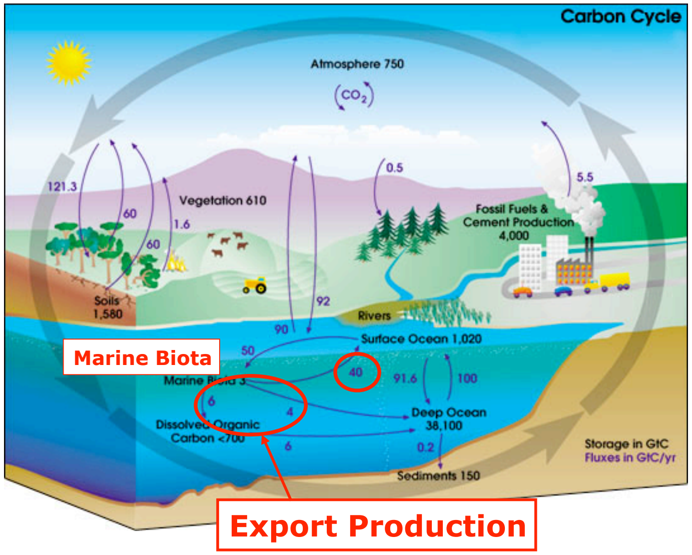
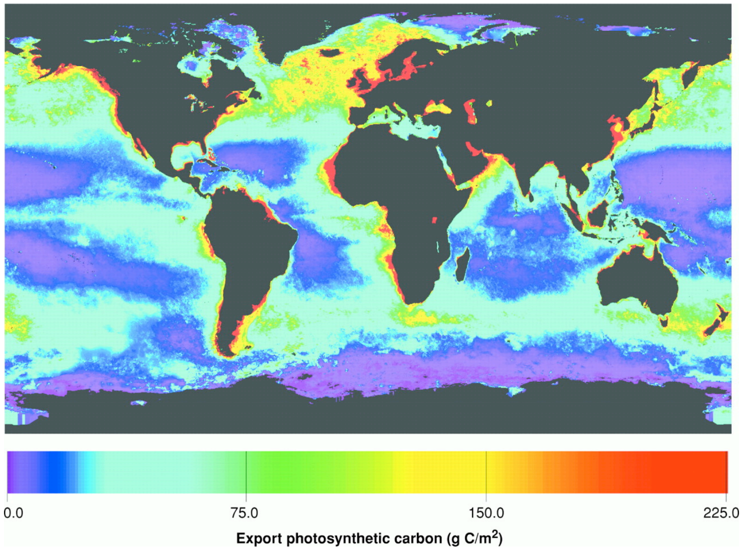
Carbon Cycle

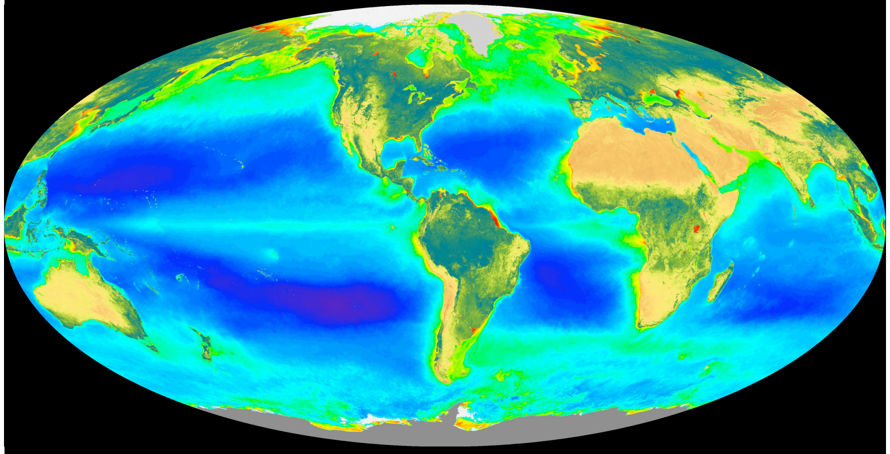


Export Production of Organic Carbon



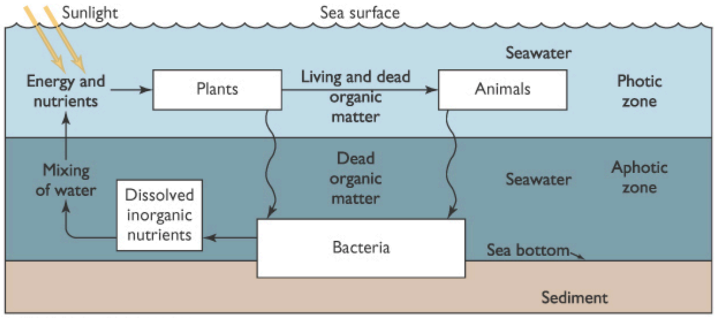
Nitrogen and Iron cycles

Understanding the marine ecosystem dynamics



Why do we care about Nitrogen?

1) N is a currency to track mass transfers in marine ecosystem
2) N dynamics important to model exchange processes



(a) NUTRIENT CYCLING

Nitrogen

- N is an essential nutrient for all living organisms (nucleic acids and amino acids)
- N has many oxidation states, which makes speciation and redox chemistry very interesting
- NH_4^+ is preferred N nutrient

Different forms of Marine N

Libes, 1992

Bioavailable/Fixed (oxidation state)

NO_3^- 5.7*10^5 Tg N (+5)

NO_2^- 500 Tg N (+3)

NH_4^+ 7.0*10^3 Tg N (-3)

Organic N 5.3*10^5 Tg N (-3)

