Nitrogen cycling in the ocean

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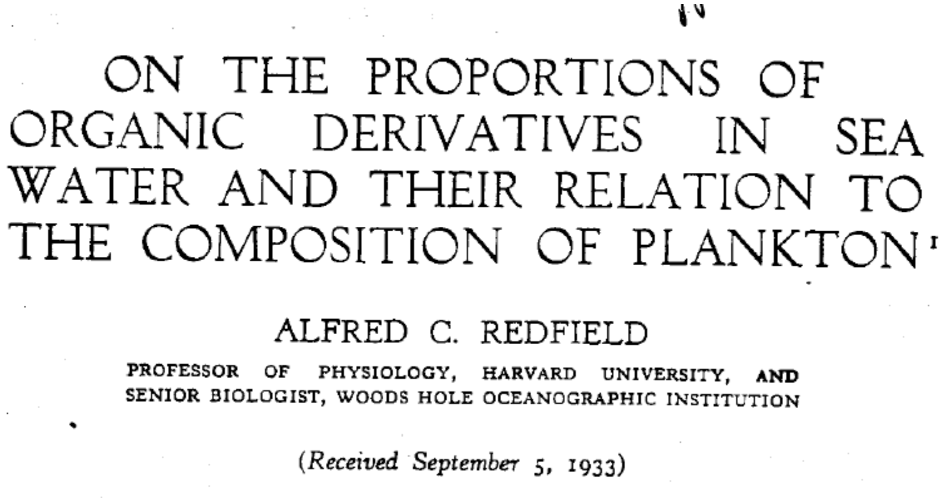
Outline:

1. The Redfield ratio
2. The nitrogen cycle
3. Liebig's Law of the Minimum
4. New & regenerated production
5. Is the N cycle in steady state?

Nitrogen Revolution
mid-1990s-present

- Nitrification
- Denitrification/anammox
- N_2 fixation
- Anthropogenic N inputs



ON THE PROPORTIONS OF ORGANIC DERIVATIVES IN SEA WATER AND THEIR RELATION TO THE COMPOSITION OF PLANKTON[1]

ALFRED C. REDFIELD

PROFESSOR OF PHYSIOLOGY, HARVARD UNIVERSITY, AND
SENIOR BIOLOGIST, WOODS HOLE OCEANOGRAPHIC INSTITUTION

(*Received September 5, 1933*)

Redfield 1934 James Johnstone Memorial Volume

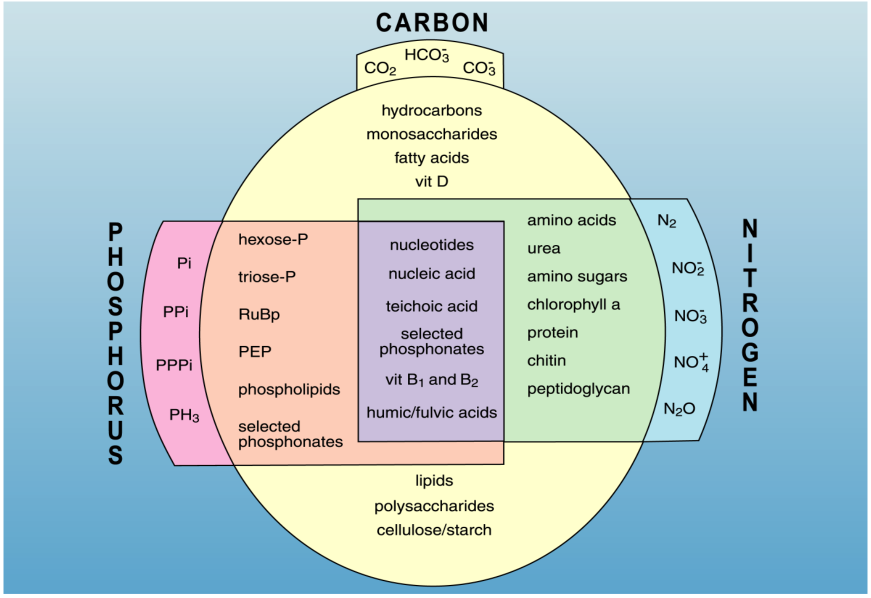
The Redfield Ratio

C:N:P = 106: 16: 1

$106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4$

$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$

detritus vs. phyto vs. bacteria?



CARBON

CO_2 HCO_3^- CO_3^-

hydrocarbons
monosaccharides
fatty acids
vit D

PHOSPHORUS

Pi
PPi
PPPi
PH_3

hexose-P
triose-P
RuBp
PEP
phospholipids
selected phosphonates

nucleotides
nucleic acid
teichoic acid
selected phosphonates
vit B_1 and B_2
humic/fulvic acids

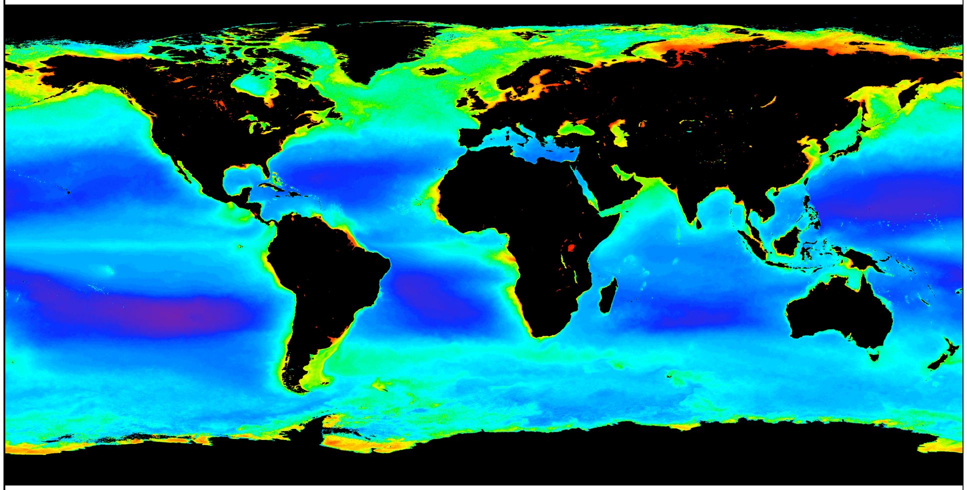
amino acids
urea
amino sugars
chlorophyll a
protein
chitin
peptidoglycan

