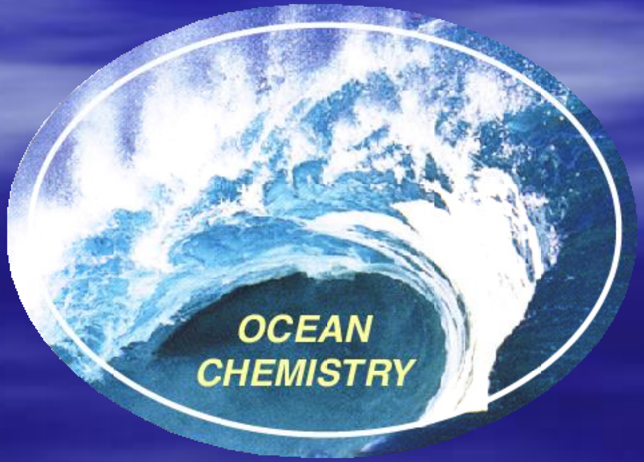
Nutrients in the Ocean- Biogeochemistry Nitrogen Cycle



What are nutrients?

- Unicellular marine organisms (phytoplankton and bacteria) require a range of elements to grow and reproduce
- Some nutrient elements abundant in seawater (e.g. inorganic C, Na, Ca)
- Other elements can be scarce e.g. N, P - These are the potentially bio-limiting nutrients

OCEAN CHEMISTRY

Nutrients

Living organic tissue contains:

- Primary (>1%): H, C, **N**, O, **P**
- Secondary (<1%): Na, Mg, S, Cl, K, Ca,
- Micro (<0.05%): B, F, **Si****, **Fe,** Mn, Co, Cu, Zn, I, others???

Of the primary constituents: N and P are often **biolimiting** in the ocean
**Silicon is important skeletal (hard-part) constituent for some organisms

<u>The ‚Major‘ or ‚Macro‘ Nutrients:</u>

Nitrogen	(redox chemistry; soft tissue)
Phosphorus	(no redox chemistry; soft and hard tissues)
Silicon	(no redox chemistry; hard tissues)

Specific uses of nutrients in organisms

- N- amino acids, RNA, enzymes
- P- cellular energy transport (ATP), phospho-lipids etc
- Si- diatoms, radiolaria
- Sr- shells of acantharians
- Metals (Fe, Mn, Cu, Zn etc)- enzyme systems

OCEAN CHEMISTRY

Nutrient limitation

- If nutrients at very low concentration, some phytoplankton may have growth limited.
- Other organisms sometimes able to move into this ecological niche (e.g. N_2 fixers)
- The main ocean bio-limiting nutrients: N, P, Si, Fe

Why are nutrients and nutrient limitation important?

- Exert a control on phytoplankton activity and marine life over long time-scales-
    - Development of early marine photosynthetic organisms is why we have an oxygen containing atmosphere
    - Phytoplankton activity leads to uptake of atmospheric carbon dioxide and transfer of C to deep waters and sediments (biological carbon pump)
    - Implications for global climate

OCEAN CHEMISTRY

Nutrient cycles in the ocean

- In the sunlit surface ocean particles almost exclusively have a biological origin
- Particle production is based on photosynthesis and phytoplankton
- About half the total photosynthetic fixation of C occurs in the ocean

OCEAN CHEMISTRY

Cycle of carbon fixation and regeneration

light

respiration CO_2 +nutrients $+H_2O$

Photosynthesis

phytoplankton

On cell death..

