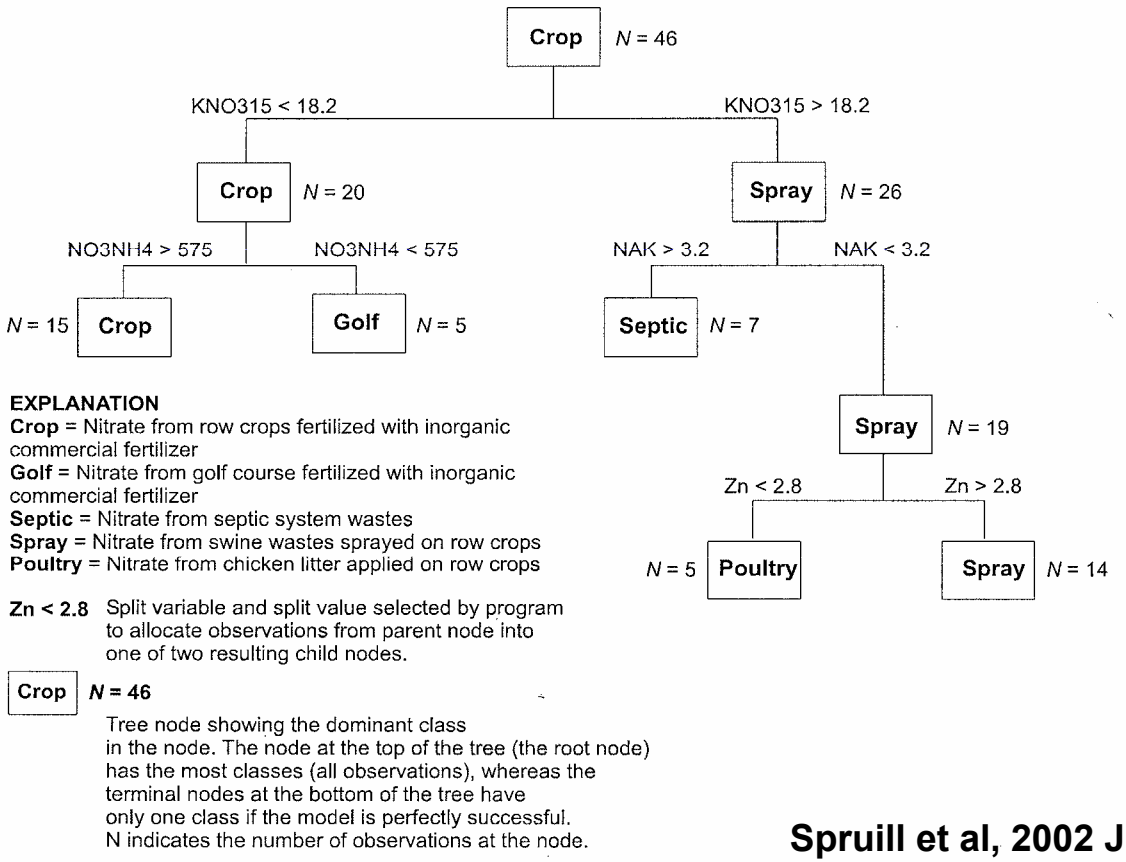
Battaglin et al 2001 Hydrological Processes

Microbial Nitrogen Source Tracking

Classification tree model of nitrate sources

Classification variables:

- $\delta^{15}N$ of NO_3
- Zinc
- NO_3/NH_4 ratio
- Na/K ratio

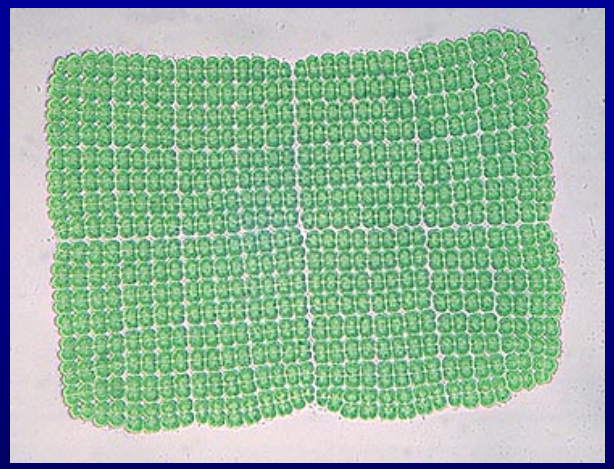


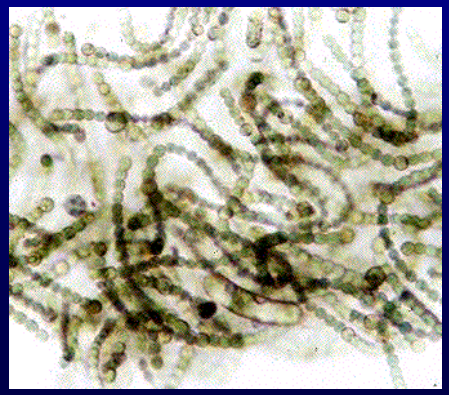
Spruill et al, 2002 JEQ

Correctly identified from 5 different NO_3 sources the correct source (80% of time) of 48 water samples. $N\delta^{18}O_3$ would probably help