N_2
NO_2^-
NO_3^-
NO_4^+
N_2O

NITROGEN

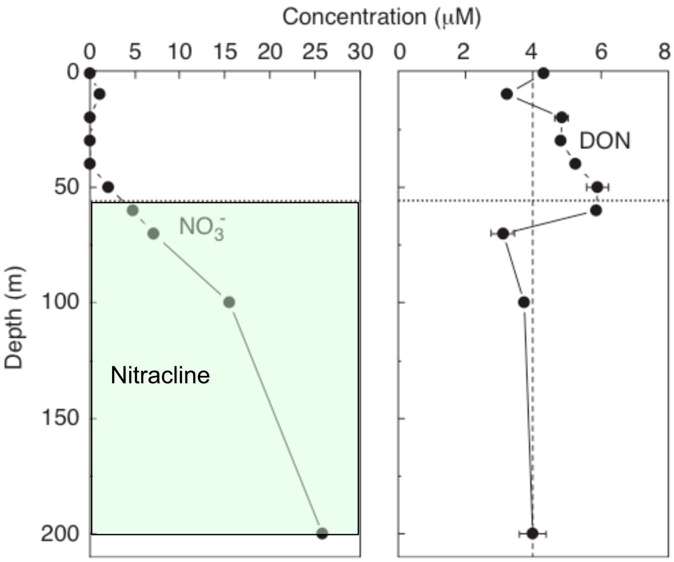
lipids
polysaccharides
cellulose/starch

Karl & Björkman 2002 DOM book



SEAWIFs chl a image

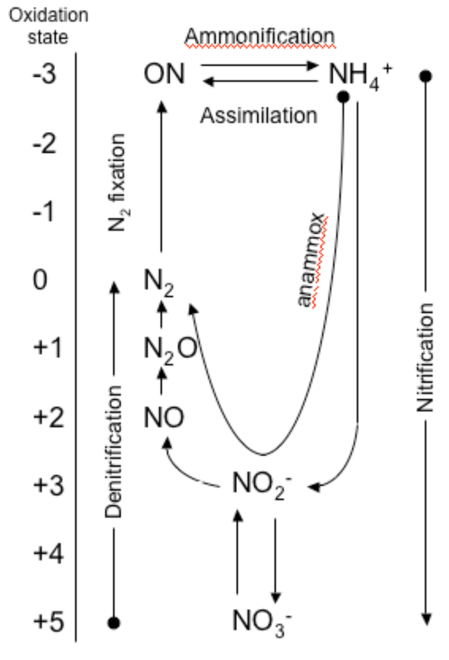
Southern California Bight



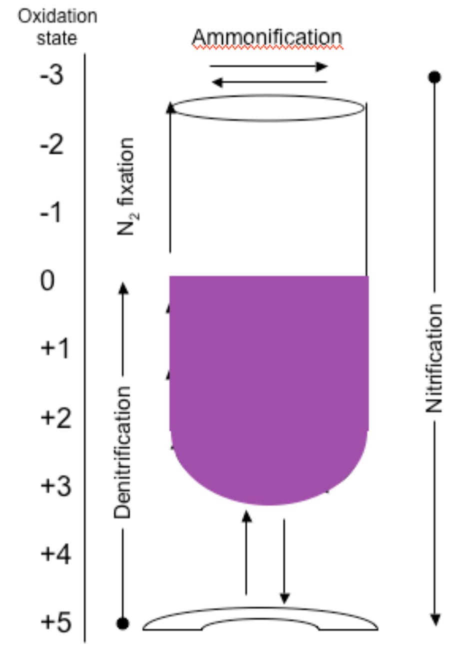
Bronk & Ward 2005 DSRI

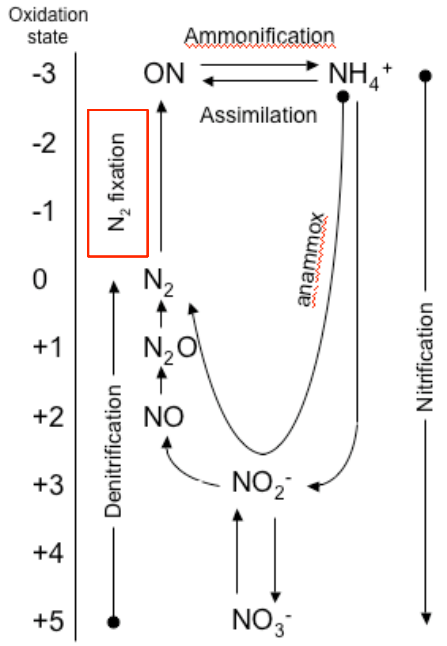
TDN - DIN = DON

$TDN - (NO_3^- + NO_2^- + NH_4^+)$



Love et al. In press





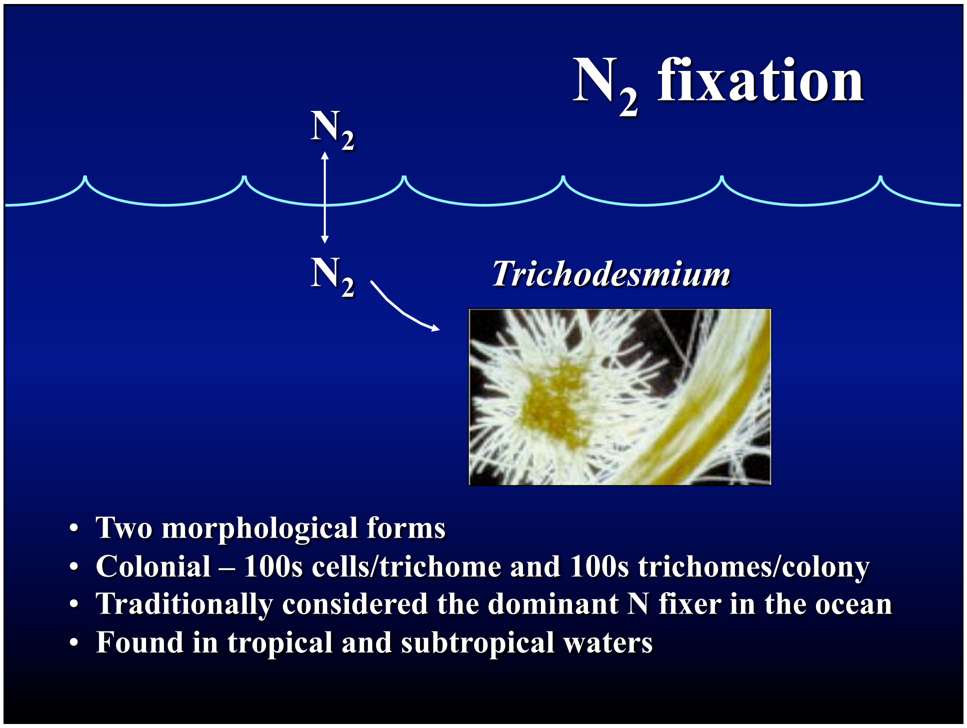
Love et al. In press

Nitrogen fixation

$$N_2 + 8H^+ + 8e- + 16\ ATP \rightarrow 2\ NH_3 + H_2 + 16\ ADP + 16P_i$$

Nitrogenase

- “Fixing” broken N_2
- Energetically very expensive – N_2 has triple bond
- Nitrogenase is irreversibly inactivated by oxygen
- Most N_2 fixers form heterocysts
- Requires P, Fe, and trace metals (Mo, Co, V)



N_2 fixation

- Two morphological forms
- Colonial – 100s cells/trichome and 100s trichomes/colony
- Traditionally considered the dominant N fixer in the ocean
- Found in tropical and subtropical waters

1987

Trichodemsium mystery

Non-heterocystous

Photosynthesis
$CO_2 \rightarrow O_2$

N_2 fixation
$N_2 \rightarrow NH_4^+$
nitrogenase

Temporal or spatial segregation?

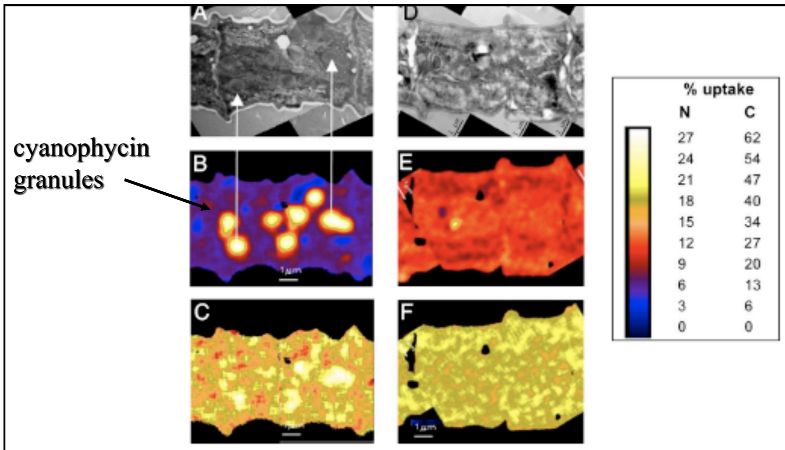


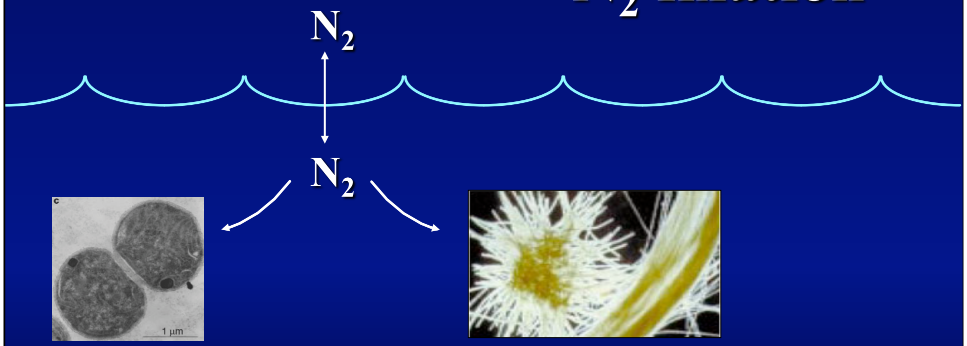
Fig. 3. TEM images of ~2 cells from a *Trichodesmium* filament after (*A*) 8-h and (*D*) 24-h incubation with $H^{13}CO_3$ and $^{15}N_2$. Correlated NanoSIMS images demonstrate percentage fixed ^{15}N after (*B*) 8 h and (*E*) 24 h, percentage fixed ^{13}C after (*C*) 8 h and (*F*) 24 h. Arrows indicate correlation between cyanophycin granules identified by TEM and ^{15}N enriched hotspots evident in NanoSIMS image. (Scale bar, 1 µm.) Because NanoSIMS analysis is a destructive process, distinct cells were imaged for the 2 different time points.

High resolution-secondary ion mass spectrometry (Nano SIMS)

Supports temporal segregation!