recycling by bacteria

Primary Production

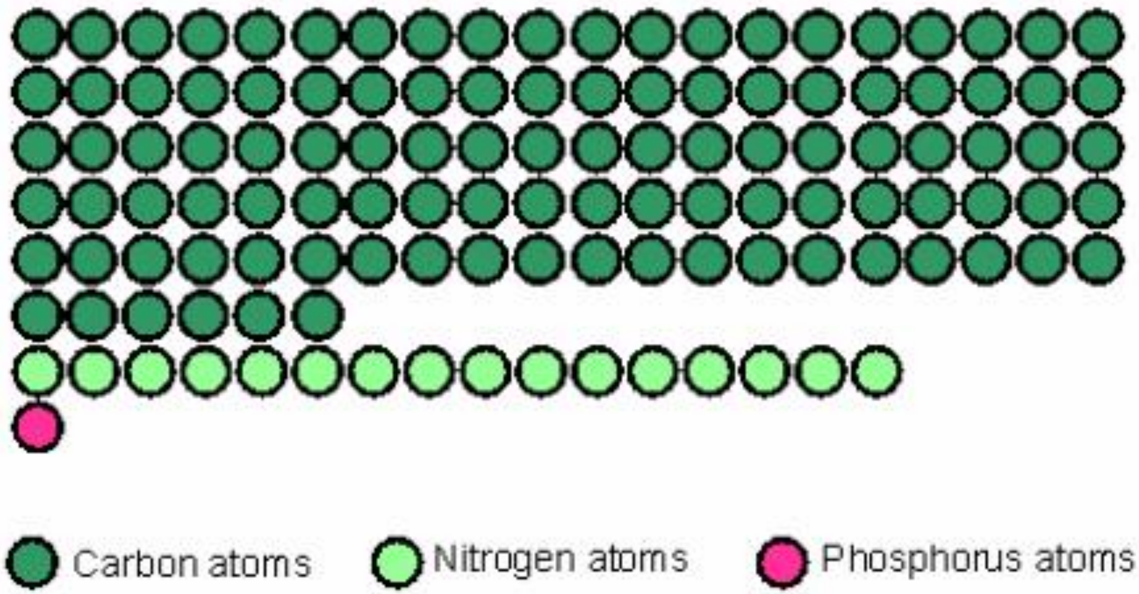
$C_{106}\ H_{263}\ O_{110}\ N_{16}\ P_1$ ….

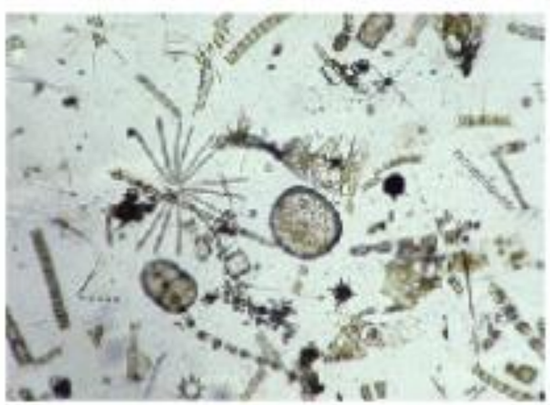
algal biomass

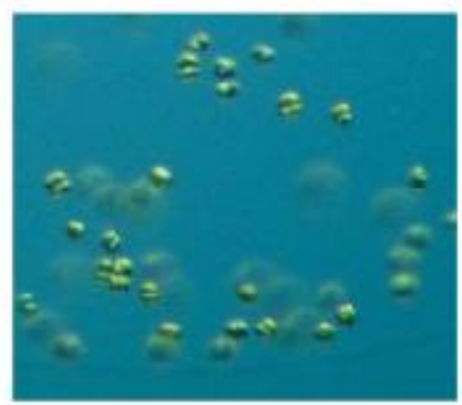
Basis of the marine food chain

Average composition of phytoplankton.