Nitrate

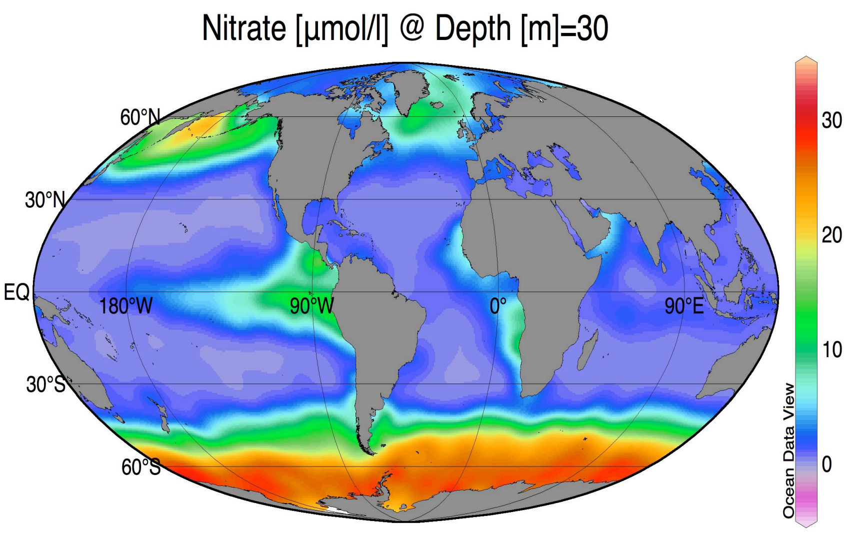
Nitrite

Ammonia

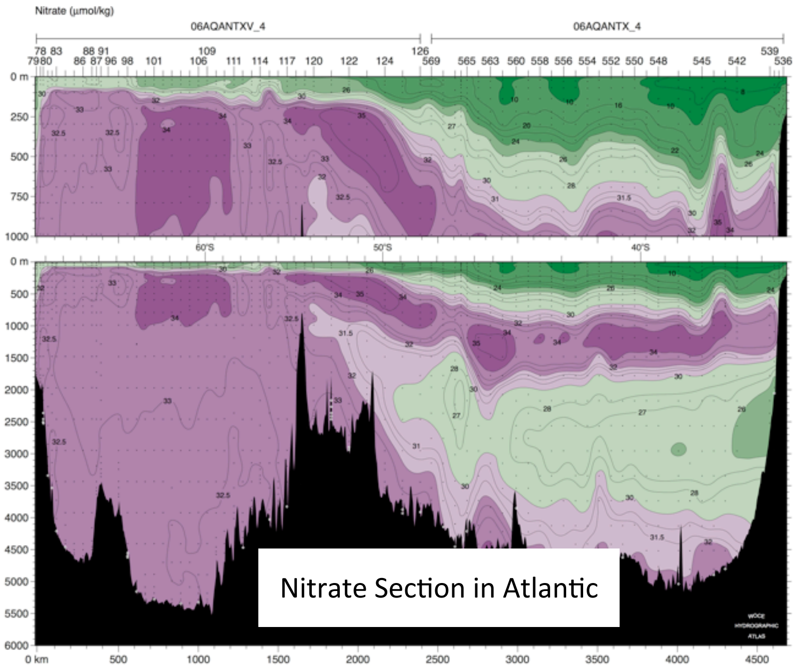
Non-bioavailable

N_2O 200 Tg N (+1)

N_2 2.2*10^7 Tg N (0)

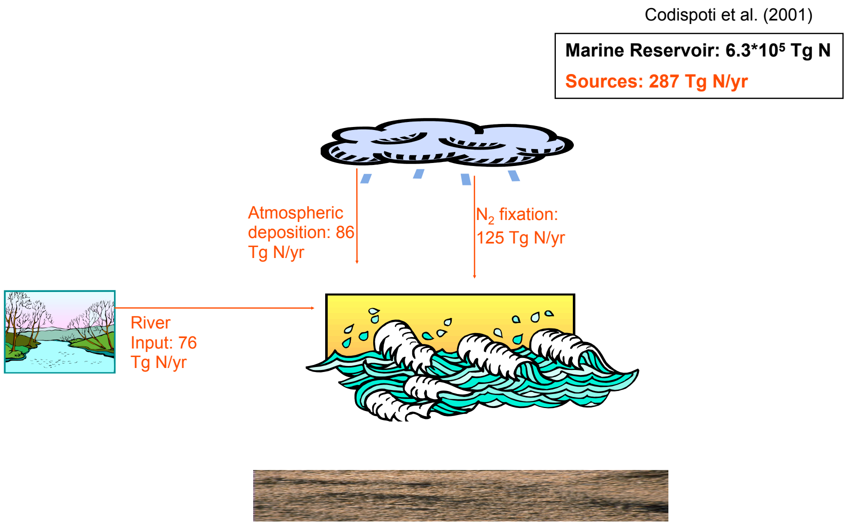


Data: eWOCE. Plot prepared with ODV



Nitrate Section in Atlantic

Marine Fixed N Budget



Codispoti et al. (2001)

Marine Reservoir: 6.3*10^5 Tg N

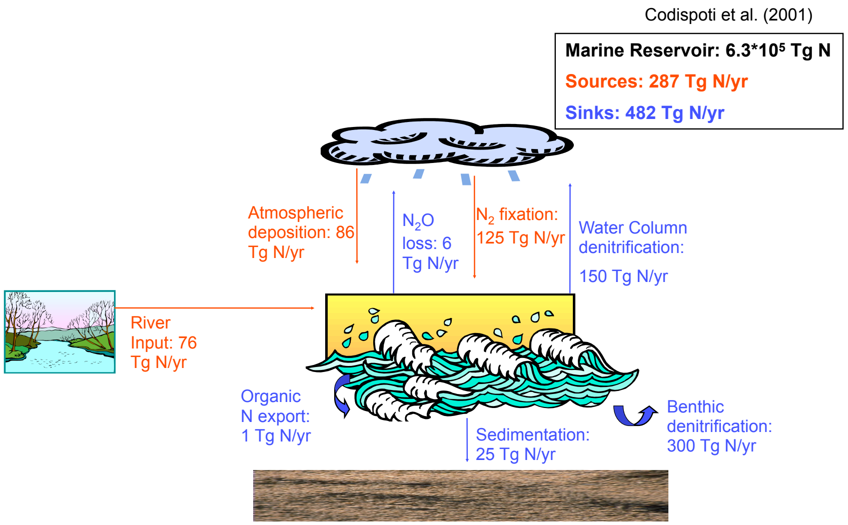
Sources: 287 Tg N/yr

Atmospheric deposition: 86 Tg N/yr

N_2 fixation: 125 Tg N/yr

River Input: 76 Tg N/yr

Marine Fixed N Budget



Codispoti et al. (2001)

Marine Reservoir: 6.3*10^5 Tg N

Sources: 287 Tg N/yr

Sinks: 482 Tg N/yr

Atmospheric deposition: 86 Tg N/yr

N_2O loss: 6 Tg N/yr

N_2 fixation: 125 Tg N/yr

Water Column denitrification: 150 Tg N/yr

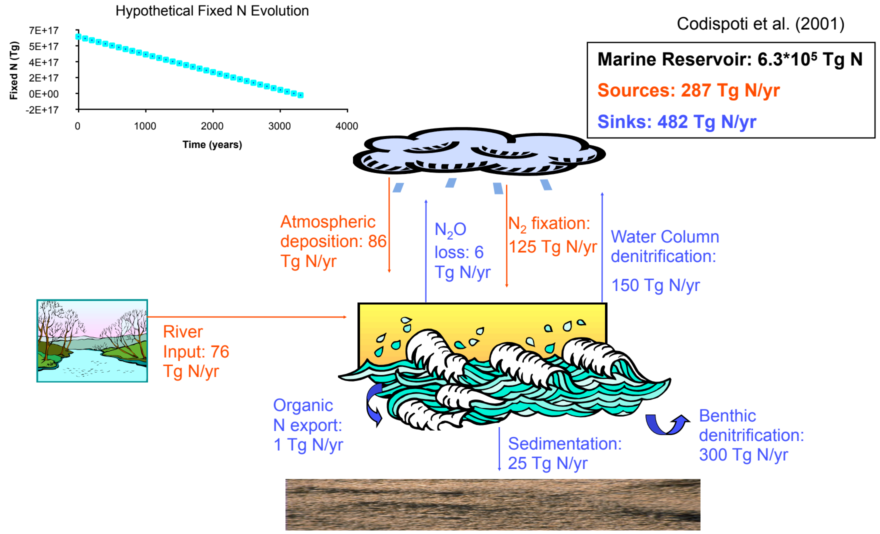
River Input: 76 Tg N/yr

Organic N export: 1 Tg N/yr

Sedimentation: 25 Tg N/yr

Benthic denitrification: 300 Tg N/yr

Marine Fixed N Budget



Codispoti et al. (2001)