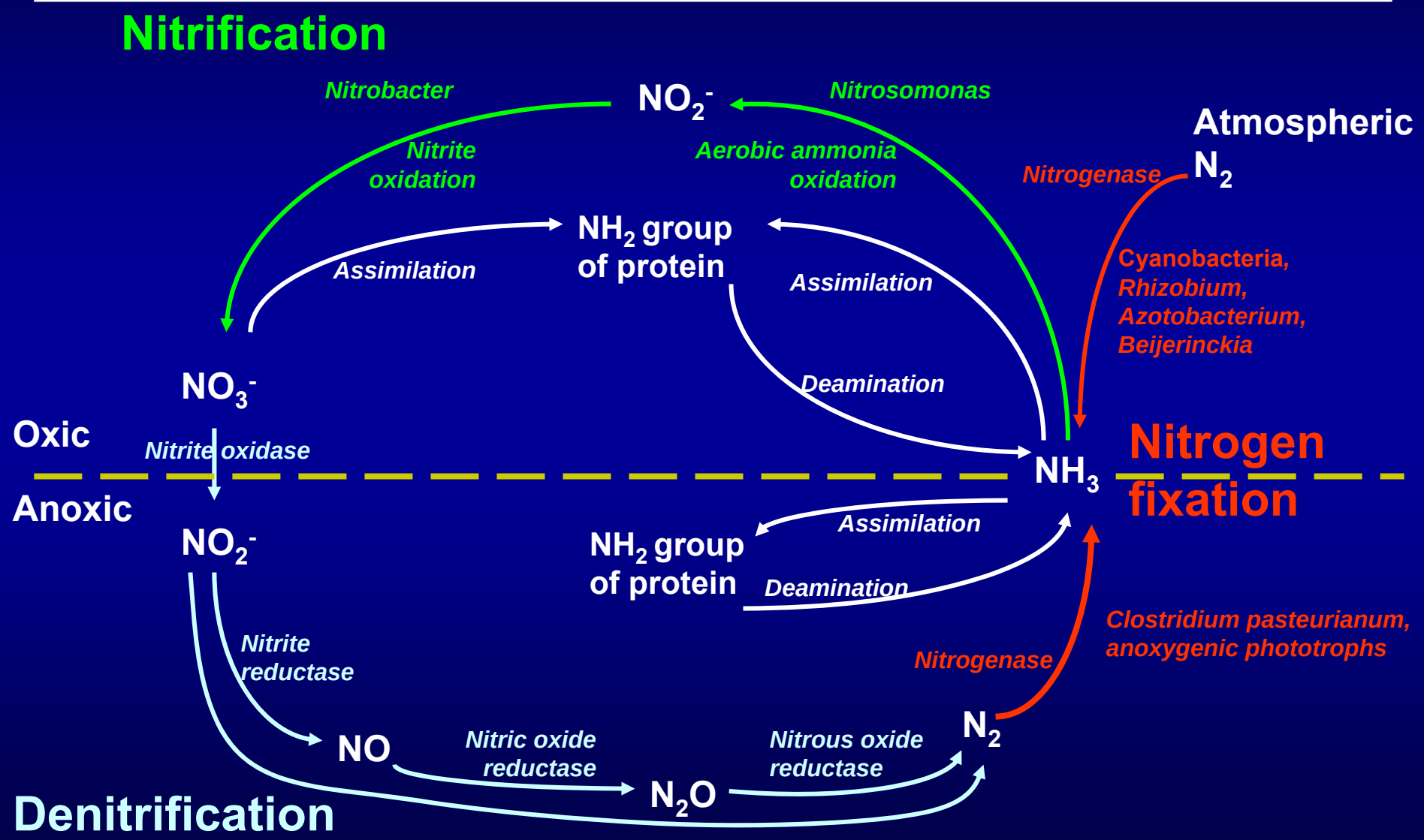
Microbial Nitrogen Cycling

- Nitrogen limits productivity of many aquatic ecosystems
- Uniquely bacterial processes
  - N_2 Fixation
  - Nitrification
  - Denitrification