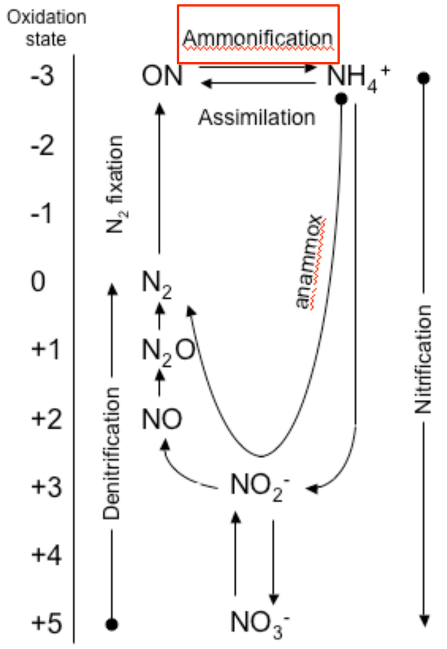
Finzi-Hart et al. 2009 PNAS

N_2 fixation



Zehr et al. 2001 Nature
Unicellular cyanobacteria that expressed nitrogenase at HOT

Montoya et al. 2004 Nature
Rates of N fixation by the single cell forms can equal or exceed rates by *Trichodemsium*



Love et al. In press

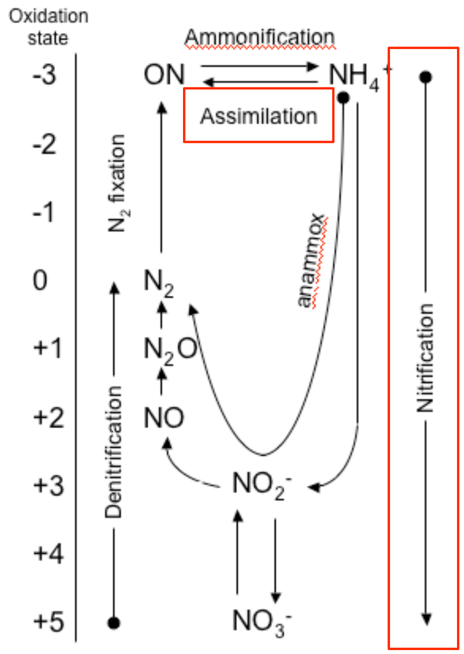
Ammonification -

the conversion of DON or PON to NH_4^+

Two types:

1. Bacterial -
   a. Traditional view of bacterial decomposition
   b. Was considered primary source of NH_4^+
   (Now primary source if believed to be grazers)

2. Photochemical (abiotic!)
   a. More recently recognized source
   b. Importance of process is still debated



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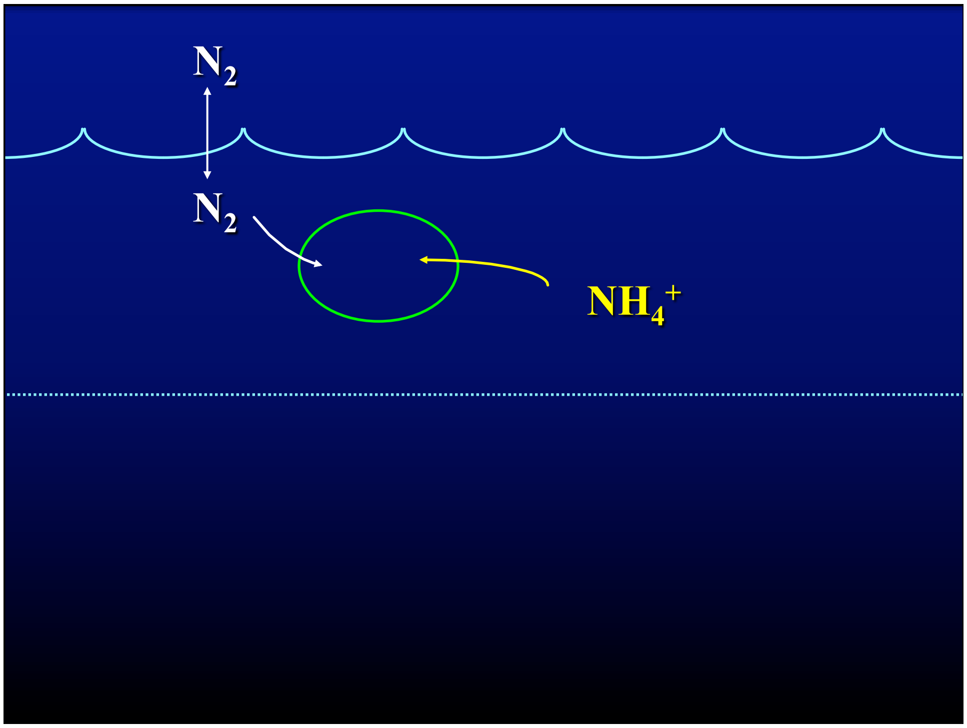
The Ocean

Euphotic zone	light - ~little N
Aphotic zone	no light - lots N



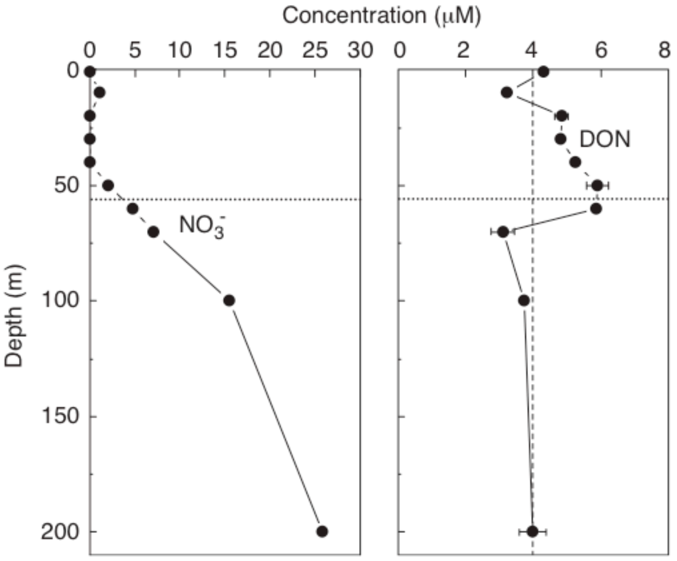
Nitrification

NH_4^+ -----------------> NO_2^- -----------------> NO_3

Ammonium oxidizers:	Nitrite oxidizers:
very slow growing	faster growing
sensitive to light	more sensitive to light

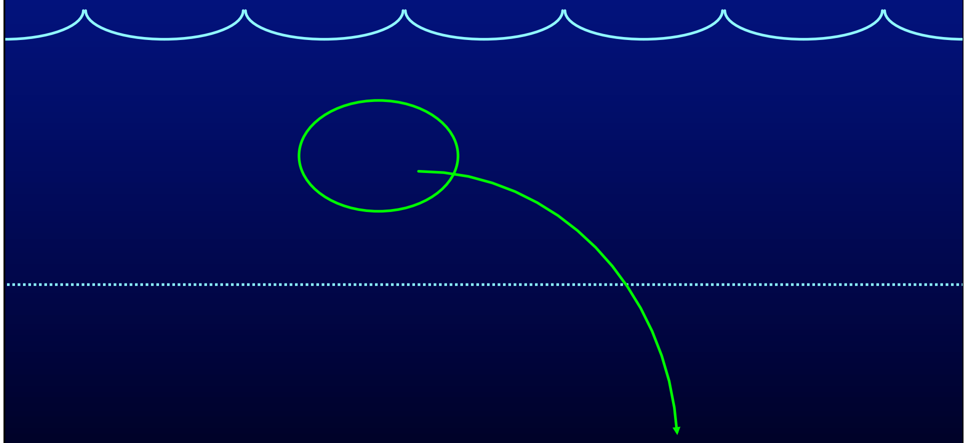
- Nitrifiers are chemolithoautotrophs.
- Maximum rates occur near the base of the euphotic zone.

Southern California Bight



Bronk & Ward 2005 DSRI

Nitrification



NO_3^- ← NO_2^- ← NH_4^+ ← PN or DON

Nitrifying bacteria - or is it??

Karner et al. 2001 Nature

39% of the picoplankton in the mesopelagic at HOT are archaea.

