Nitrogen and phosphorus cycling in the ocean

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Outline:

1. The Redfield ratio
2. Liebig's Law of the Minimum
3. The nitrogen cycle
4. The phosphorus cycle
5. New & regenerated production

The Redfield Ratio

C:N:P = 106: 16: 1

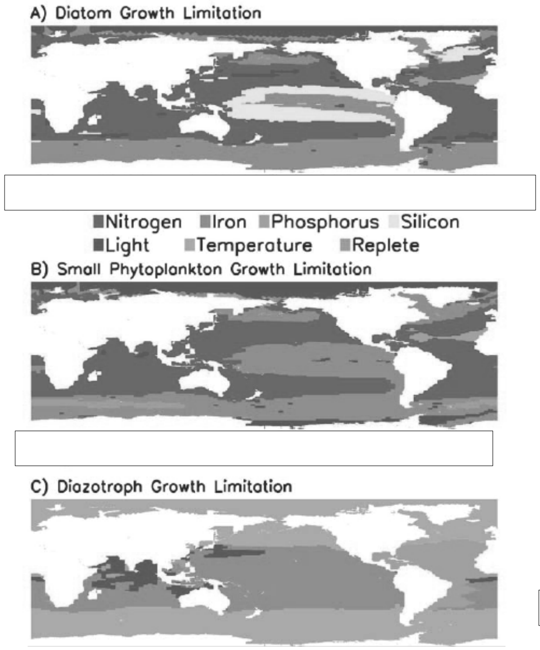
$$106CO_2 + 122H_2O + 16HNO_3 + H_3PO_4 \longrightarrow (CH_2O)_{106}(NH_3)_{16}(H_3PO_4)$$

detritus vs. phyto vs. bacteria?

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

co-limitation - biochemical or community
Ex. biochemical - P & Zn limitation
Ex. community - Si and diatoms

Arrigo 2005 Nature

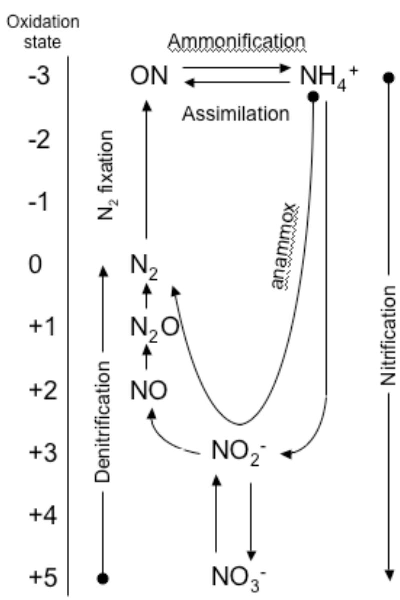


Factor limiting growth rates during summer

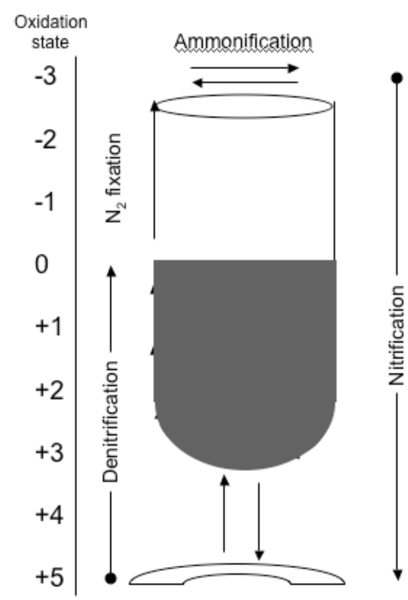
Moore et al. 2004 GBC

Nitrogen Revolution mid-1990s-present

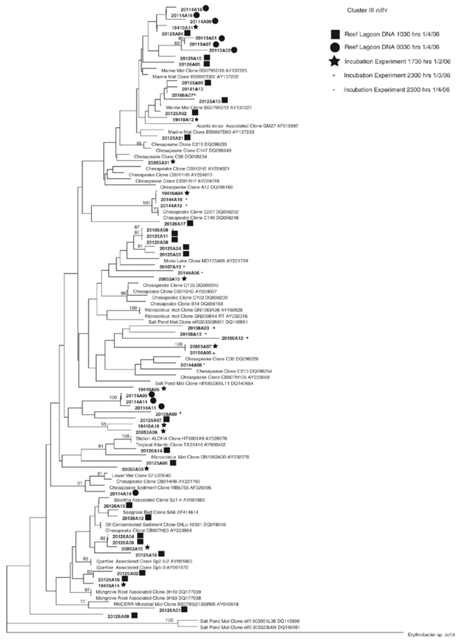
- Nitrification
- Denitrification/anammox
- N_2 fixation
- Anthropogenic N inputs