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Water Column denitrification: 150 Tg N/yr

River Input: 76 Tg N/yr

Organic N export: 1 Tg N/yr

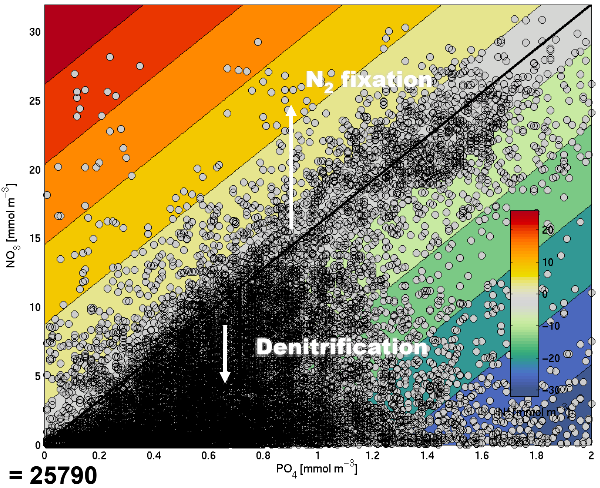
Sedimentation: 25 Tg N/yr

Benthic denitrification: 300 Tg N/yr

Oceanic Nitrogen Budget Estimates

N Budget Terms (Tg N y^{-1})	1970 (Delwiche)	1979 (Liu)	1985 (Codispoti & Christensen)	1997 (Gruber & Sarmiento)	2001 (Codispoti et al.)
Inputs					
atmospheric	4.1	49	40	15	56
runoff	30	17	25	41	41
N_2-fixation	**10**	**30**	**25**	**125**	**125**
Total Inputs	**44.1**	**96**	**90**	**181**	**222**
Outputs					
pelagic denitrification	40	50	60	85	150
sedimentary denitrification	0	10	60	85	300
burial & other	0.2	36	38	19	32
Total Outputs	**40.2**	**96**	**158**	**189**	**482**

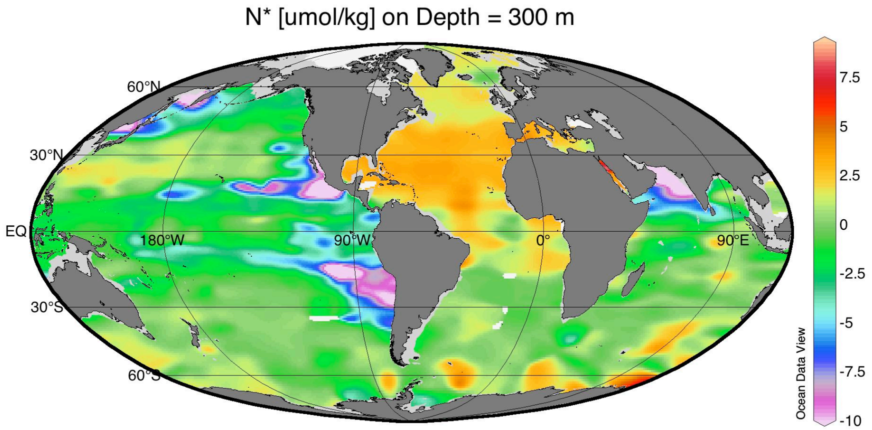
Modern TIME



N = 25790

N* = N – 16 P (Gruber & Sarmiento 1997)

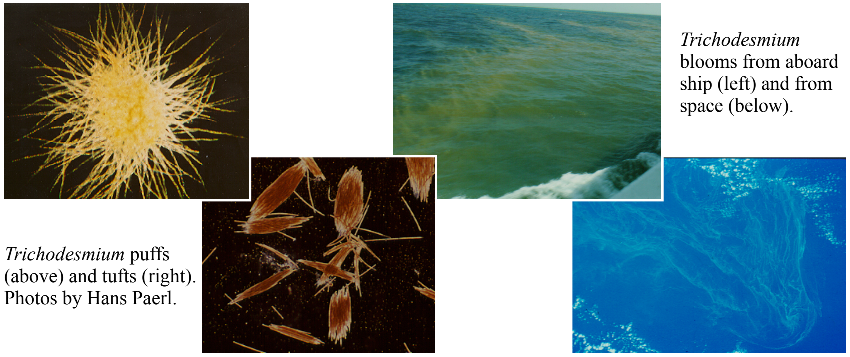
N* Distribution Shows Interplay Between N_2-Fixation and Denitrification



$$N^* = 0.87([NO_3^-] - 16[PO_4^{3-}] + 2.9)$$ (Gruber & Sarmiento 1997)

Trichodesmium: The Usual Suspect

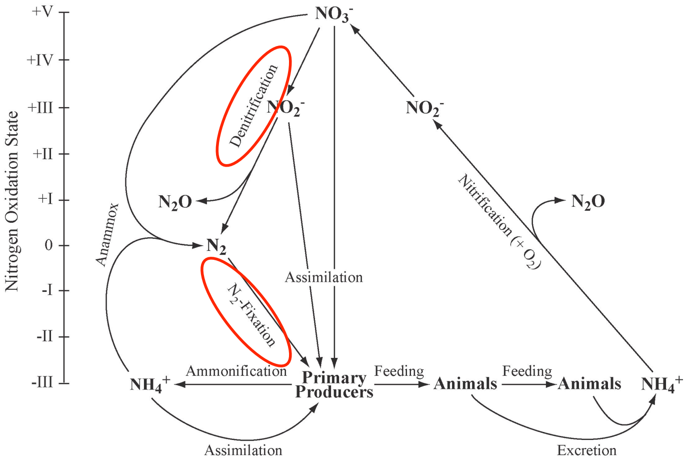
- Diazotrophs, including *Trichodesmium*, are broadly distributed in nutrient poor oceanic waters, but their contribution to the marine N budget remains poorly constrained.



Trichodesmium blooms from aboard ship (left) and from space (below).