Microbial Nitrogen Cycling

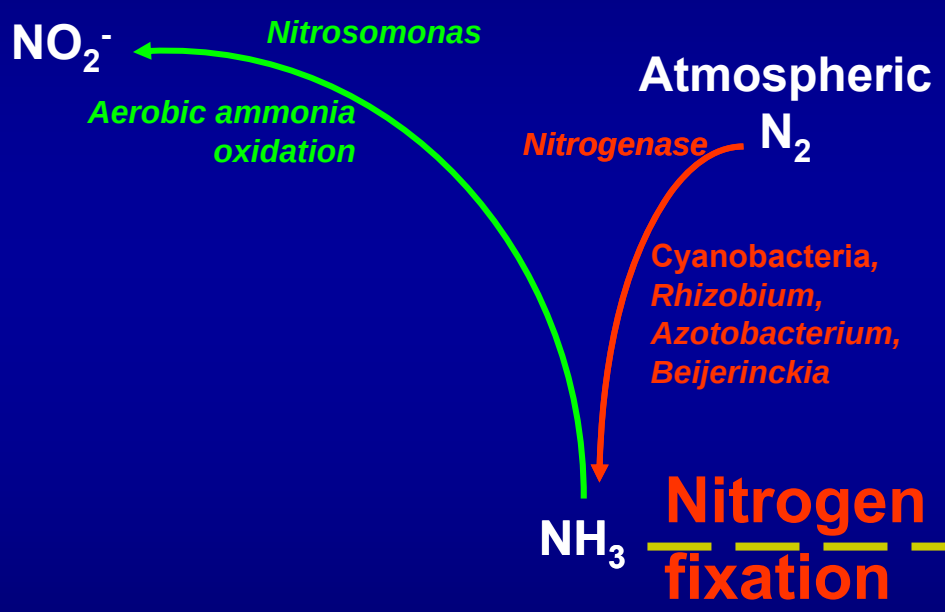


Pseudomonas, Bacillus, facultative aerobes

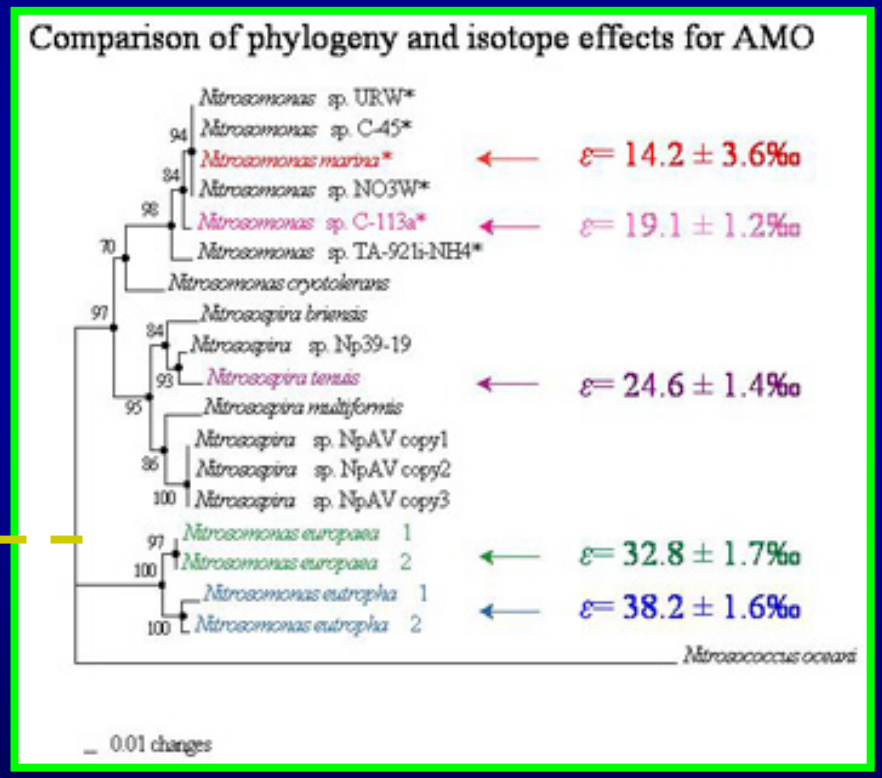
After Brock 1997

Microbial Nitrogen Cycling

Interpretation of natural isotopic N ratios in N pools



Ammonia monooxygenase



Still trying to deconvolute.

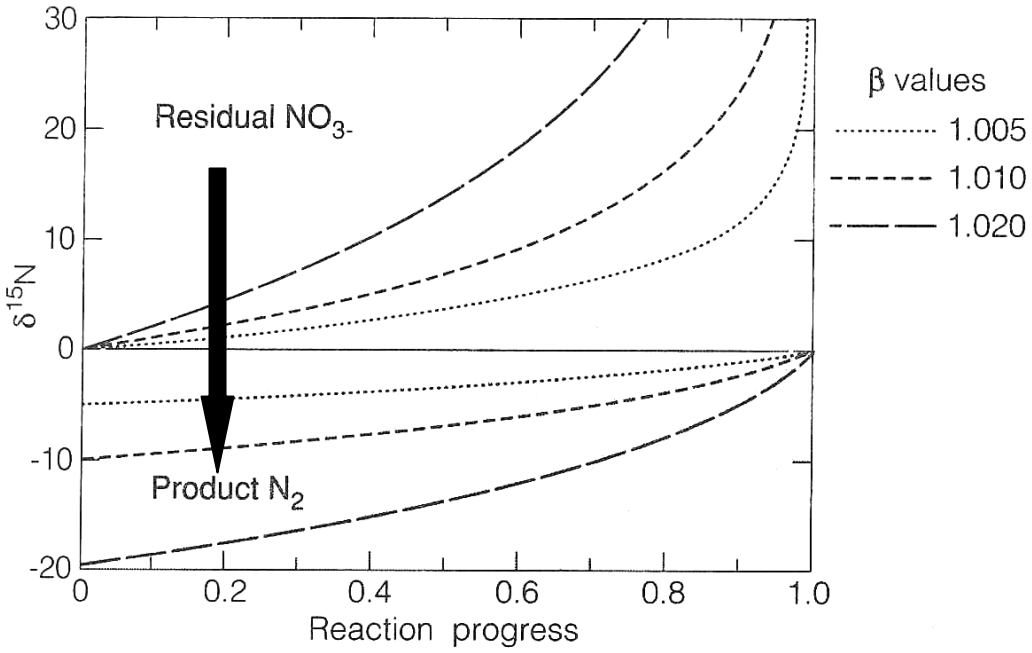
Karen L. Casciotti - Department of Marine Chemistry and Geochemistry
Woods Hole Oceanographic Institution

Isotopic Tracers in Kinetic Studies

Biological Fractionations and The Rayleigh Effect

- Initial products are relatively light.
- Residual reactants become progressively heavier.
- In a series of reactions the final isotopic fraction depicts the rate limiting step.