Love et al. In press



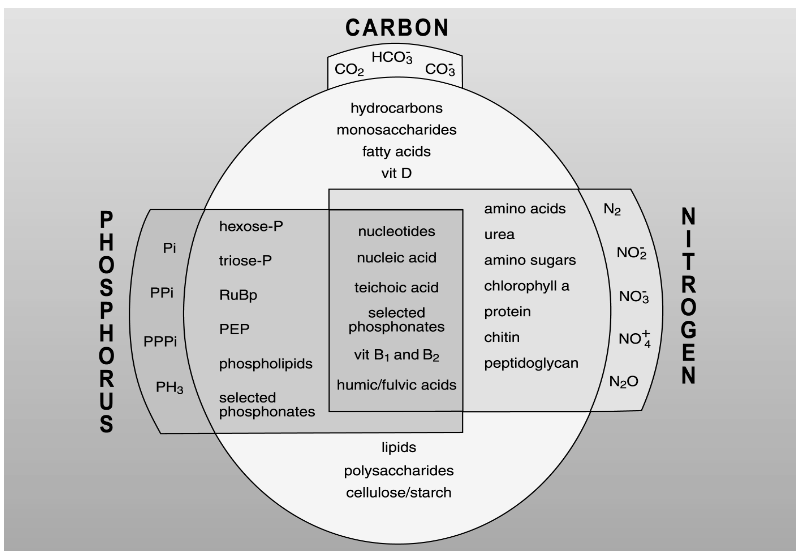
A plea and a warning!



Hewson et al. 2007 ISME

Types of nitrogen

Inorganic	**Organic**
nitrogen gas (N_2)	urea
ammonium (NH_4^+)	amino acids
nitrate (NO_3^-)	proteins
nitrite (NO_2^-)	humic substances
	more later….