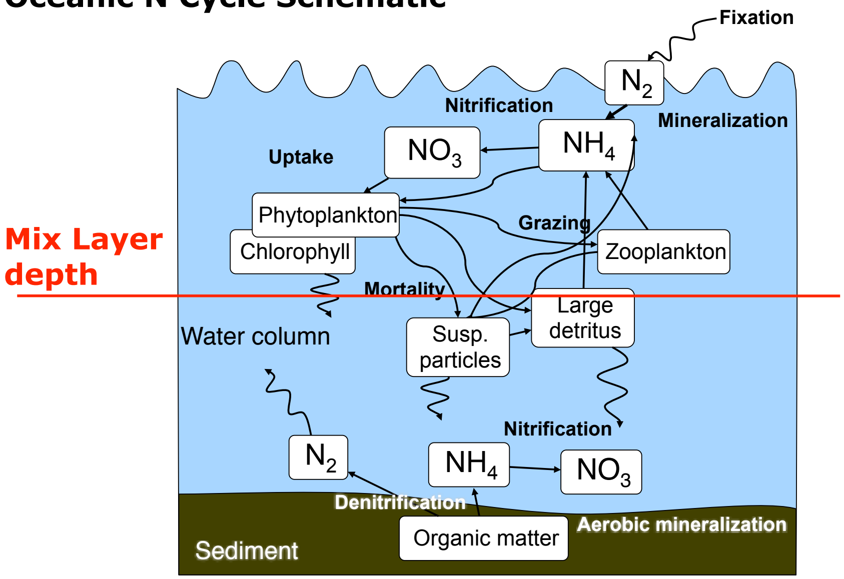
Trichodesmium puffs (above) and tufts (right). Photos by Hans Paerl.

Major Biological Transformations of Nitrogen

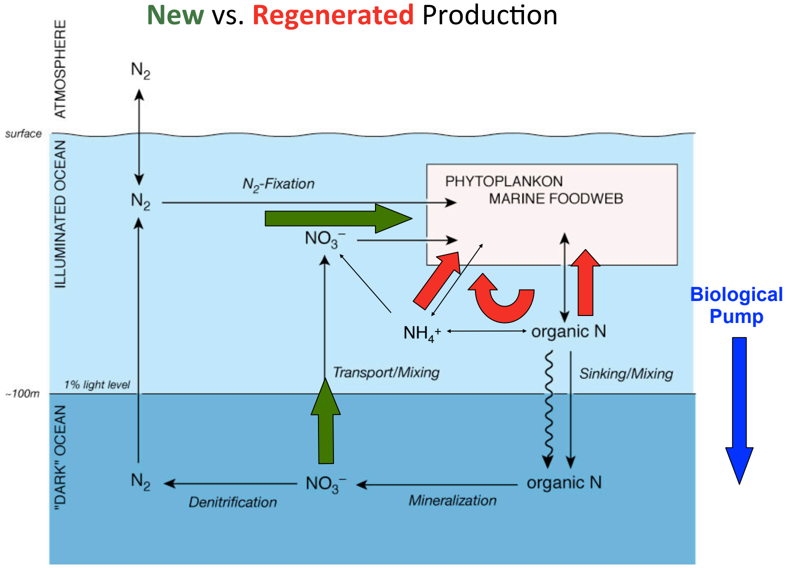


(Inspired by Codispoti 2001and Liu 1979)

Oceanic N Cycle Schematic



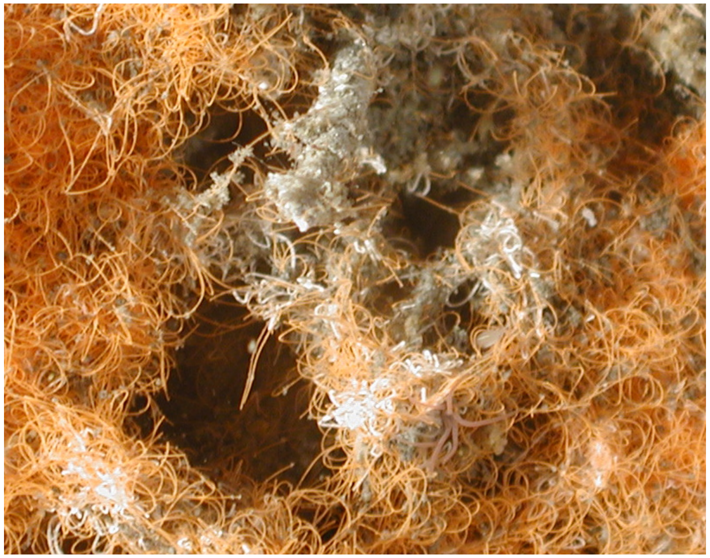
New vs. Regenerated Production



Organic Matter Oxidation Sequence

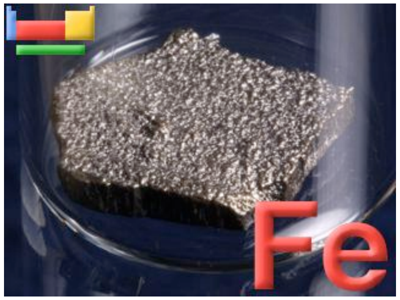
Morel & Herring, 1993

	ΔG° (kJ/mol)
Respiration $\frac{1}{4}CH_2O + \frac{1}{4}O_2 \leftrightharpoons \frac{1}{4}CO_2 + \frac{1}{4}H_2O$	-119
Denitrification $\frac{1}{4}CH_2O + \frac{1}{5}NO_3^- + \frac{1}{5}H^+ \leftrightharpoons \frac{1}{4}CO_2 + \frac{1}{10}N_2 + \frac{1}{2}H_2O$	-113
MnO$_2$ reduction $\frac{1}{4}CH_2O + \frac{1}{8}MnO_2 + H^+ \leftrightharpoons \frac{1}{4}CO_2 + \frac{1}{2}Mn^{2+} + \frac{3}{4}H_2O$	-96.9
Fe oxide reduction $\frac{1}{4}CH_2O + Fe(OH)_3 + 2H^+ \leftrightharpoons Fe^{2+} + \frac{1}{4}CO_2 + \frac{11}{4}H_2O$	-46.7
Sulfate reduction $\frac{1}{4}CH_2O + \frac{1}{8}SO_4^{2-} + \frac{1}{8}H^+ \leftrightharpoons \frac{1}{8}HS^- + \frac{1}{4}CO_2 + \frac{1}{4}H_2O$	-20.5
Methanogenesis $\frac{1}{4}CH_2O \leftrightharpoons \frac{1}{8}CH_4 + \frac{1}{8}CO_2$	-17.7



Georgia Tech Biological Oceanography

Iron and Biogeochemical Cycles



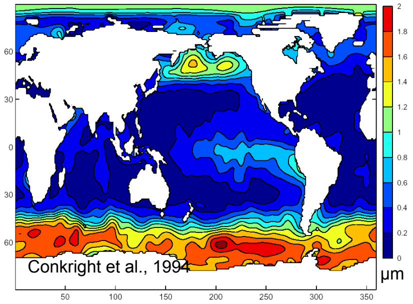
Redfield Ratio

- C:N:P
- 106:16 :1 (Redfield, 1958)
- Could there be other essential micro-nutrients?