Denitrification $NO^3 \rightarrow\rightarrow\rightarrow N_2$



Introduction to Stable Isotopes

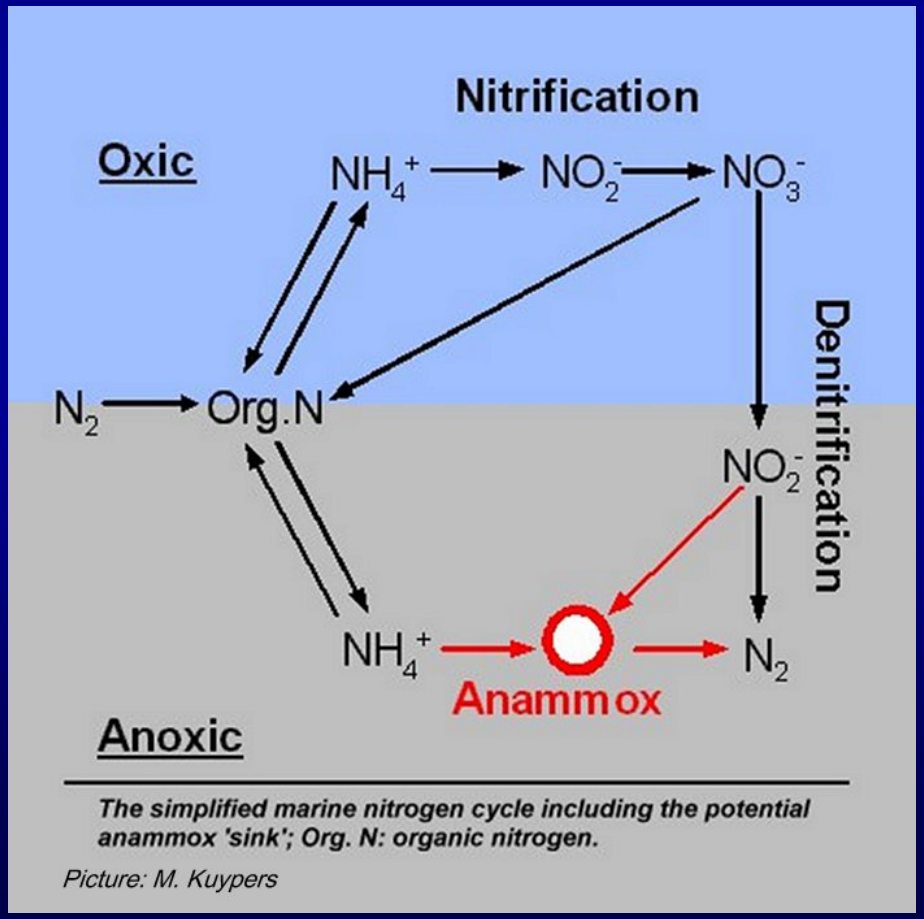
Two General Types of Use

1. Natural abundances of light stable isotopes
   - Know ratios of potential sources
   - Know causes/extents of isotopic discrimination
2. Spike into system a heavy isotope of the element in the appropriate chemical species.
   - Microcosms
   - Pulse-chase field spikes

Microbial Nitrogen Cycling

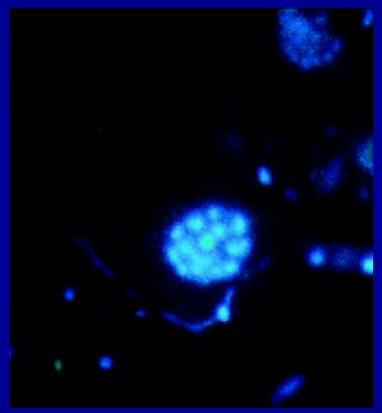
The anoxic ammonium oxidation reaction:

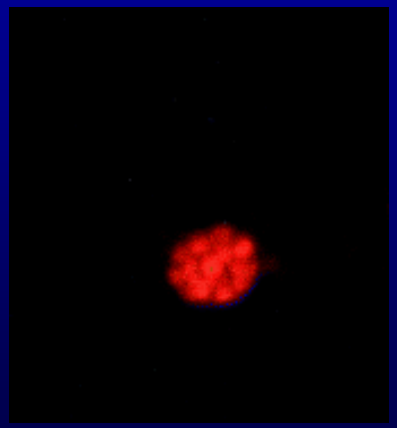
$$^{15}NH_4^+ + {}^{14}NO_2^- = {}^{15}N^{14}N + 2H_2O$$



The simplified marine nitrogen cycle including the potential anammox 'sink'; Org. N: organic nitrogen.