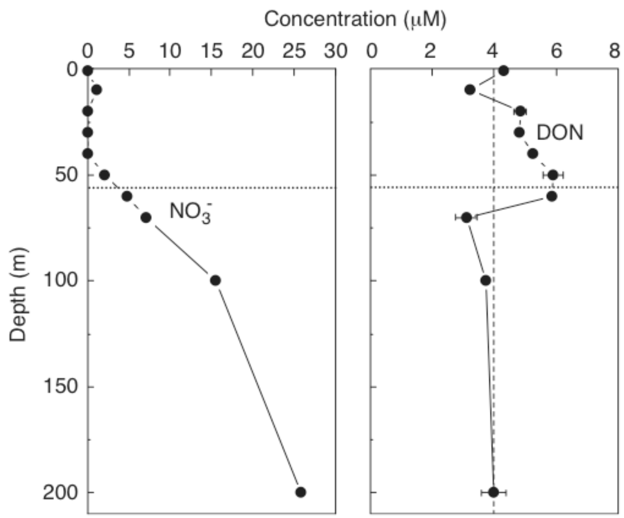


Karl & Björkman 2002 DOM book

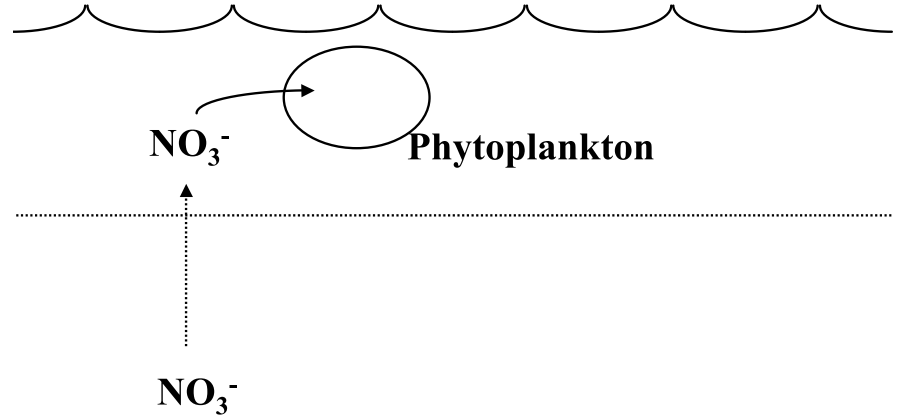
TDN - DIN = DON

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

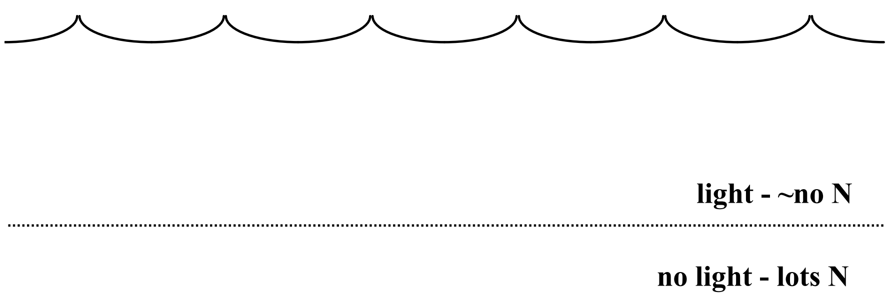
Southern California Bight

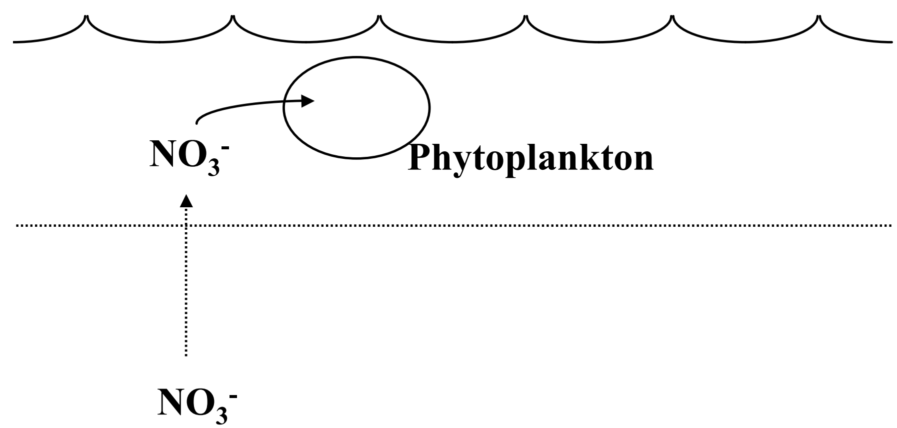


Bronk & Ward 2005 DSRI



The Ocean



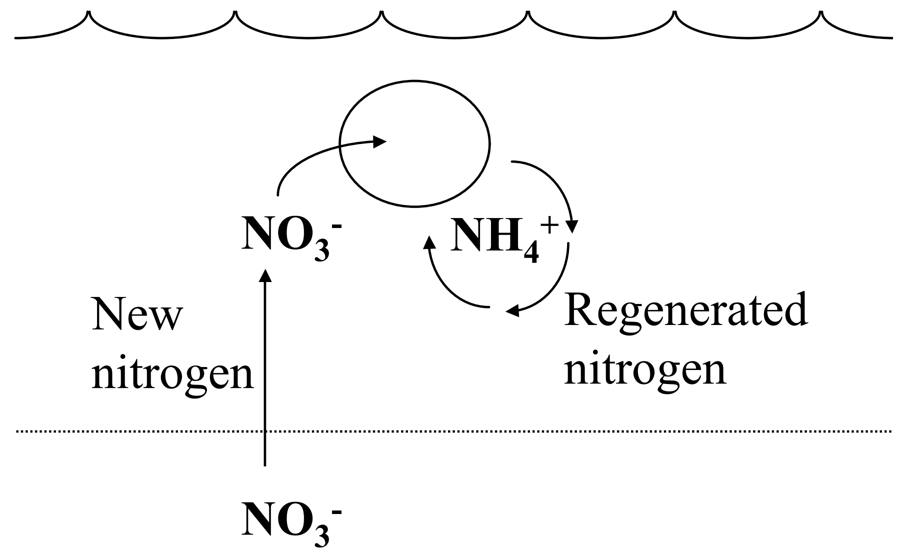


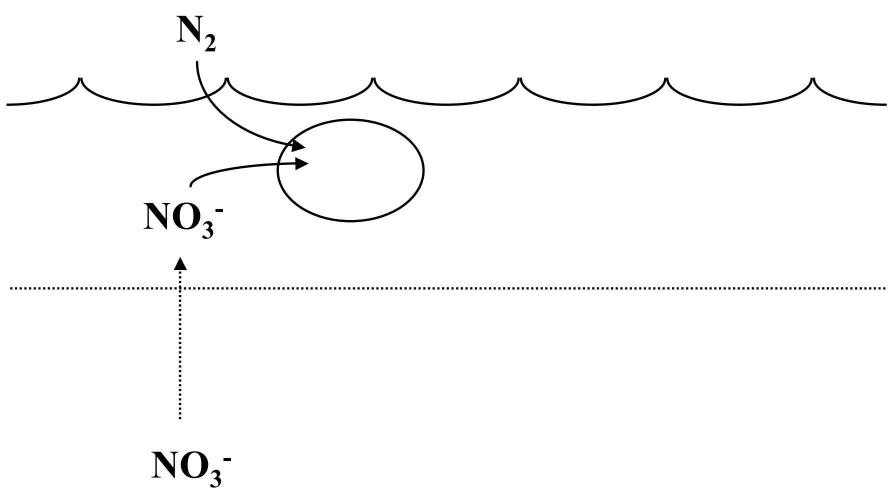
UPTAKE OF NEW AND REGENERATED FORMS OF NITROGEN IN PRIMARY PRODUCTIVITY[1]