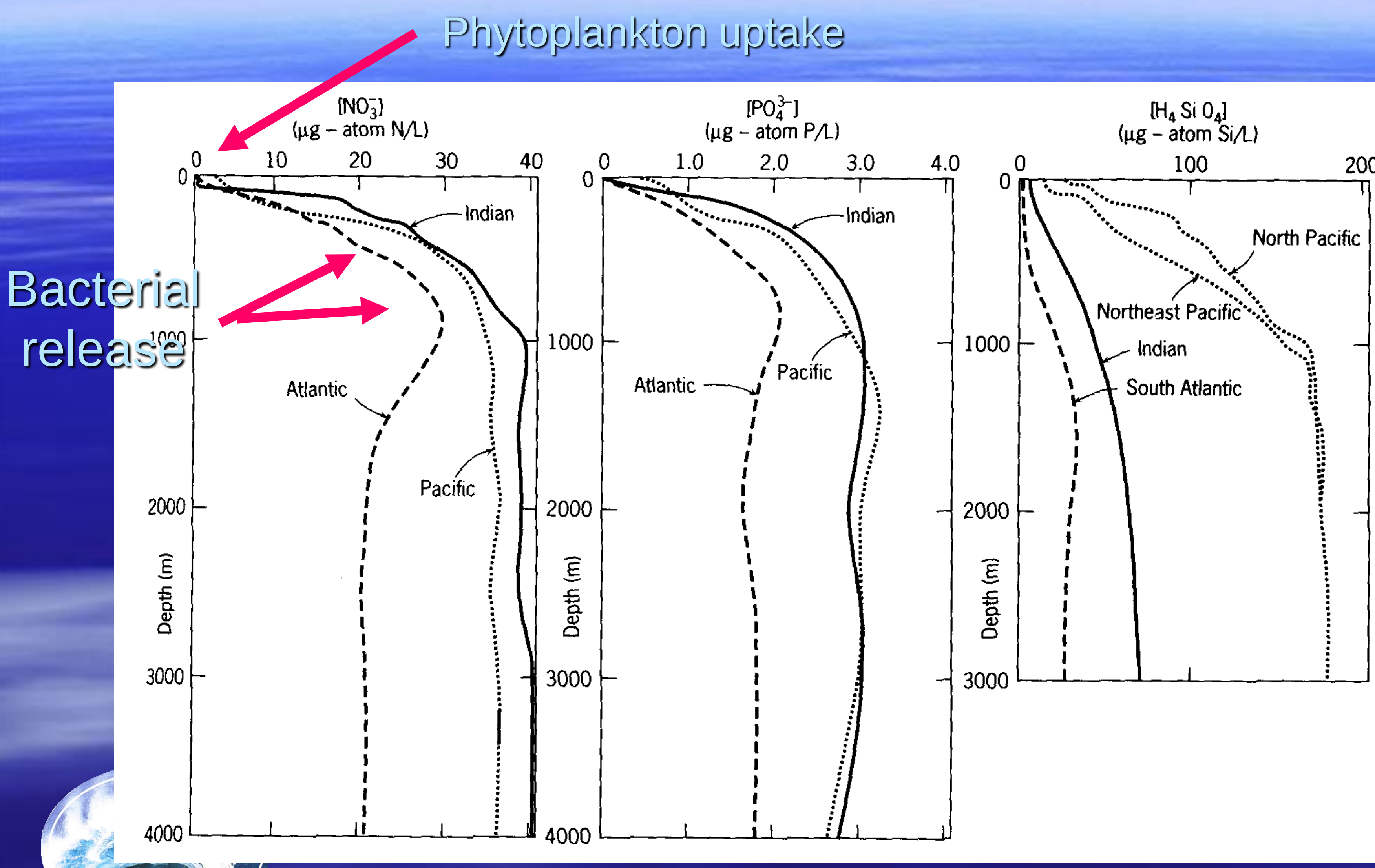
"Recipe for Phytoplankton"