Picture: M. Kuypers

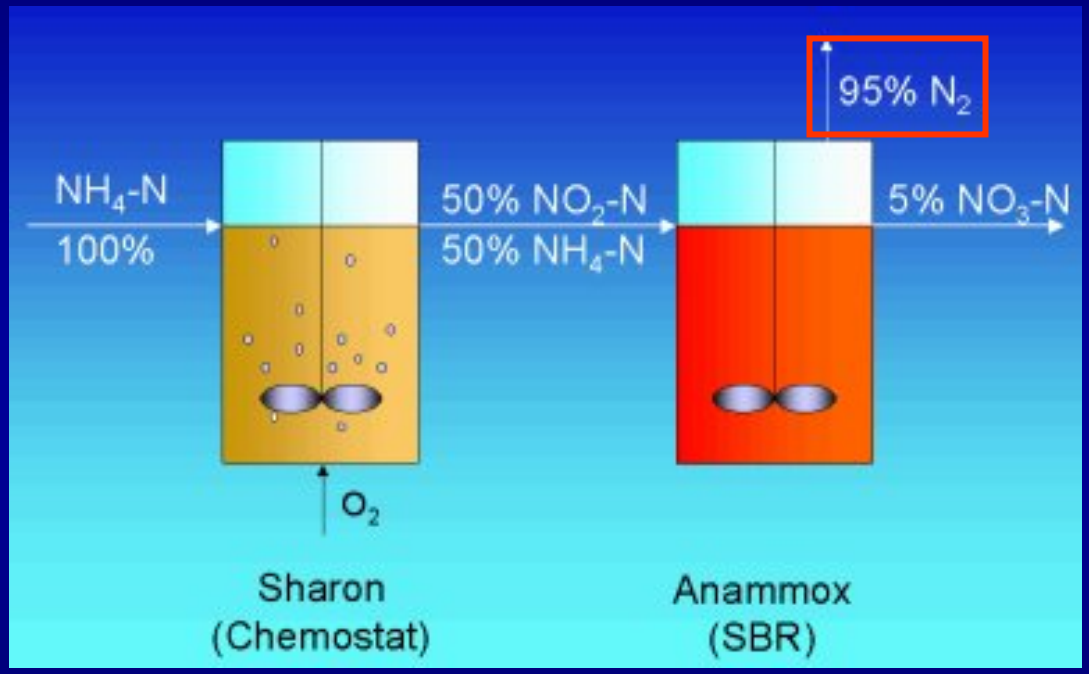




Kuypers, Marcel M. M. et al. (2005) Proc. Natl. Acad. Sci. USA 102, 6478-6483

Anoxic Ammonium Oxidation

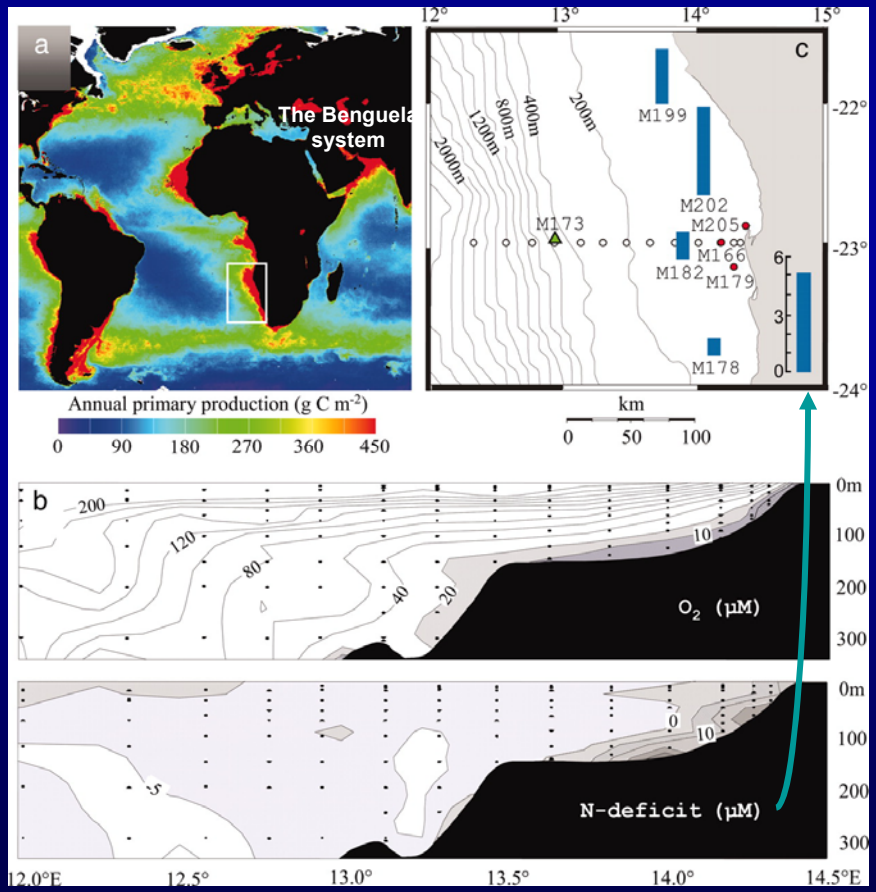
ANAMMOX Wastewater Treatment Process

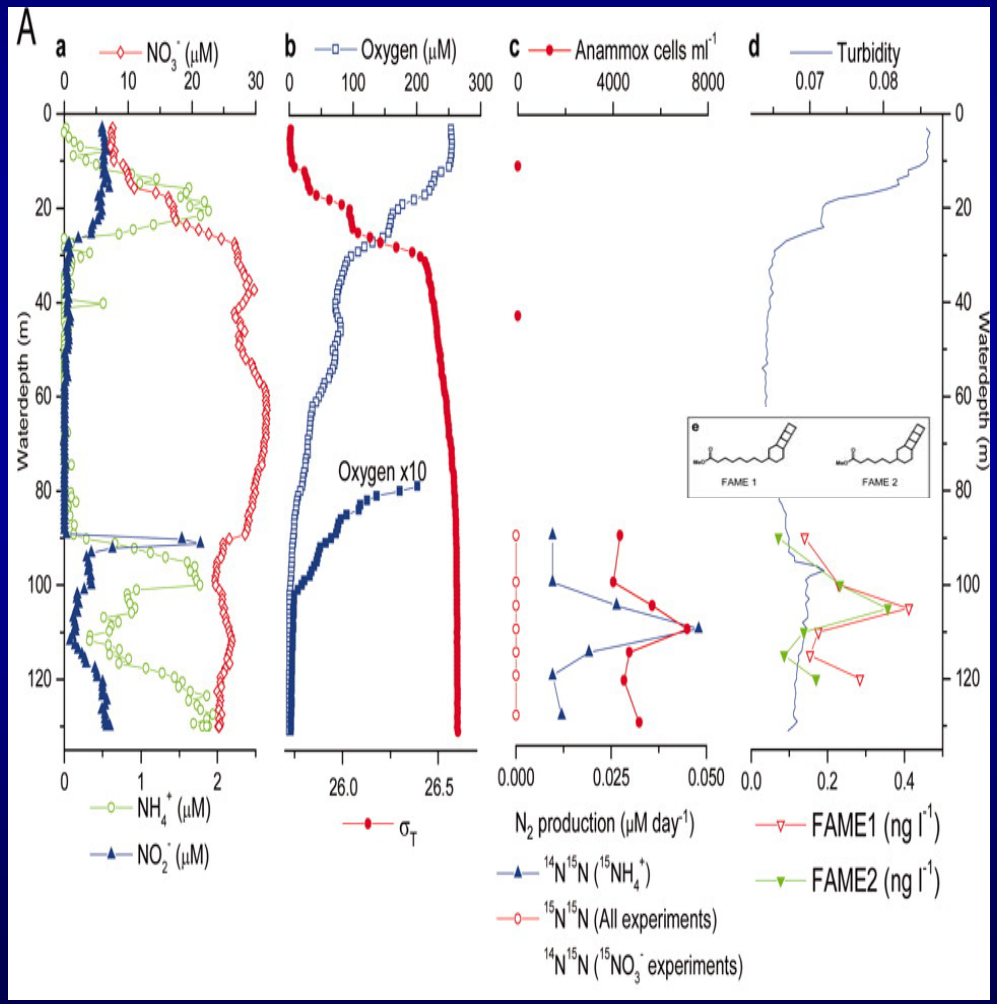


(partial nitrification)	2NH4+ + 1.5O2 = NH4+ + NO2- + H2O + 2H+
(anammox)	NH4+ + NO2- = N2 + 2H2O
(total)	2NH4+ + 1.5O2 = N2 + 3H2O + 2H+

Anoxic Ammonium Oxidation

Benguela Upwelling, 20-70% of total N_2 production





Kuypers, Marcel M. M. et al. (2005) Proc. Natl. Acad. Sci. USA 102, 6478-6483

Anoxic Ammonium Oxidation

How important is ANAMMOX?