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





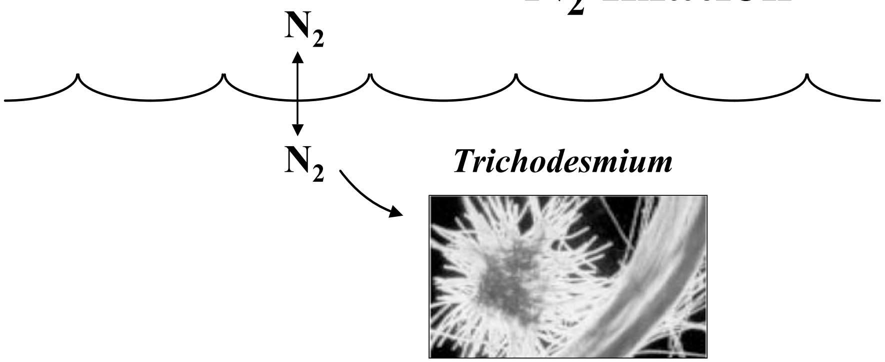
Nitrogen fixation

$$N_2 + 8H^+ + 8e^- + 16\ MgATP \rightarrow 2\ NH_3 + H_2 + 16\ MgADP + 16P_i$$

Nitrogenase

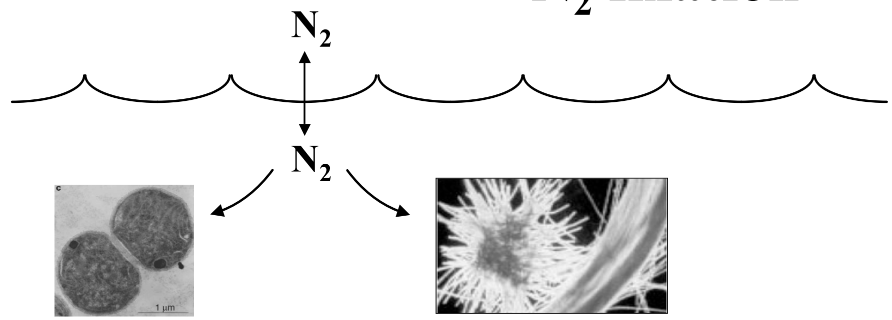
- **"Fixing" broken N_2**
- **Energetically very expensive**
- **Nitrogenase is irreversibly inactivated by oxygen**
- **Most N_2 fixers form heterocysts**

N_2 fixation



- Colonial, non-heterocystous diazotroph
- Two morphological forms
- Found in tropical and subtropical waters
- Traditionally considered the dominant N fixer in the ocean

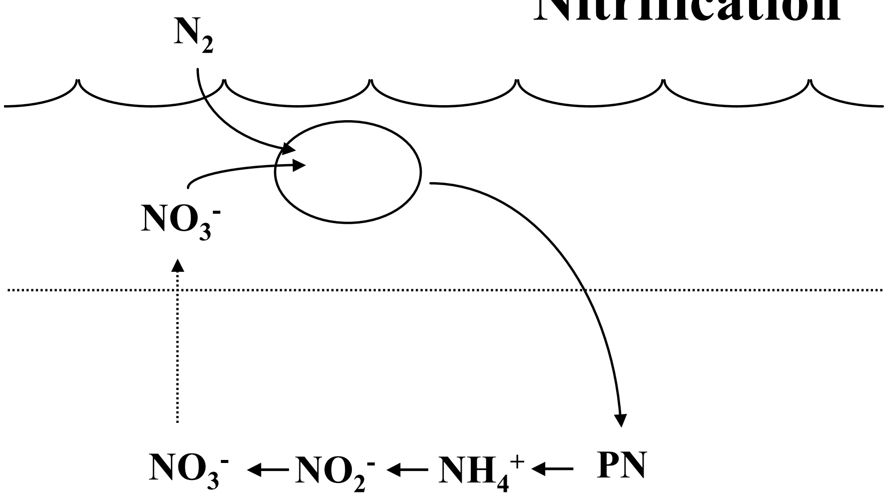
N_2 fixation



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*

Nitrification



Nitrifying bacteria - or is it??

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.

Karner et al. 2001 Nature

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

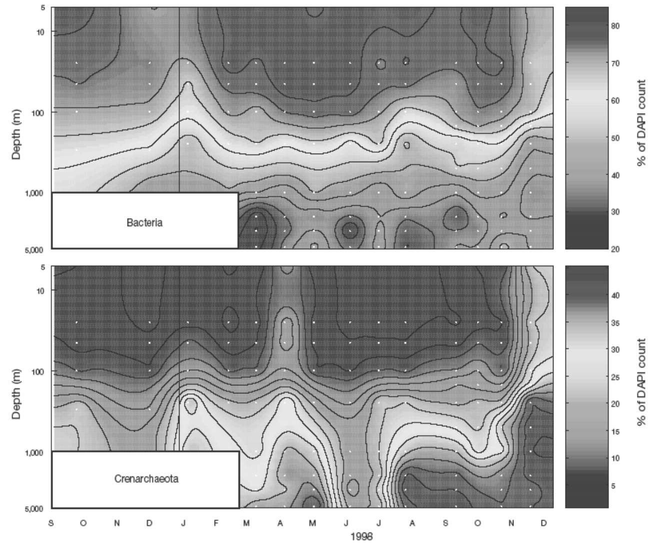


Figure 1 Contour plots of relative abundances with depth of bacteria and pelagic crenarchaeota during a 1-yr sampling effort at the Hawai'i Ocean Time-series station, ALOHA, in the North Pacific subtropical gyre. White dots indicate dates and depths where samples were collected. Contour lines are percentages 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

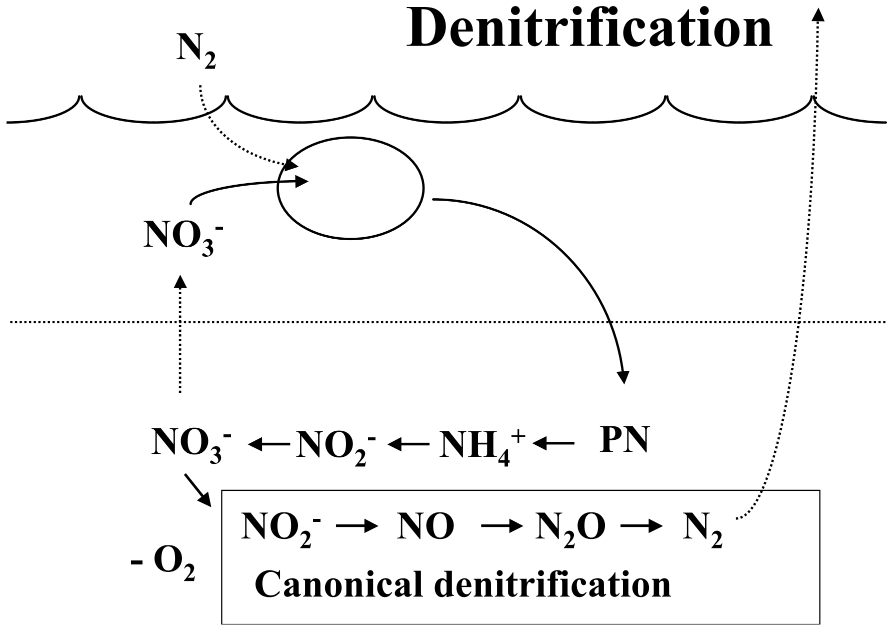
Isolated a marine crenarchaeota that can grow by aerobically oxidizing NH_4^+ to NO_2^-.