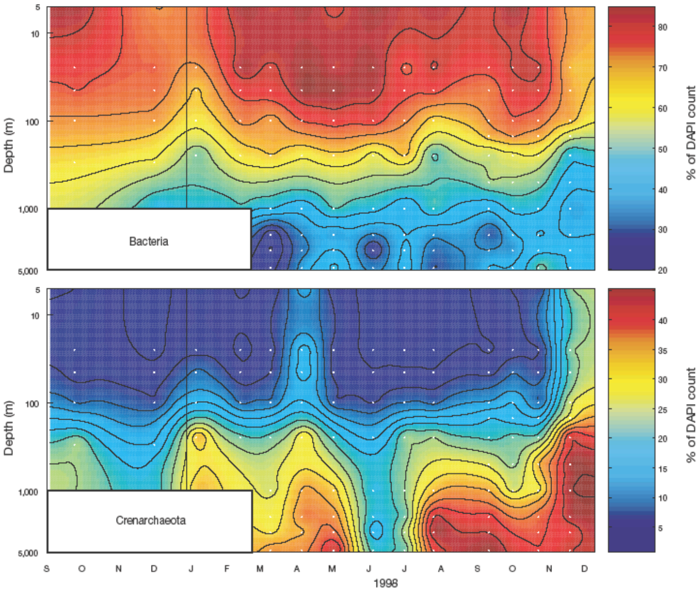


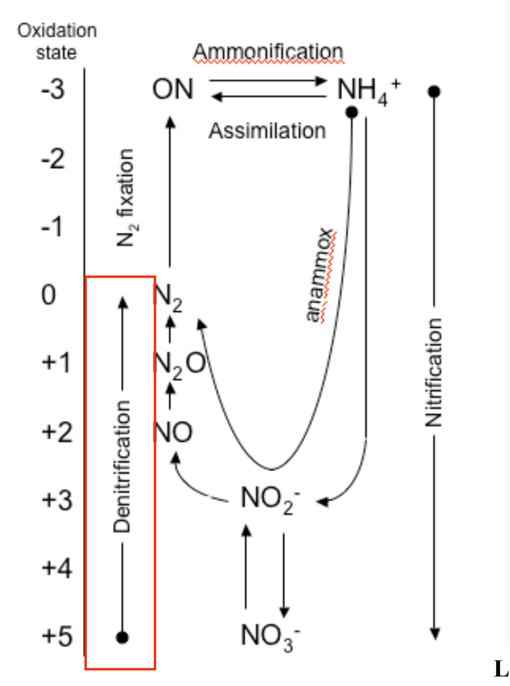
Figure 1 Contour plots of relative abundances with depth of bacteria and pelagic crenarchaeota during a 1-yr sampling effort at the Hawai'i Ocean Time-series station, ALOHA, in the North Pacific subtropical gyre. White dots indicate dates and depths where samples were collected. Contour lines are percentages of bacteria and pelagic crenarchaeota as compared with total microbial abundance at each depth. Total cell abundance was assessed using the DAPI nucleic acid stain. Bacteria and archaea were enumerated using whole-cell rRNA targeted fluorescent *in situ* hybridization with fluorescein-labelled polynucleotide probes. See also Supplementary Information.

Könneke et al. 2005 Nature

Isolated a marine crenarchaeota that can grow by aerobically oxidizing NH_4^+ to NO_2^-.

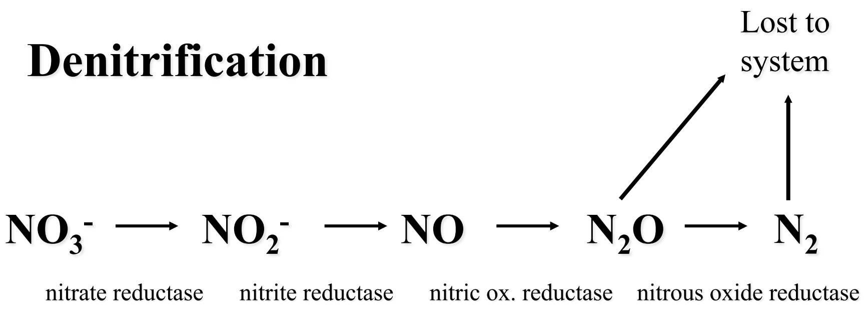
Ingalls et al. 2006 PNAS

An isotopic mass balance of radiocarbon signatures of archaeal membrane lipids indicates that 83% of their carbon is obtained autotrophically at depth.



Love et al. In press

Denitrification



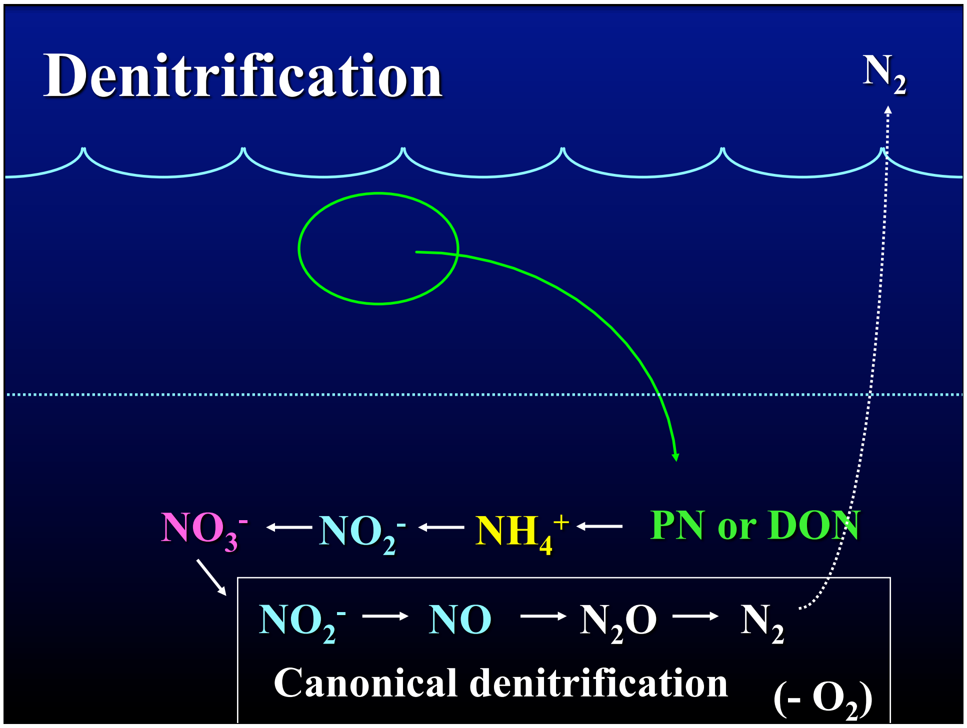
Lost to system

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

nitrate reductase nitrite reductase nitric ox. reductase nitrous oxide reductase

- N is used as an electron acceptor, not as a N source
- Lots of organisms can reduce NO_3^-
- Fewer can reduce NO_2^-
- All the enzymes are induced by anoxia
- NO is very labile and does not accumulate