Study	% of N_2 production
Benguela Upwelling	20-70%
Gulf Dulce, CR	20-50%
Global Redfield-based estim.	30-50%
Artic marine sediments	1-35%
Thames Estuary	1–15 % (salinity gradient)
Sewage Treatment	90%
Lake Tanganyika (freshwater)	5-15% C. Schubert-AWAG
Other freshwater systems	?????

Denitrification

Various Methods - Pros and Cons Steingruber et al 2001 AEM 69:3771-3778.

1. N mass balance — Ahlgren 1967 Hydrologia 29:53-90
2. N_2 production — Seitzinger et al 1980 Geochim. Cosmochim Acta 44:1853
3. Nitrate disappearance — Anderson 1977 Arch. Hydrobiol. 80:147-159
4. Pore water Z profiles — Mengis et al 1997 L&O 421530-1543
5. ^{15}N dilution — Koike & Hattoti 1978 AEM 35:278-282
6. ^{15}N isotope paring — Nielsen 1992 FEMS Microb. Ecol. 86:357-362
7. Acetylene inhibition — Sørensen 1978 AEM 36:139-143

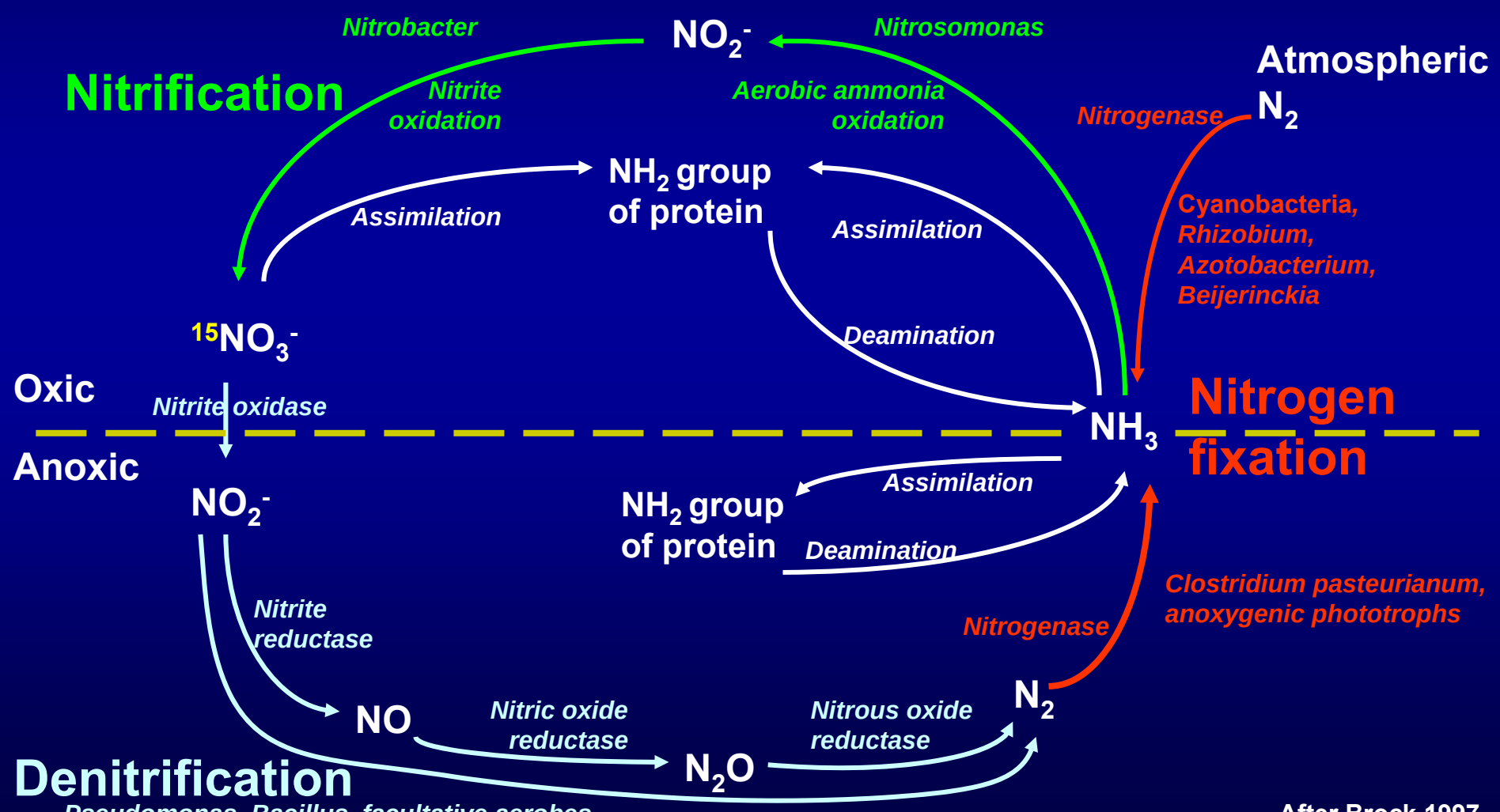
Pro – Easy & field portable

Con – Can underestimate denitrification

- Acetylene inhibition of coupled nitrification-denitrification
- Incomplete blockage of N20 reductase at low NO_3 levels or when S^- present
- Etc.