?

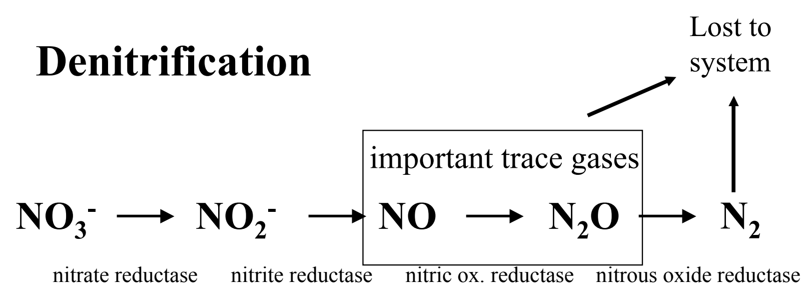
Ingalls et al. 2006 PNAS

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

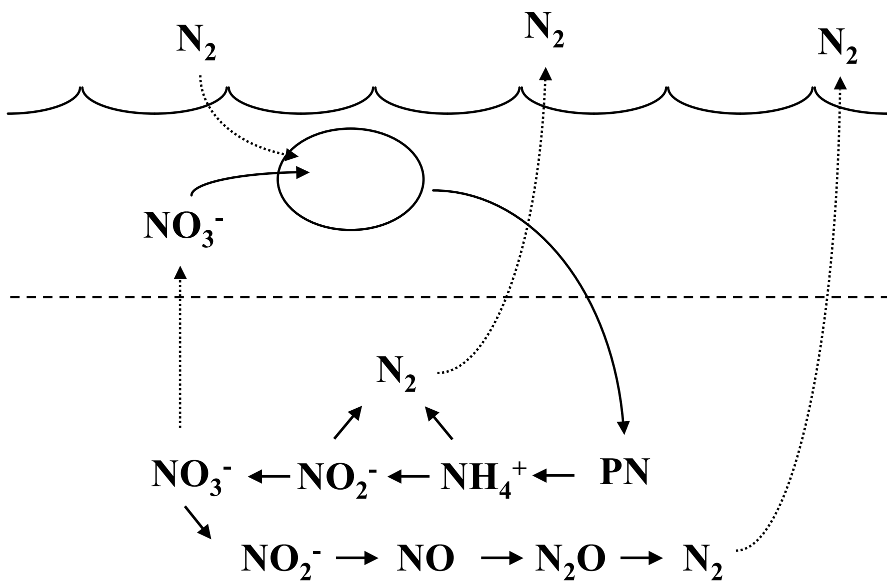
Denitrification



Denitrification



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



ANAMMOX

ANaerobic AMMonium OXidation

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

- First described in a wastewater treatment plant in the Netherlands in 1995.
- Oxygen inhibition is reversible.

Canonical denitrification? OR Anammox??

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

obligate anaerobic autotrophs

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

facultative anaerobic heterotrophs

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	

REACTION	ENERGY YIELD (KILOCALORIES)
DENITRIFICATION	
1 $C_6H_{12}O_6 + 6KNO_3 \longrightarrow 6CO_2 + 3H_2O + 6KOH + 3N_2O$ (GLUCOSE, POTASSIUM NITRATE, POTASSIUM HYDROXIDE, NITROUS OXIDE)	545
2 $5C_6H_{12}O_6 + 24KNO_3 \longrightarrow 30CO_2 + 18H_20 + 24KOH + 12N_2$ (NITROGEN)	570 (PER MOLE OF GLUCOSE)
3 $5S + 6KNO_3 + 2CaCO_3 \longrightarrow 3K_2SO_4 + 2CaSO_4 + 2CO_2 + 3N_2$ (SULFUR, POTASSIUM SULFATE, CALCIUM SULFATE)	132 (PER MOLE OF SULFUR)
RESPIRATION	
4 $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$ (CARBON DIOXIDE, WATER)	686
AMMONIFICATION	
5 $CH_2NH_2COOH + 1\frac{1}{2}O_2 \longrightarrow 2CO_2 + H_2O + NH_3$ (GLYCINE, OXYGEN, AMMONIA)	176
NITRIFICATION	
6 $NH_3 + 1\frac{1}{2}O_2 \longrightarrow HNO_2 + H_2O$ (NITROUS ACID)	66
7 $KNO_2 + \frac{1}{2}O_2 \longrightarrow KNO_3$ (POTASSIUM NITRITE)	17.5
NITROGEN FIXATION	
8 $N_2 \longrightarrow 2N$ "ACTIVATION" OF NITROGEN	−160
9 $2N + 3H_2 \longrightarrow 2NH_3$	12.8

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 In press N in the Marine Env.