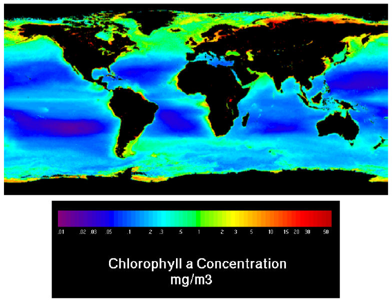
-Trace metals such as Fe, Zn, Co are important!

High Nutrient, Low (Medium) Chlorophyll Regions

Phosphorous



Chlorophyll



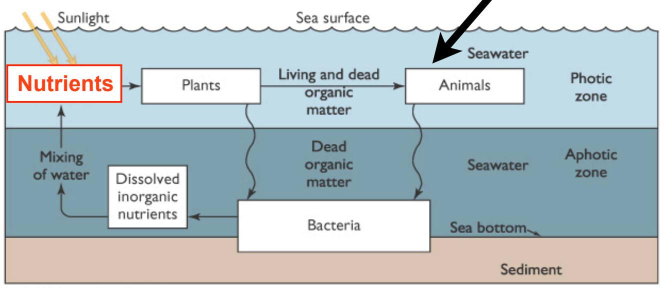
SeaWiFs

Why aren't the nutrients being completely utilized by phytoplankton?

Hypotheses

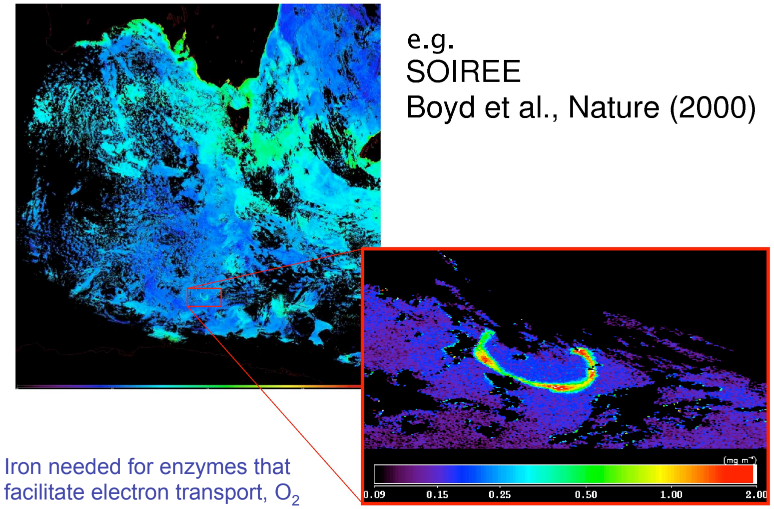
- Light
- Grazing
- Micronutrient limitation

Top Predators



(a) NUTRIENT CYCLING

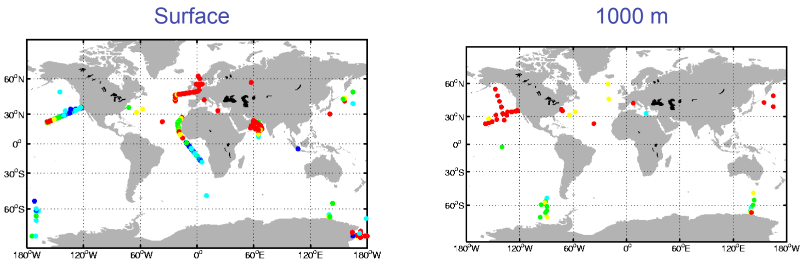
In situ Fertilization experiments: Is iron limiting?



e.g.
SOIREE
Boyd et al., Nature (2000)

Iron needed for enzymes that facilitate electron transport, O_2 transport and other important functions.

‘Dissolved’ Iron distribution



Surface

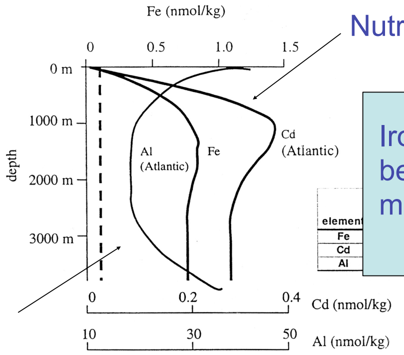
1000 m

- 🟥 >0.6 nM
- 🟨 0.4 – 0.6 nM
- 🟩 0.2 – 0.4 nM
- ● 0.1 – 0.2 nM
- 🟦 <0.1 nM

Why are there so few measurements?

- Difficult to measure

Iron Profile



Nutrient

Metal

Iron has a profile between a typical metal and nutrient

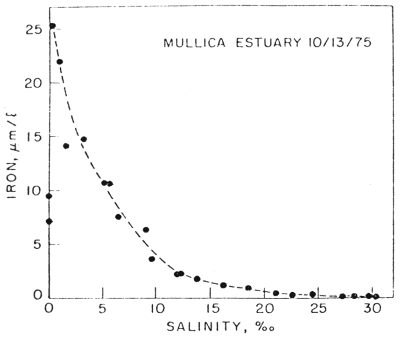
What controls the distribution (vertically and horizontally) of Iron?

Sources of Iron

- Riverine
- Continental Shelves
- Dust

Riverine

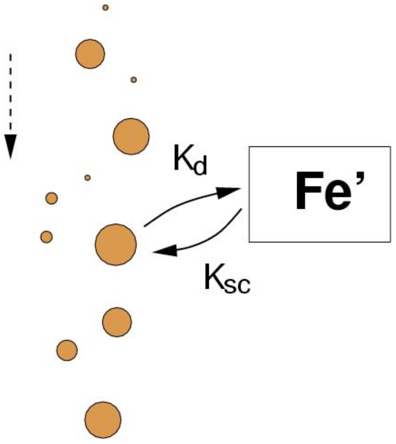
- [Fe'] decreases further from coast.
- This is due to scavenging of Fe by particles.
- We can conclude that rivers are not an important source for the open ocean



Boyle et al. (1977)

Scavenging: Iron sink

- Iron lost to the ocean by scavenging – the process of sticking onto particles
- Rate of scavenging not well-known
- *loss=-ksc[Fe'][P]*



Continental Shelves

1. Resuspension of sediments can release Fe

2. When organic matter decomposes, Fe can diffuse or be bio-irrigated into the water column

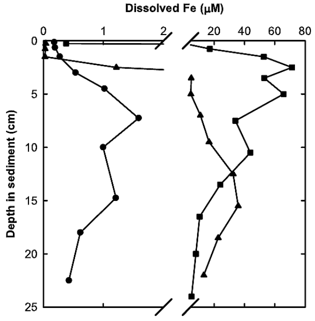
$C_{106}H_{263}O_{110}N_{16}P_1Fe_{.0001}+138O_2=106CO_2+16NO^-_3+H_2PO^-_4+0.0001Fe(OH)_2$

Estimate global flux of 0.2-9 x 10^{10} mol y^{-1}

Is this Fe upwelled to the surface before being scavenged?