Denitrification



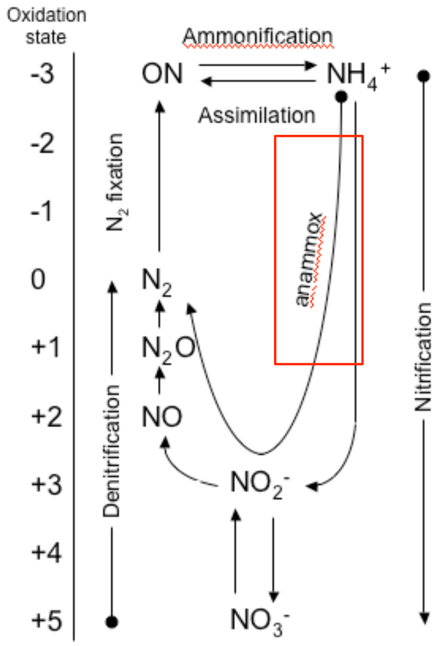
N_2

$NO_3^- \longleftarrow NO_2^- \longleftarrow NH_4^+ \longleftarrow$ PN or DON

$NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$

Canonical denitrification

$(- O_2)$



Love et al. In press

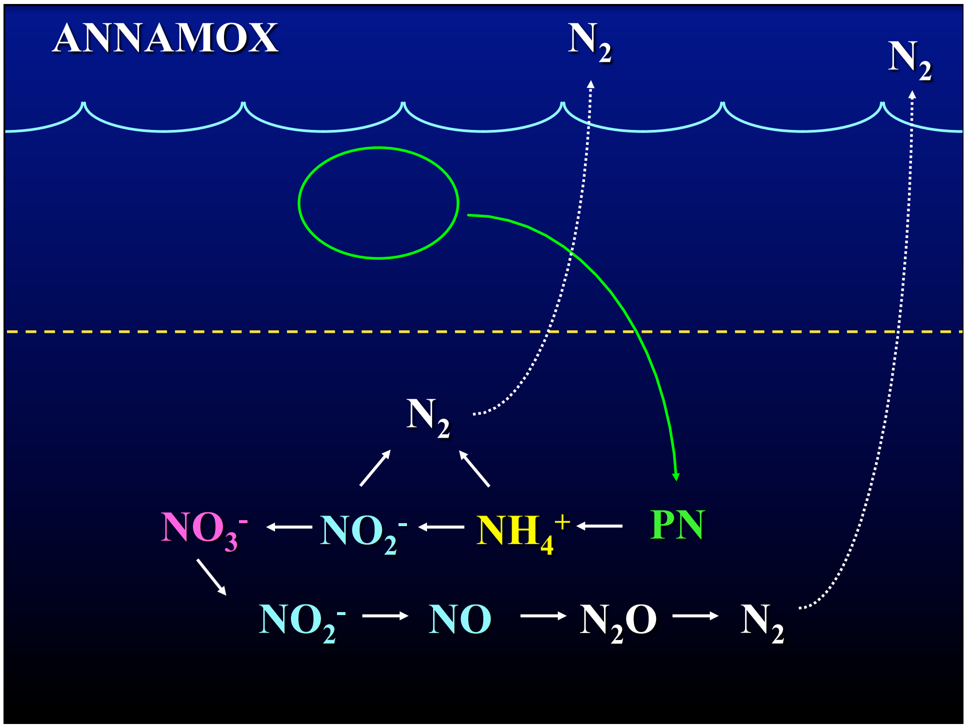
ANAMMOX

ANaerobic AMMonium OXidation

$$NO_2^- \quad + \quad NH_4^+ \longrightarrow N_2$$

- First described in a wastewater treatment plant in the Netherlands in 1995.
- Oxygen inhibition is reversible.
- Thandrup & Dalsgaard (2002) published the first marine data (sediment study)

ANNAMOX



N_2 N_2

N_2

$NO_3^- \leftarrow NO_2^- \leftarrow NH_4^+ \leftarrow$ PN

$NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$

Canonical denitrification? OR Anammox??

$$NO_2^- + NH_4^+ \longrightarrow N_2$$

obligate anaerobic autotrophs

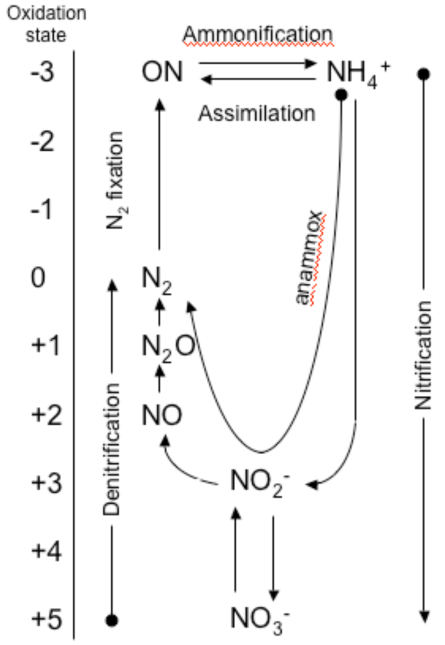
$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow \enclose{circle}{N_2O} \longrightarrow N_2$$

facultative anaerobic heterotrophs

Greenhouse Gases

The most abundant greenhouse gases
(in order of relative abundance)

- water vapor
- CO_2
- methane
- N_2O
- ozone
- CFCs

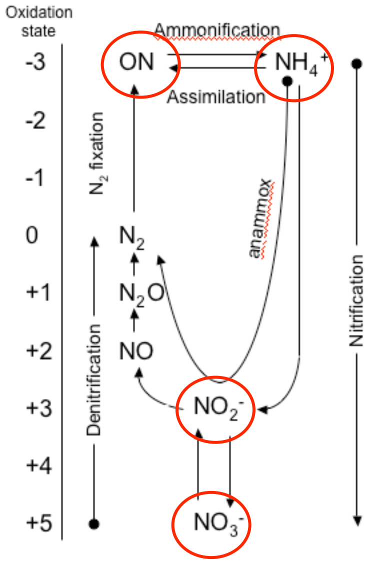


Love et al. In press

What's the best way to make a living in a given place?

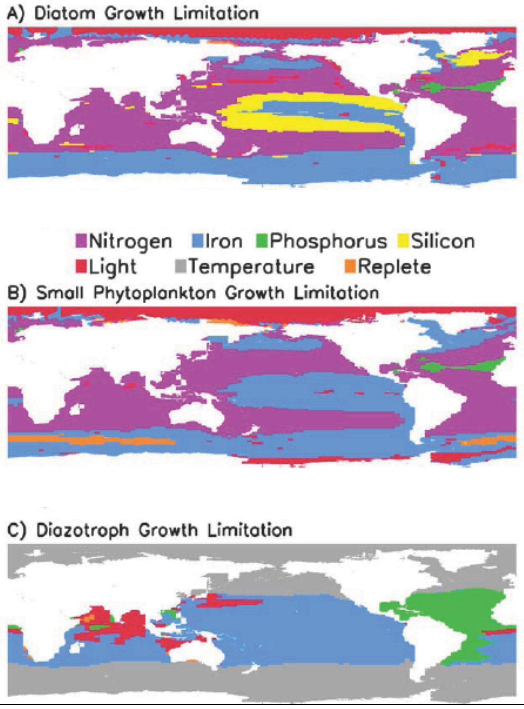
Reaction		Energy yield (kcal)	
Aerobic respiration		686	
Denitrification		545	($-O_2$)
Nitrification	NH_4^+ oxidation	66	
	NO_2^- oxidation	17	
N_2 fixation		-147	

Uptake and regeneration in the surface ocean



Liebig's Law of the Minimum (1840) - the resource in smallest supply relative to what the organism needs is the limiting factor.

Growth versus biomass



Factor limiting growth rates during summer

Moore et al. 2004 GBC

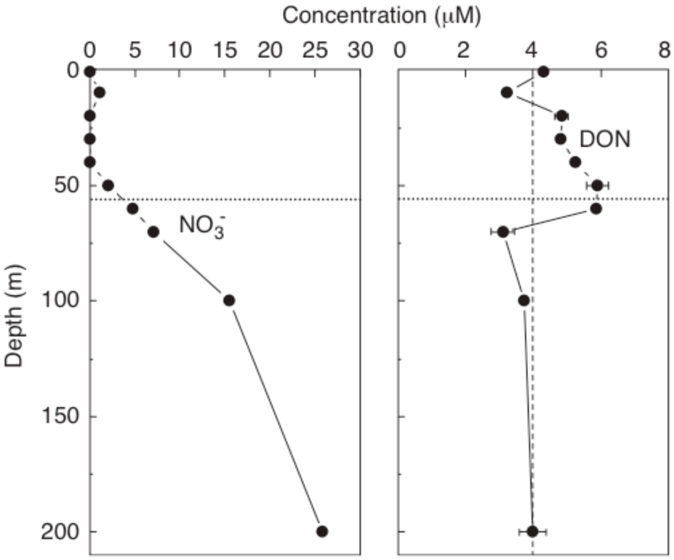
UPTAKE OF NEW AND REGENERATED FORMS OF NITROGEN IN PRIMARY PRODUCTIVITY[1]

R. C. Dugdale and J. J. Goering
Institute of Marine Science, University of Alaska, College 99735

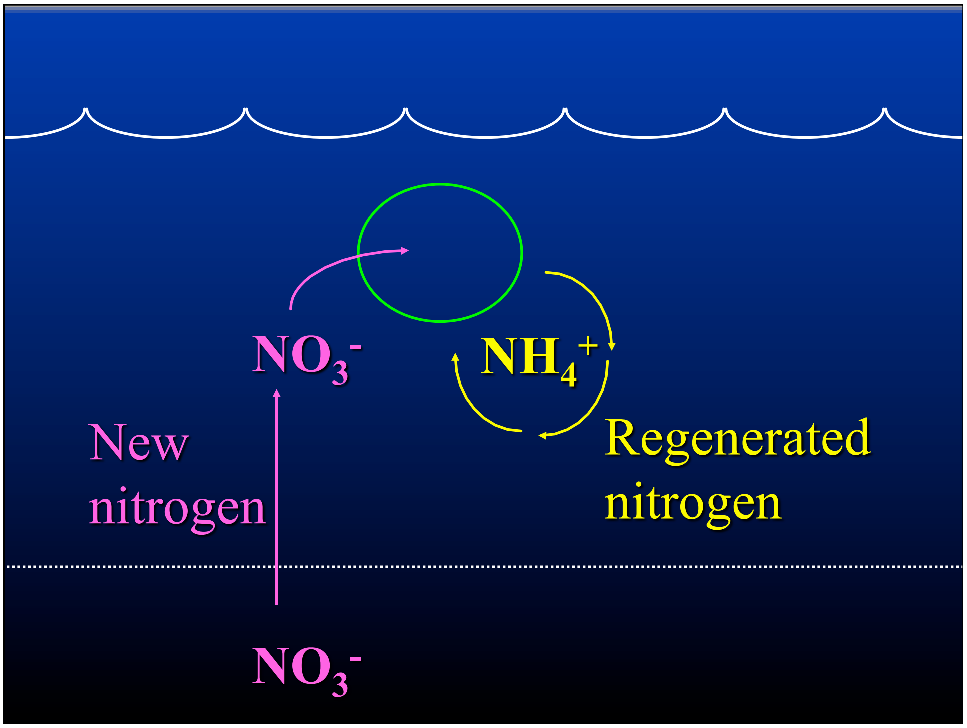
Production can be defined as new or regenerated based on the source of the nitrogen that fueled it.