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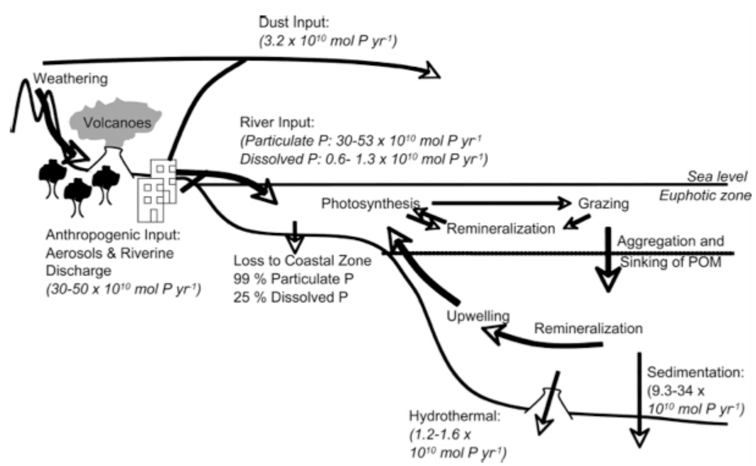
Big Picture Phosphorus Cycle



Paytan & McLaughlin 2007 Chem. Reviews

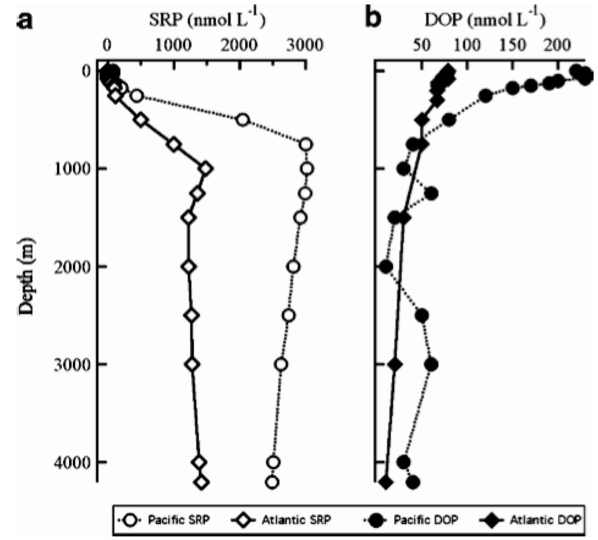
Phosphorus

Dissolved inorganic phosphorus (DIP)
Orthophosphate

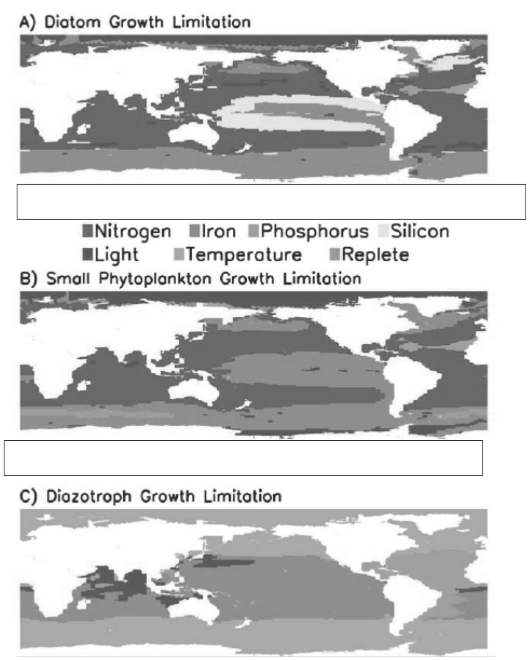
4		3		1		2
H_3PO_4	⇔	$H_2PO_4^-$	⇔	HPO_4^{2-}	⇔	PO_4^{3-}
phosphoric acid		di-hydrogen phosphate		hydrogen phosphate		phosphate

Polyphosphates

Solubable reactive phosphorus (SRP) - P that reacts with a molybdate solution. Includes primarily HPO_4^{2-} (~87%), PO_4^{3-}, and some reactive organic species.



Paytan & McLaughlin 2007 Chem. Reviews



Factor limiting growth rates during summer

Moore et al. 2004 GBC

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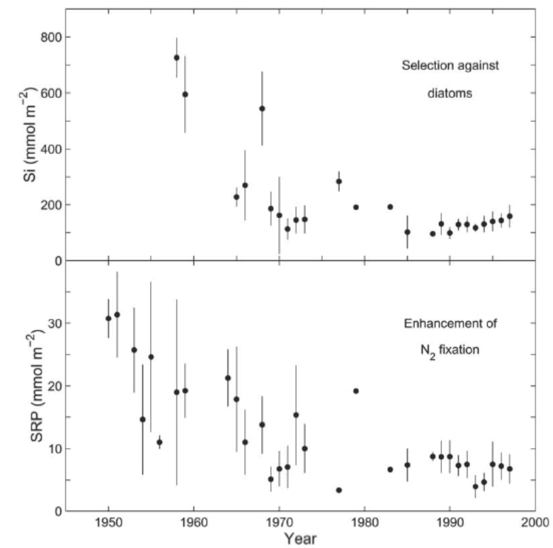
Gruber, In press, N in the Marine Env.

If nitrogen is queen, phosphorus is king!