Microbial Nitrogen Cycling

Use appropriate ^{15}N label to measure any rate



After Brock 1997

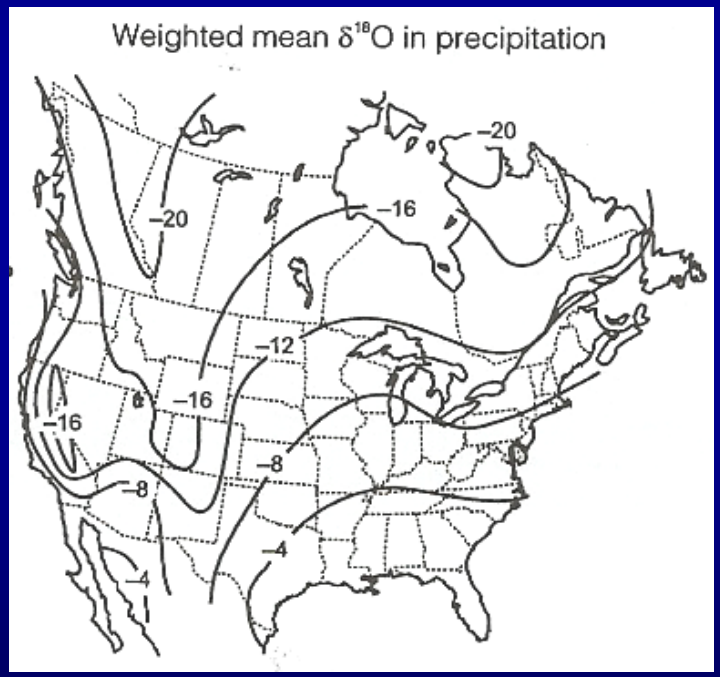
Opinion

- Bulk elemental and isotopic surveys help frame/delimit issues
- δ^2H and $\delta^{18}O$ of H_2O – validate hydrological models
- $\delta^{15}N$ provides N-cycle kinetic data
- $\delta^{15}N$, $\delta^{13}C$ and $\delta^{34}S$ used to link hydrological to biological models

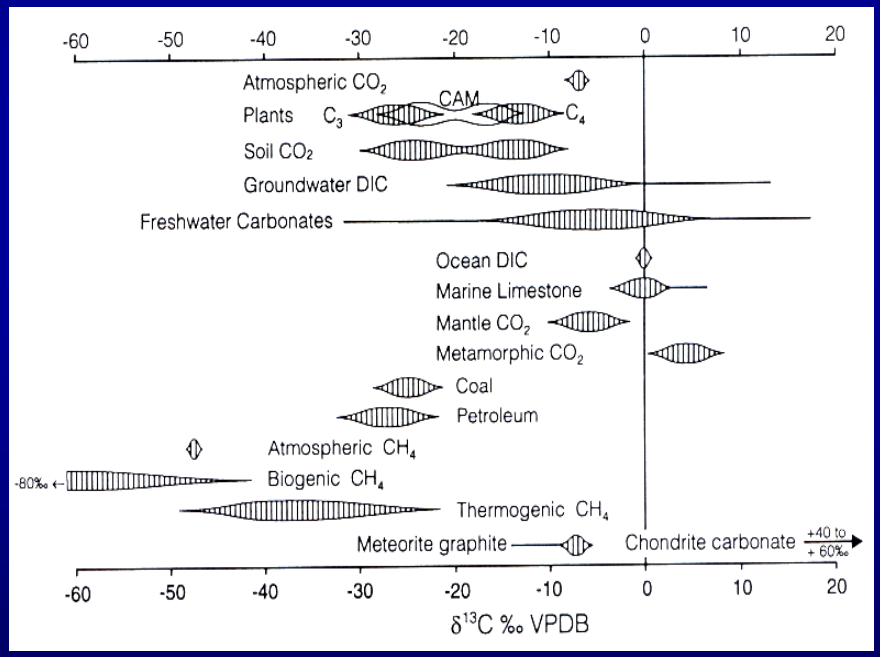
$\delta^{15}N$ and $\delta^{13}C$ used to link hydrological to biological models