Dugdale & Goering 1967 L&O

Southern California Bight



Bronk & Ward 2005 DSRI



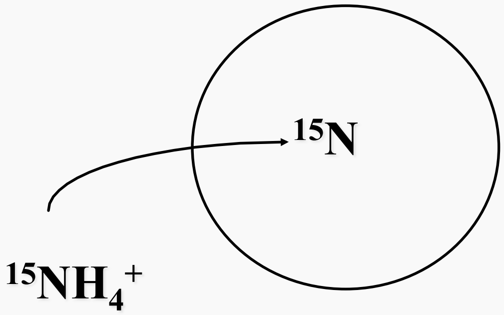
NO_3^-

NH_4^+

New
nitrogen

Regenerated
nitrogen

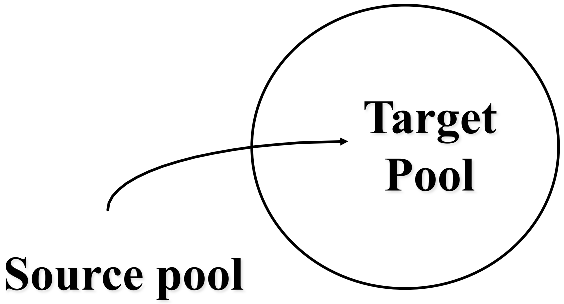
NO_3^-



^{15}N

$^{15}NH_4^+$

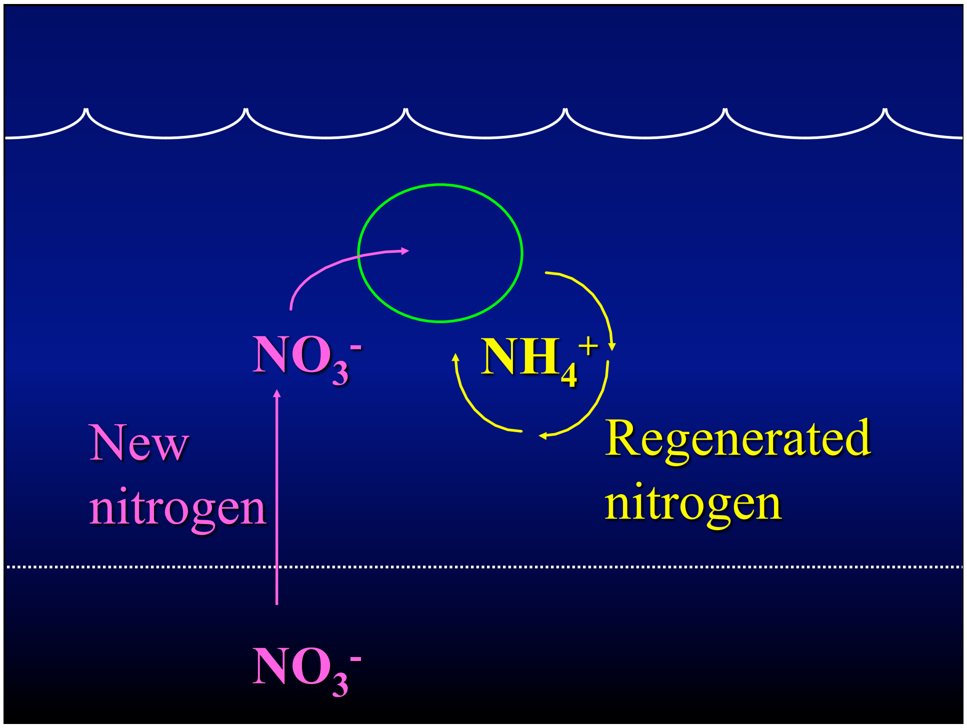
$$\text{Net Uptake Rate} = \frac{\text{atom\% PN}}{\text{atom \% } NH_4^+ \times \text{Time}} \times [\text{PN}]$$



Target Pool

Source pool

$$\text{Rate} = \frac{\text{atom \% of target}}{\text{atom \% of source} \times \text{Time}} \times [\text{target}]$$



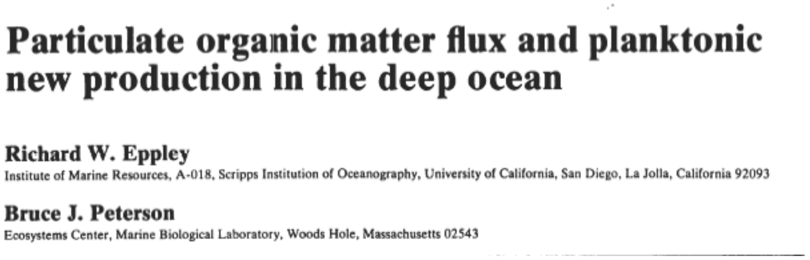
NO_3^-

NH_4^+

New nitrogen

Regenerated nitrogen

NO_3^-



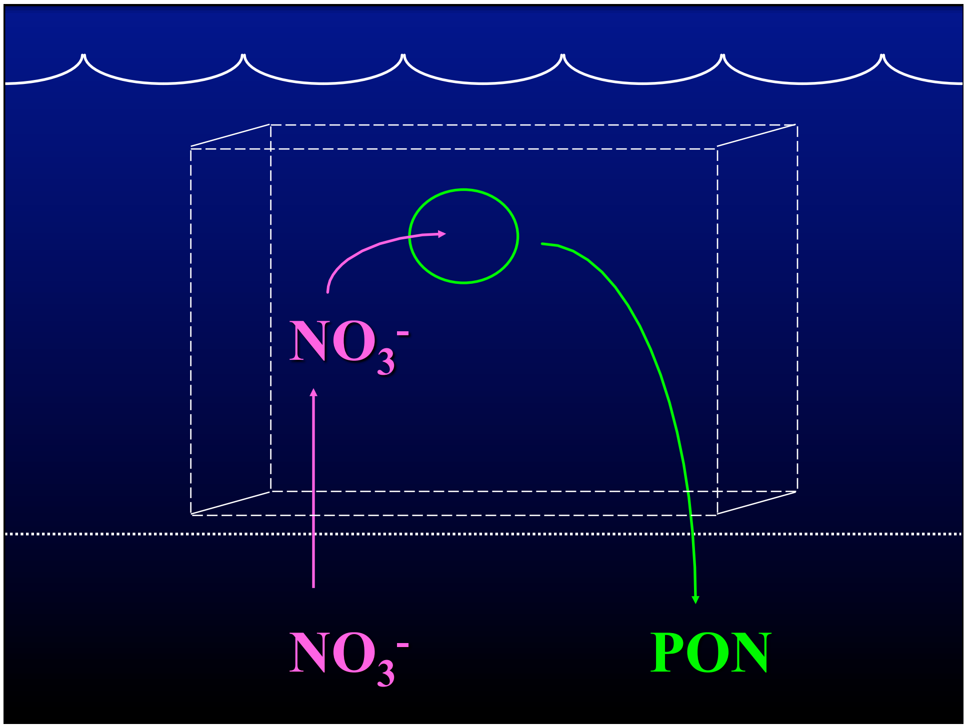
Particulate organic matter flux and planktonic new production in the deep ocean

Richard W. Eppley
Institute of Marine Resources, A-018, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093

Bruce J. Peterson
Ecosystems Center, Marine Biological Laboratory, Woods Hole, Massachusetts 02543

New production over appropriate spatial and temporal scales equals export flux.