Active area of research

Results from flux chamber experiment (Elrod et al., 2004)



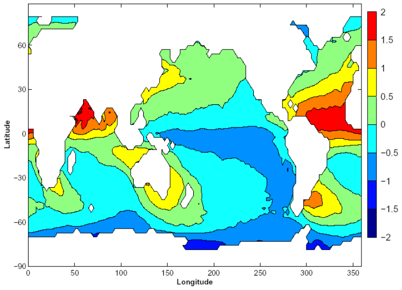
Aeolian-derived Iron

- Major source of iron
- How much of the iron is soluble?
  - 1-10%

  Active area of research:

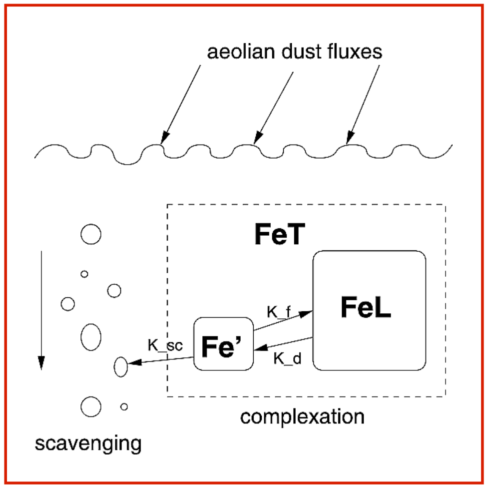
  differences by provenance, processing in cloud, surface waters
- Flux: 0.2-1.2 X 10^{10} mol y^{-1} (assuming 2% solubility)

Annual Fe flux (mg Fe m^{-2} y^{-1})



Mahowald et al. (2003)

Iron Speciation : Complexation



$$Fe_T = Fe' + FeL$$

$$Fe' + L' \Leftrightarrow FeL$$

$$K = \frac{[FeL]}{[Fe'][L']}$$

K = cond. stability constant

specifies strength of ligand

Iron Speciation : Complexation

- Inorganic iron: Fe^{2+}, Fe^{3+}, $Fe(OH)_3$
  - Since ocean is oxidizing medium, reduced iron (Fe^{2+}) concentrations are low.
  - Most Fe^{2+} produced by photochemistry, has a short lifetime
- 99% of Fe found bound to organic ligands
  - Increases solubility of iron in water column

$$Fe_T = Fe' + FeL$$

$$Fe' + L' \Leftrightarrow FeL$$

$$K = \frac{[FeL]}{[Fe'][L']}$$

K = cond. stability constant

specifies strength of ligand

Complexation: Active areas of research

- What is the structure of the ligand?

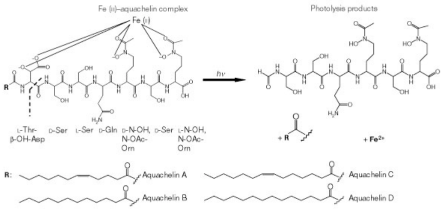
  -messy organic molecular structure

- How do organisms produce it?

  -current research suggest marine bacteria produce the ligands.

- How do organisms utilize FeL?

  -Light breaks down FeL so organisms can grab the Fe'

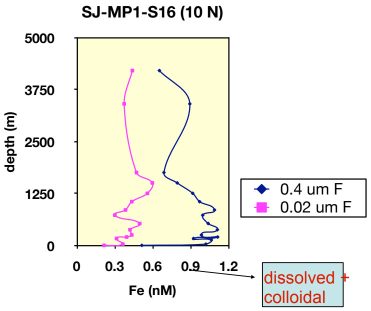


Barbeau et al. (2004)

Forms of Iron

- Dissolved iron: <0.02 µm
- Colloidal: 0.02-0.4 µm
- Particulate: >0.4 µm

Active area of research: Role of colloidal matter

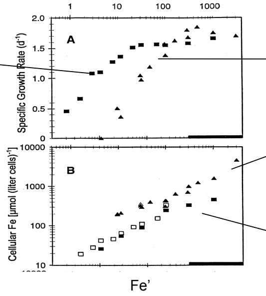


dissolved + colloidal

dissolved

Data from Boyle, 10N (Atlantic)

Biological Uptake of Iron



Oceanic

Coastal

Coastal

Oceanic

Sunda and Huntsman (1995)

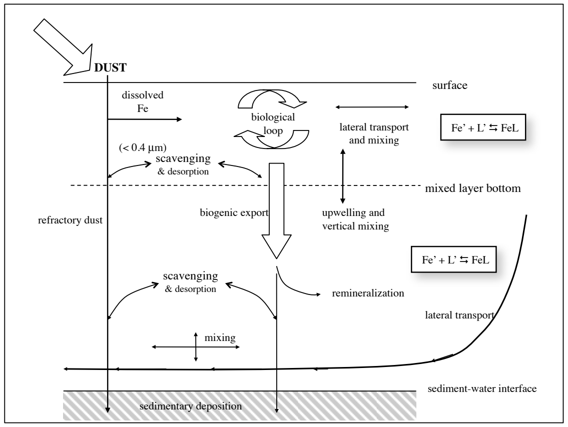
•Oceanic species have higher growth rates at lower [Fe]

•They have adapted

•Their Fe requirement is lower (small Fe:C ratio)

•Oceanic species are smaller, so they have higher surface area:volume ratio

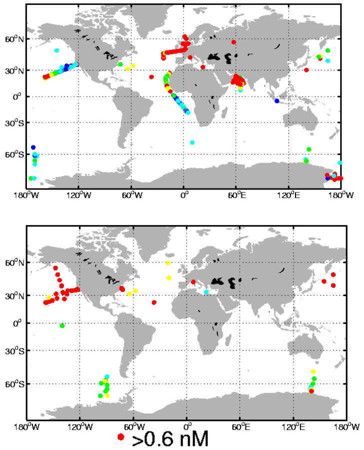
Putting it all together



Developing mathematical model to understand the various processes affecting Fe

Model Results: Iron

Observations

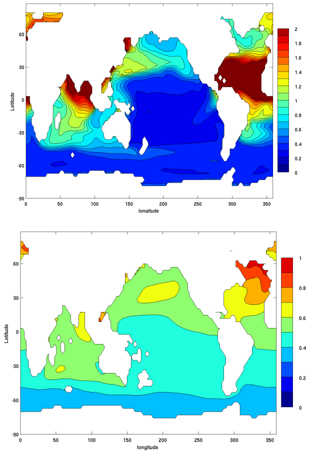


- ● >0.6 nM
- ● 0.4 – 0.6 nM
- ● 0.2 – 0.4 nM
- ● 0.1 – 0.2 nM
- ● <0.1 nM

Model

Surface

1000 m



Parekh et al. (2004b)

Link between dust flux and CO$_2$?