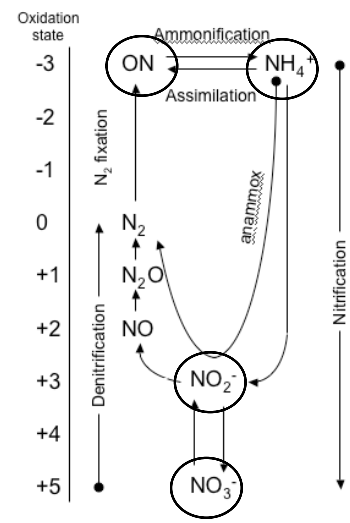
Flip Froelich

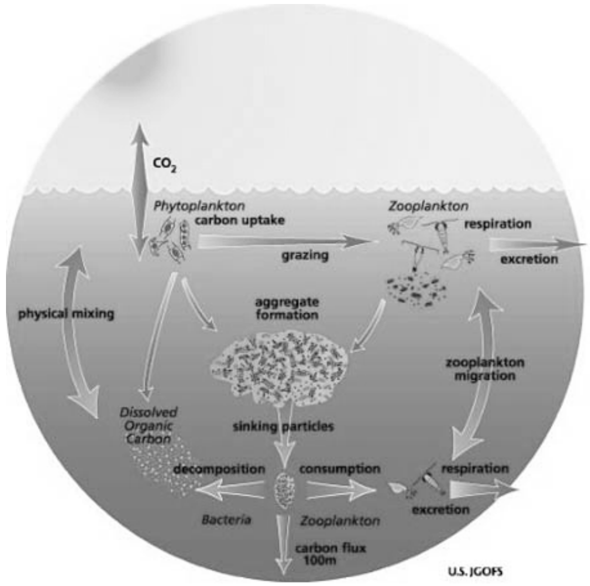
The domain shift hypothesis

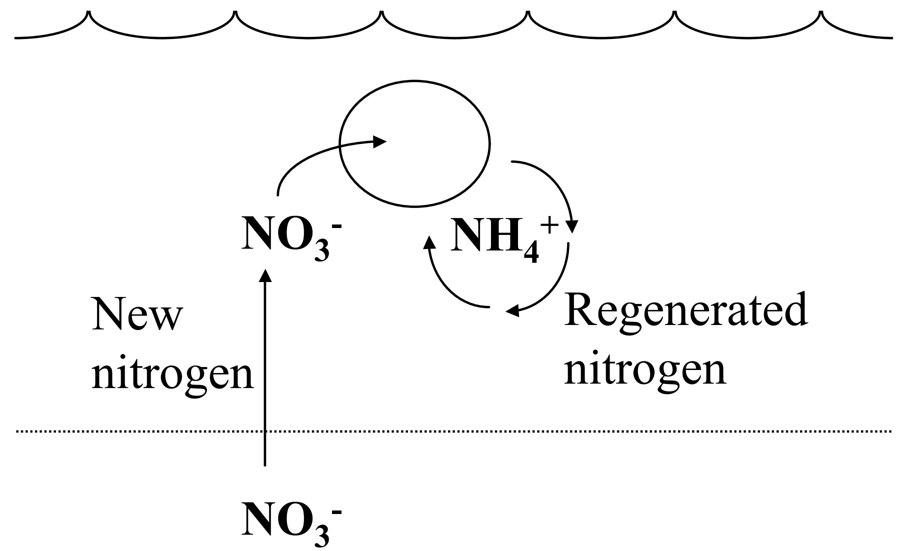


Karl et al. 2001 DSRII

Uptake and regeneration in the surface ocean







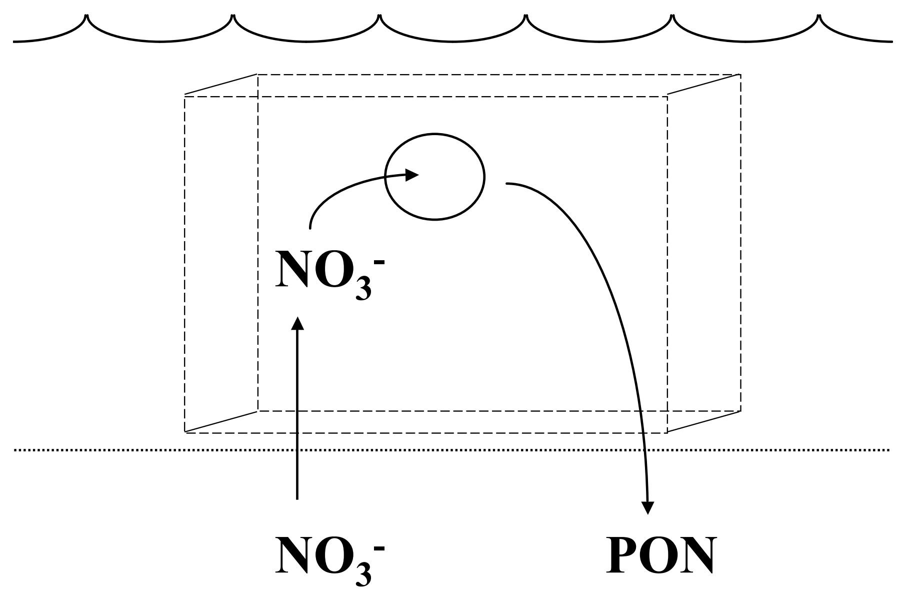
Particulate organic matter flux and planktonic new production in the deep ocean