Eppley & Peterson 1979 Nature



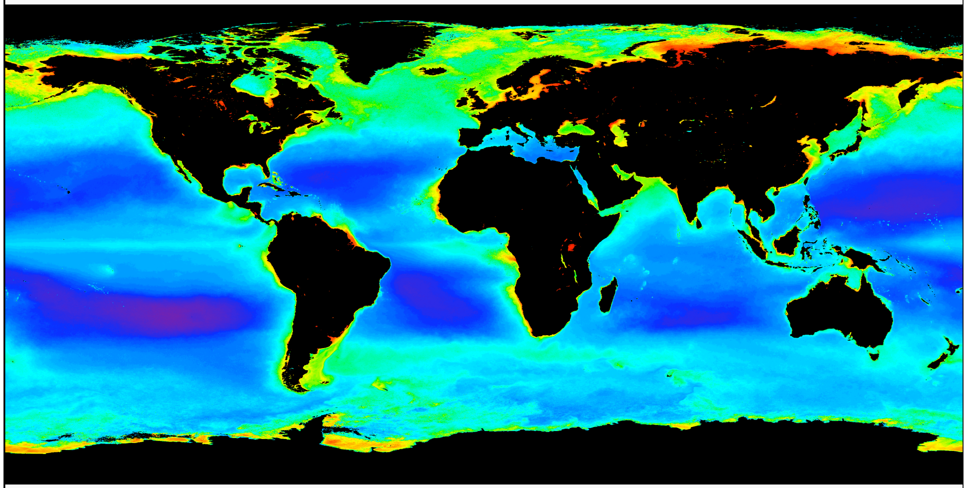
NO_3^-

NO_3^-

PON

$$\text{f-ratio} = \frac{\text{New production}}{\text{New + Regenerated Production}}$$

$$\text{f-ratio} = \frac{NO_3^- \text{ uptake}}{NH_4^+ + NO_3^- \text{ uptake}}$$



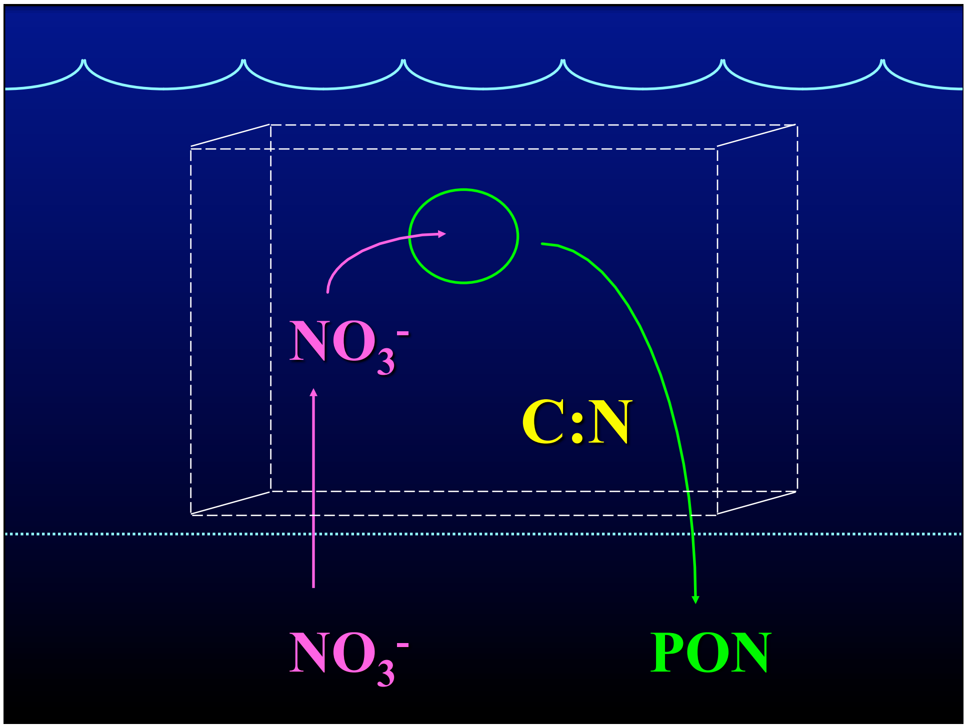
SEAWIFs chl a image

The Redfield Ratio

C:N:P = 106: 16: 1

$$106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4 \longrightarrow$$

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$$

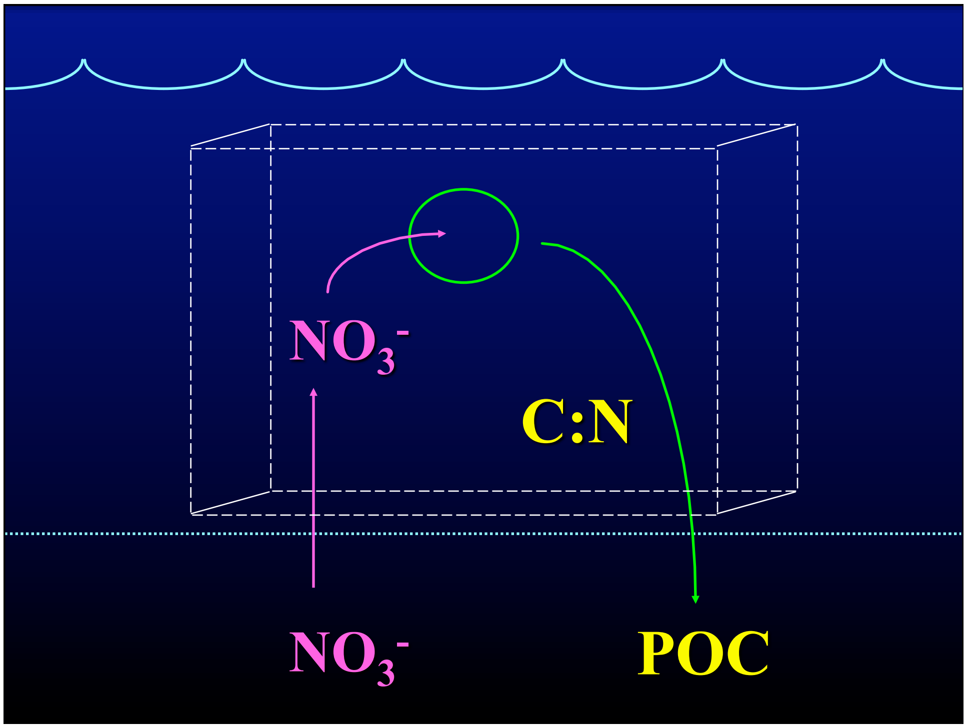


NO_3^-

C:N

NO_3^-

PON

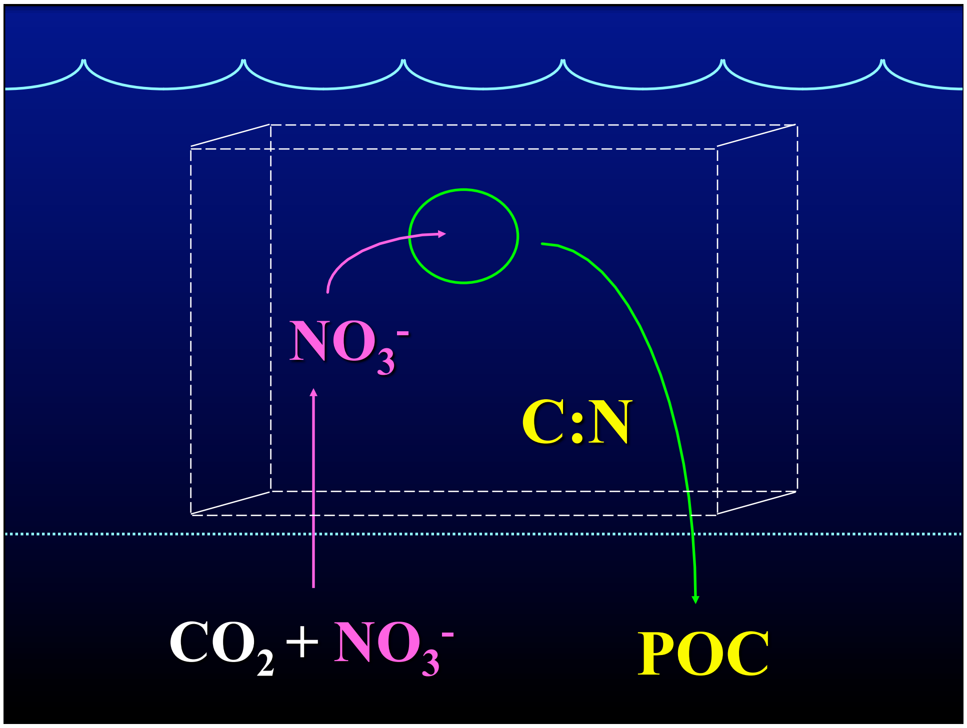


NO_3^-

C:N

NO_3^-

POC



Is the amount of N in the ocean in steady state?