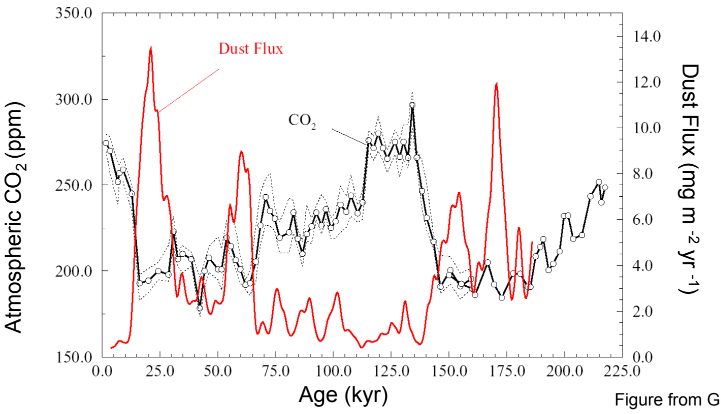
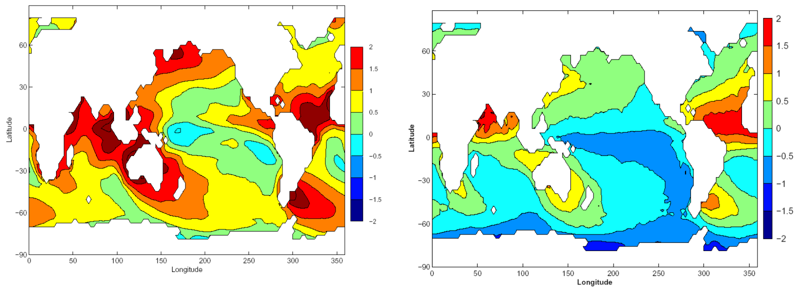


Figure from Gruber from Martin (1990)

+dust → +Fe→ +bio. Productivity→ +Export→ +CO$_2$ drawdown

Atmospheric CO$_2$ Sensitivity to Increased Dust Flux

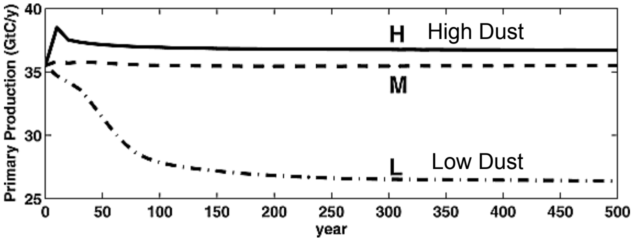


LGM dust flux

Present dust flux

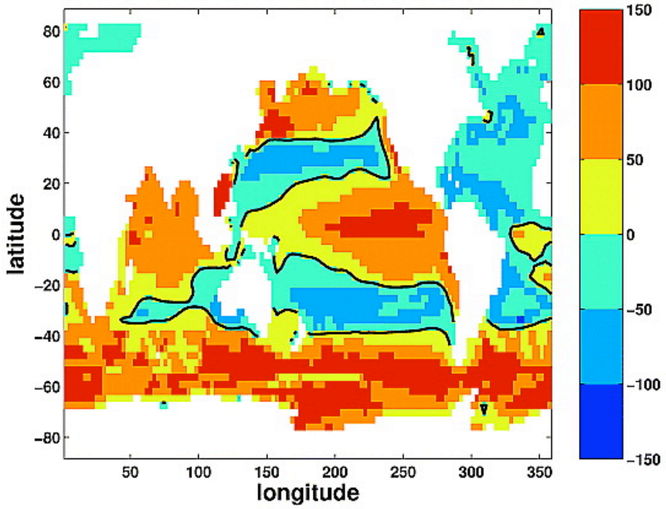
- ‘Paleo’ dust estimate from Mahowald *et al.* (1999)
- Dust flux greater 5.5 times globally

Model result



Time series of total global primary production (GtC yr−1) for high (solid line), medium (dashed line), and low (dash-dotted line) dust sensitivity studies.

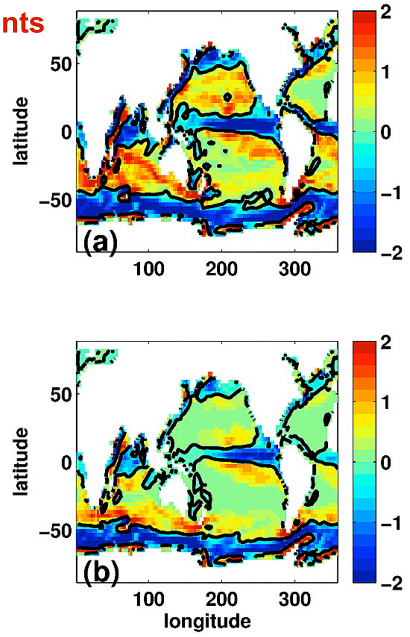
Difference in primary production (gC m−2 yr−1) between high and low dust sensitivity studies. Solid line is zero contour. Positive values indicate higher production when aeolian dust supply is enhanced.



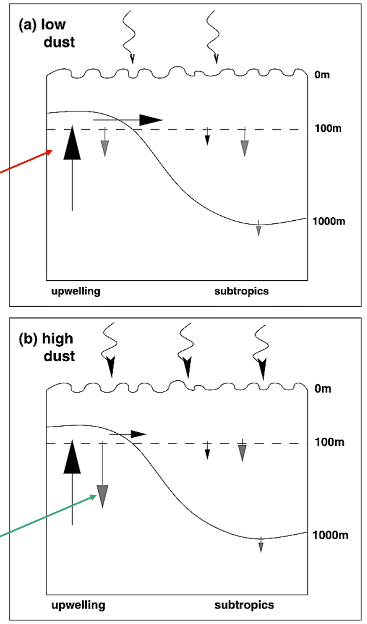
Convergence of Macro Nutrients in surface waters

Low Dust

High Dust



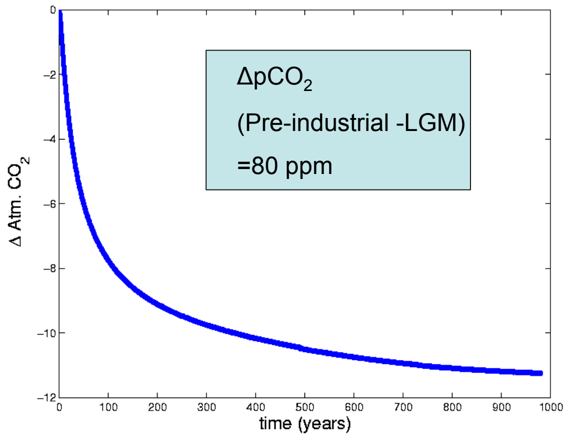
Changes in Biogeochemical Cycling



Macro Nutrients

Export of Organic Matter

Model result



The effect of additional Fe is quite small.