Examples

Hydrological Models

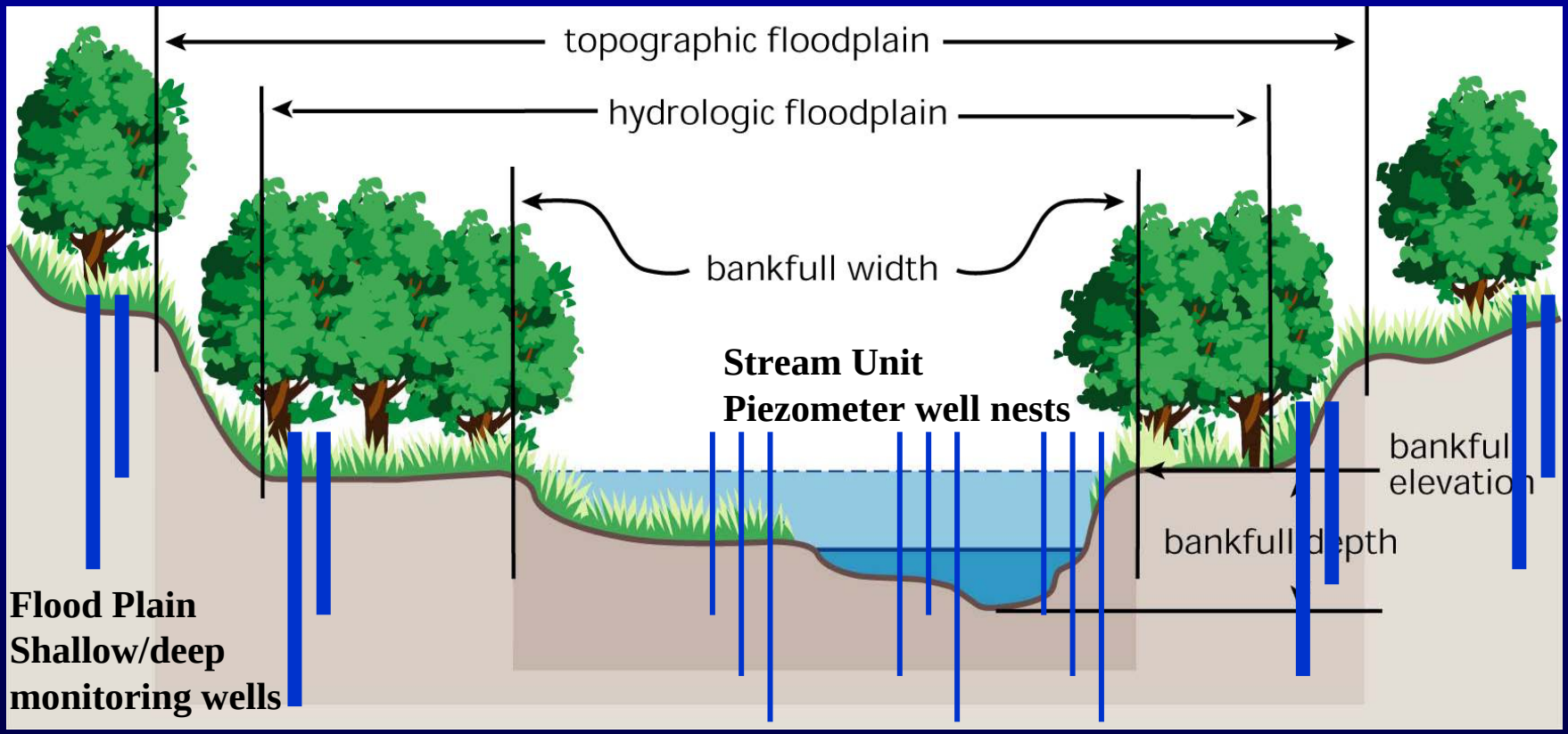


Sediment Transport Models



Link biological models ($\delta^{15}N$, $\delta^{13}C$ $\delta^{34}S$) to hydrological models ($\delta^{2}H$ and $\delta^{18}O$)

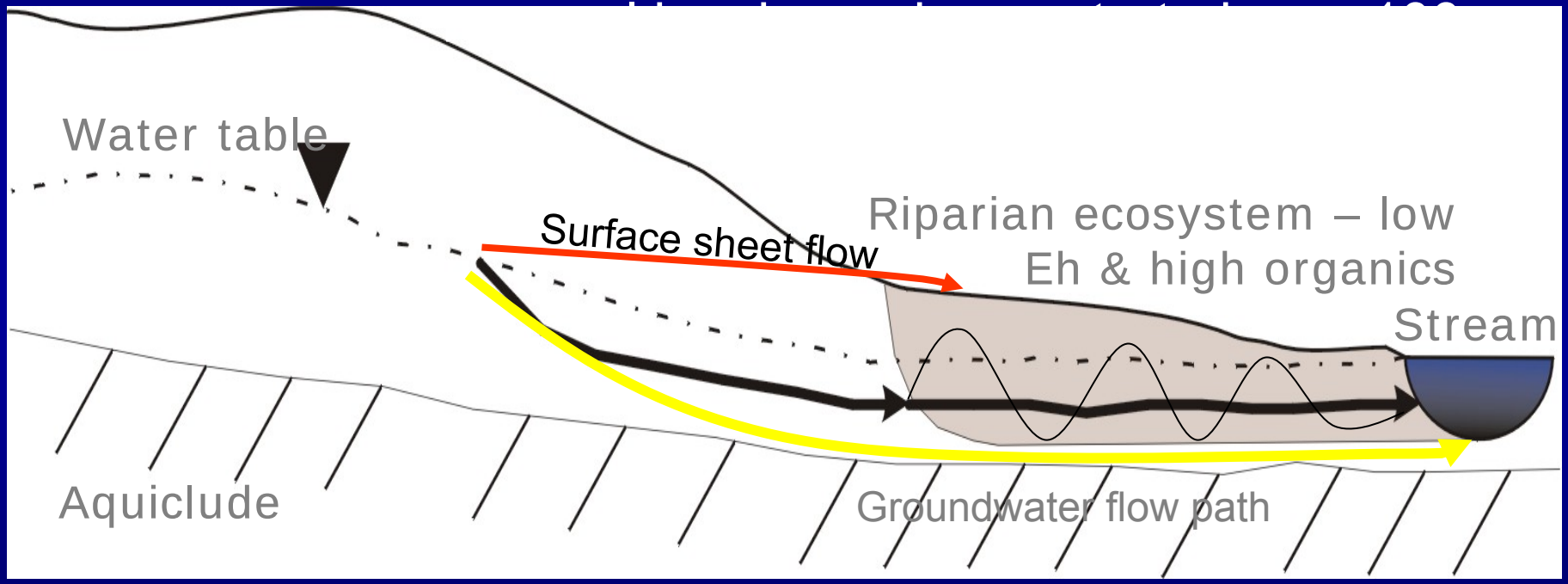
Hydrobiogeochemically active "edges" between streams, riparian and hyporheic zones



Source: Paul Mayer, EPA ESA 2005

Link biological models ($\delta^{15}N$, $\delta^{13}C$ $\delta^{34}S$) to hydrological models ($\delta^{2}H$ and $\delta^{18}O$)

- Ideal - Shallow groundwater moves through anaerobic organic rich denitrifying riparian zone. 32-98% NO_3



Aerobic surface flow lowers denitrification rates

Low carbon aquifers lower rates of denitrification

Source: Paul Mayer, EPA ESA 2005

Link biological models ($\delta^{15}N$, $\delta^{13}C$ $\delta^{34}S$) to hydrological models ($\delta^{2}H$ and $\delta^{18}O$)

QUESTIONS

fredrih@wes.army.mil
beste@wes.army.mil