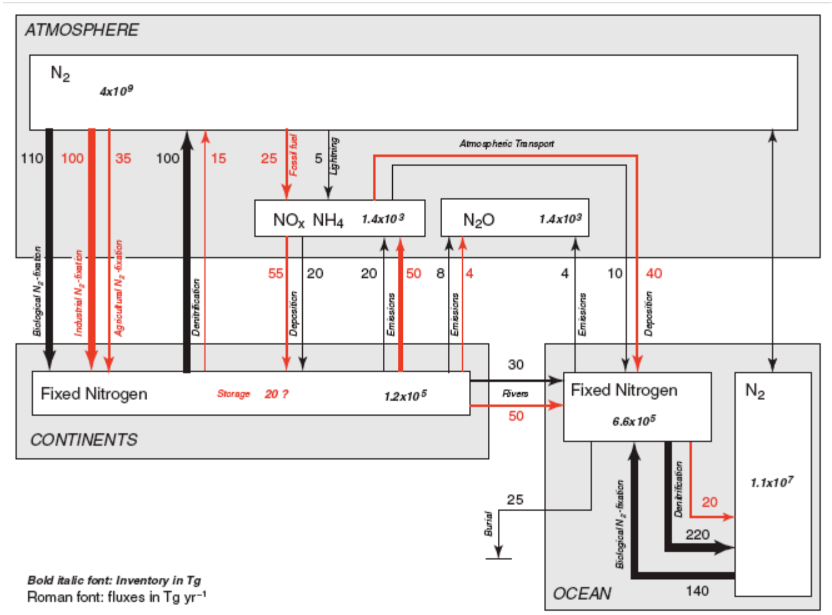
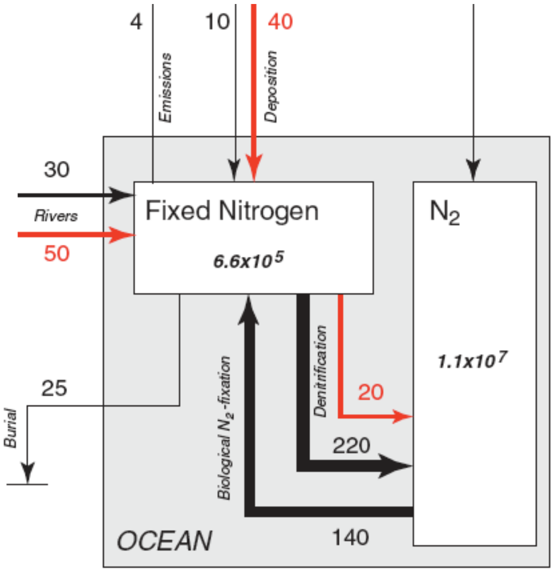


Figure 1.15 Schematic budget of the global nitrogen cycle in preindustrial times (black) and how it changed as a result of human intervention (red). Fluxes are in units of Tg N year^{-1} and inventories (bold italics) in Tg N. The flux estimates are based on Gruber and Galloway (2008).



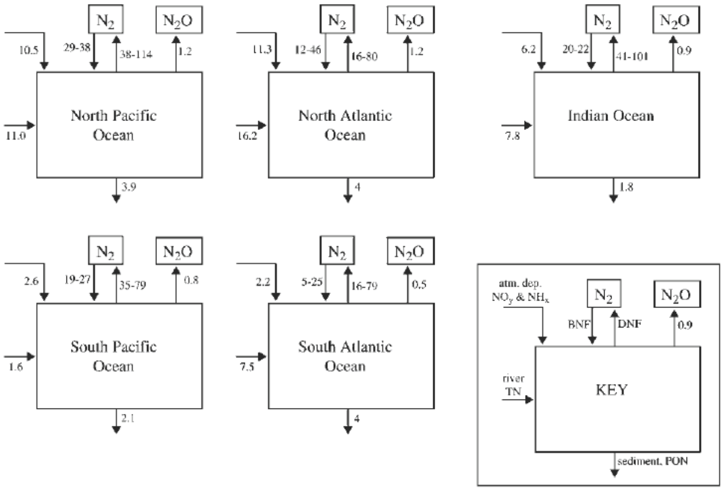


Figure 4. Nr creation and distribution by ocean basin, Tg N yr^{-1}, in the early 1990s.

Galloway et al. 2004 Biogeochemistry

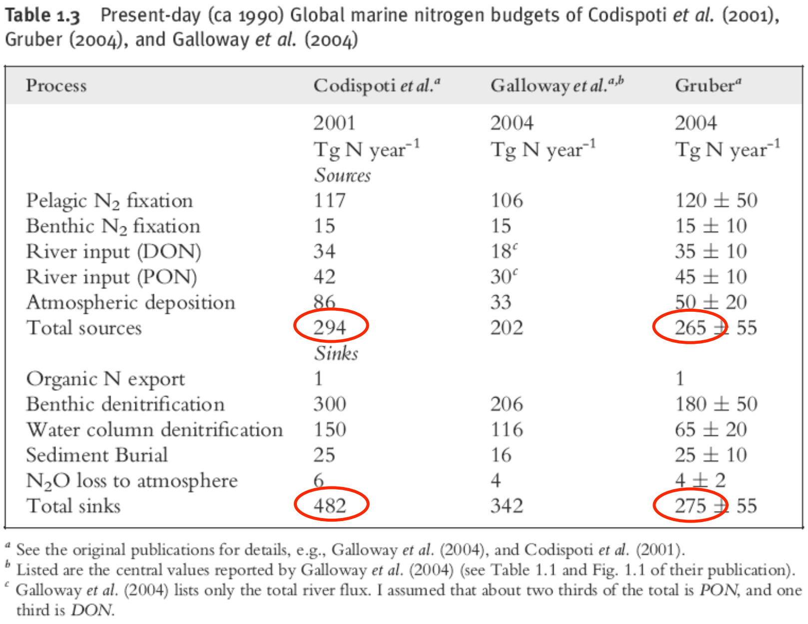


Table 1.3 Present-day (ca 1990) Global marine nitrogen budgets of Codispoti *et al.* (2001), Gruber (2004), and Galloway *et al.* (2004)

Process	Codispoti *et al.*[a]	Galloway *et al.*[a,b]	Gruber[a]
	2001 Tg N year^{-1}	2004 Tg N year^{-1}	2004 Tg N year^{-1}
	Sources		
Pelagic N_2 fixation	117	106	120 ± 50
Benthic N_2 fixation	15	15	15 ± 10
River input (DON)	34	18[c]	35 ± 10
River input (PON)	42	30[c]	45 ± 10
Atmospheric deposition	86	33	50 ± 20
Total sources	294	202	265 ± 55
	Sinks		
Organic N export	1		1
Benthic denitrification	300	206	180 ± 50
Water column denitrification	150	116	65 ± 20
Sediment Burial	25	16	25 ± 10
N_2O loss to atmosphere	6	4	4 ± 2
Total sinks	482	342	275 ± 55

[a] See the original publications for details, e.g., Galloway *et al.* (2004), and Codispoti *et al.* (2001).

[b] Listed are the central values reported by Galloway *et al.* (2004) (see Table 1.1 and Fig. 1.1 of their publication).

[c] Galloway *et al.* (2004) lists only the total river flux. I assumed that about two thirds of the total is *PON*, and one third is *DON*.

Gruber 2008 N in the Marine Env.

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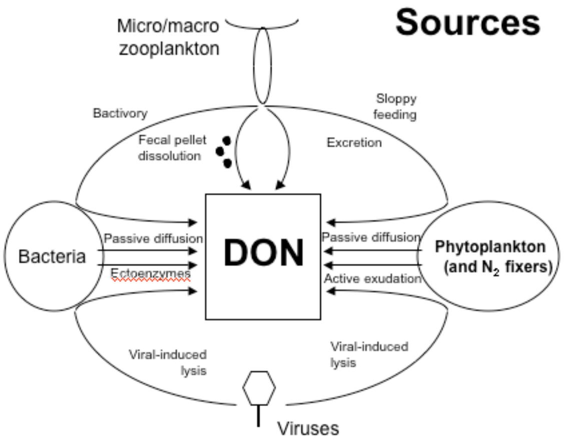
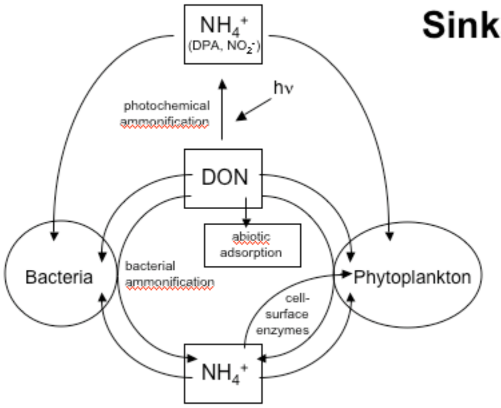
5. Is the N cycle in steady state?

Tomorrow……



Sinks



NH_4^+
(DPA, NO_2^-)

photochemical ammonification

hν

DON

abiotic adsorption

Bacteria

bacterial ammonification

Phytoplankton

cell-surface enzymes

NH_4^+