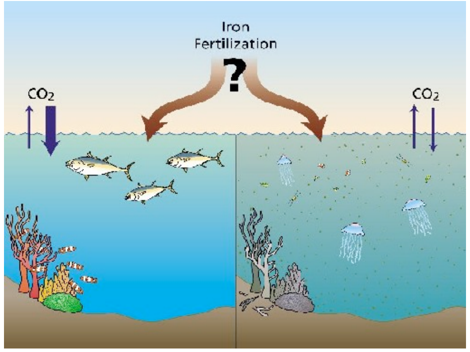
~11 ppm

Iron Fertilization

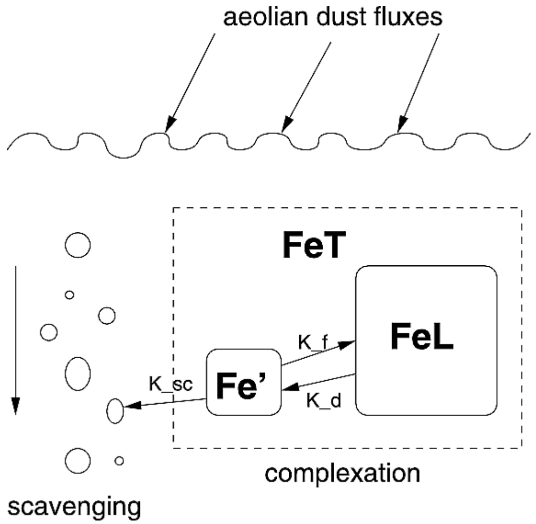
- Adding Fe artificially to transfer CO_2 from atmosphere to the sea

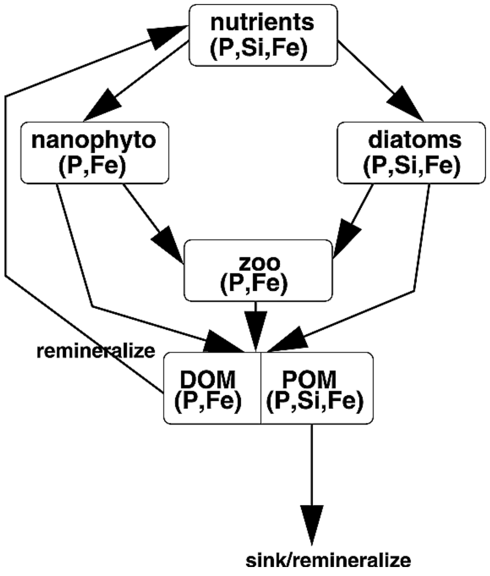
Open questions:

- How effective will it be?
- Effect on marine ecology?

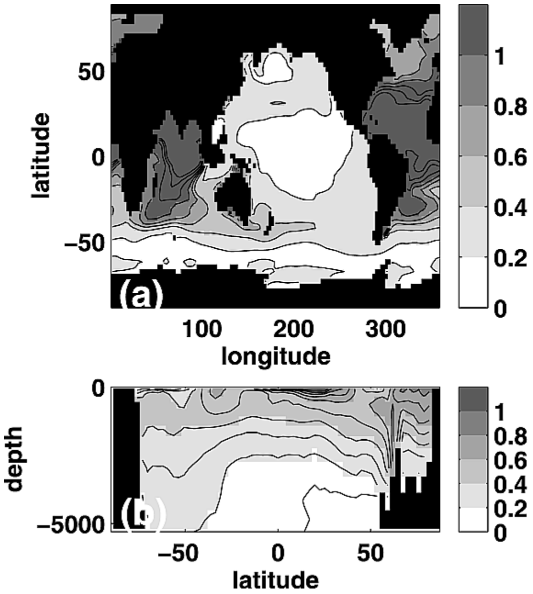


End





Model IRON



Alternative pathways to N_2

Microbially mediated

Nitrification

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$$

Heterotrophic Denitrification

$$5CH_2O + 4NO_3^- + 4H^+ \rightarrow 2N_2 + 5CO_2 + 7H_2O$$

Anammox

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O$$

OLAND

$$NH_4^+ + \tfrac{3}{4}O_2 \rightarrow \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2O + H^+$$

Nitrogen Fixation

$$N_2 + 5H_2O \rightarrow 2NH_4^+ + 2OH^- + \tfrac{3}{2}O_2$$

Chemical Reactions

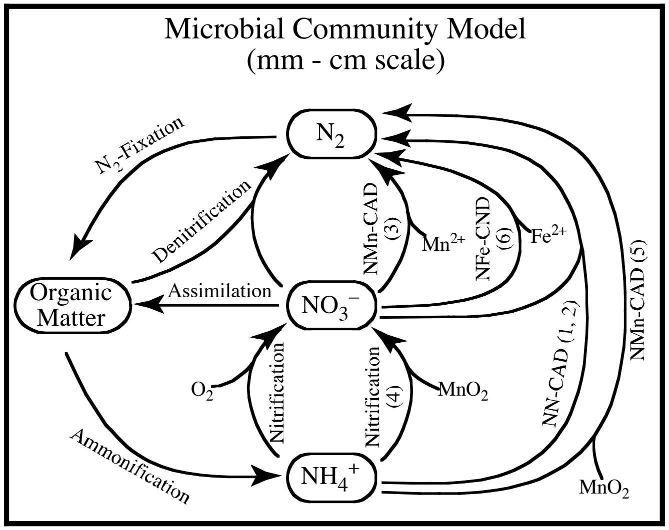
MnO_2 Reduction

$$3MnO_2 + 2NH_4^+ + 4H^+ \rightarrow 3Mn^{2+} + N_2 + 6H_2O$$

$$4MnO_2 + NH_4^+ + 6H^+ \rightarrow 4Mn^{2+} + NO_3^- + 5H_2O$$

Mn^{2+} Oxidation

$$5Mn^{2+} + 2NO_3^- + 4H_2O \rightarrow 5MnO_{2(solid)} + N_2 + 8H^+$$



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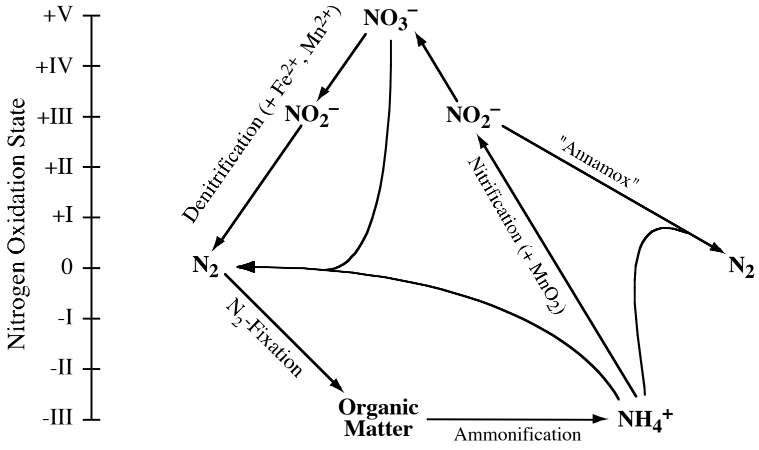
Alternative Pathways to N_2



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