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

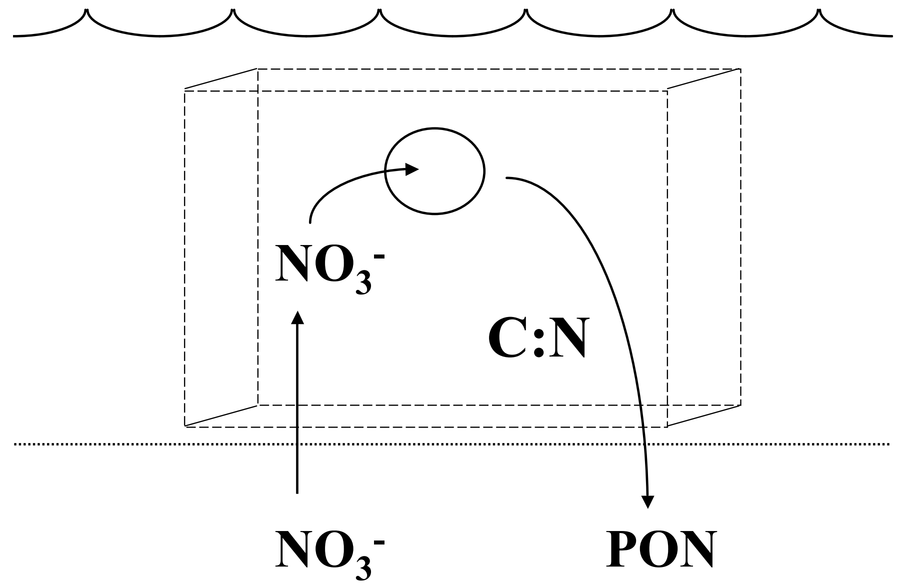
New production over appropriate spatial and temporal scales equals export flux.

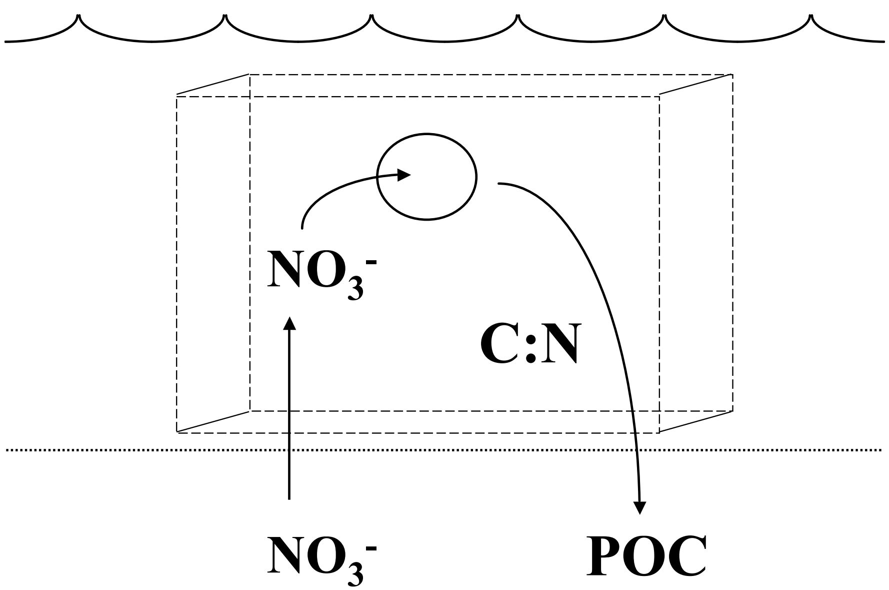
Eppley & Peterson 1979 Nature



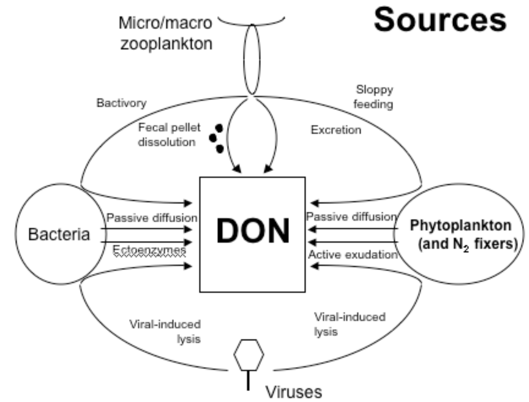
$$\text{f-ratio} = \frac{\text{New production}}{\text{New + Regenerated Production}}$$

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

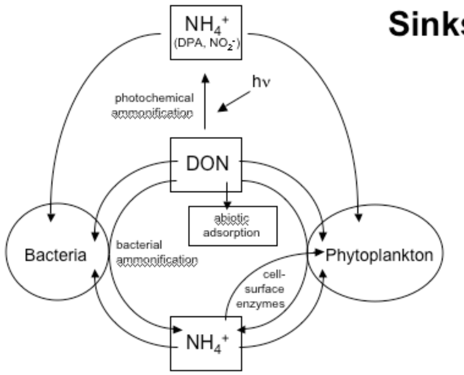




Tomorrow……



Sinks



NH_4^+
(DPA, NO_2^-)
hν
photochemical
ammonification
DON
abiotic
adsorption
Bacteria
bacterial
ammonification
Phytoplankton
cell-
surface
enzymes
NH_4^+