Vertical Distributions of Nutrients

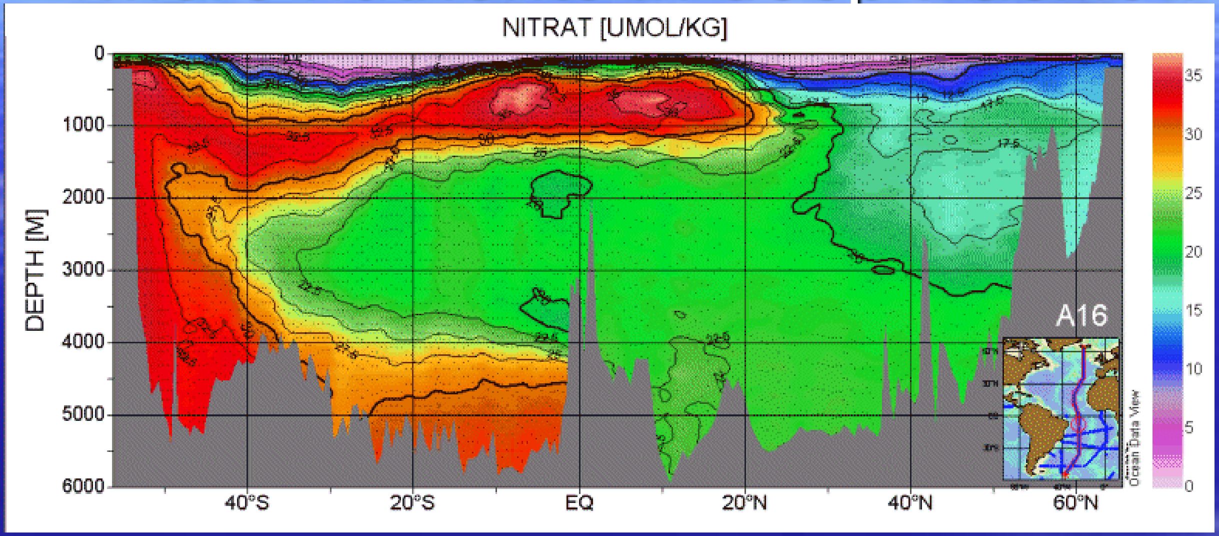


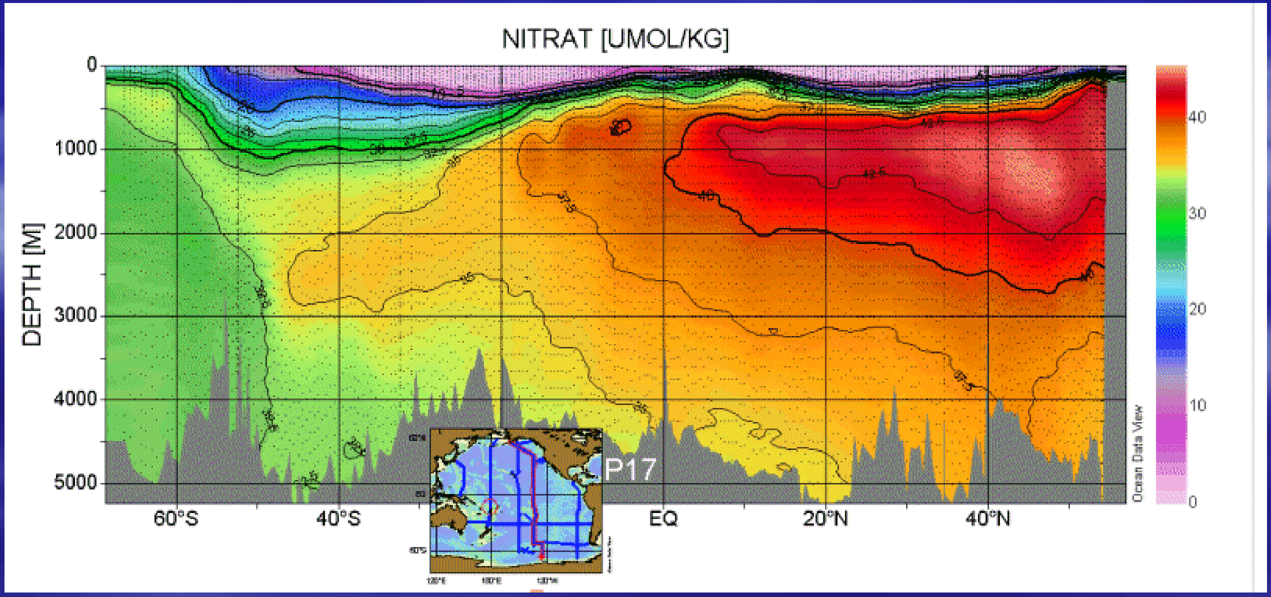
Nutrient Distributions

- Profiles have characteristic shape
  - low (near zero) in surface layers
  - mid-depth maxima at intermediate depths (500 – 1500 m).
- In most oceans, rate of carbon fixation limited by availability of nutrients (N and P).
- BUT why are concentrations greater in Pacific than Atlantic deep waters??

Horizontal distribution and circulation of nutrients in the Ocean

- More nutrients in deep Pacific *vs.* deep Atlantic



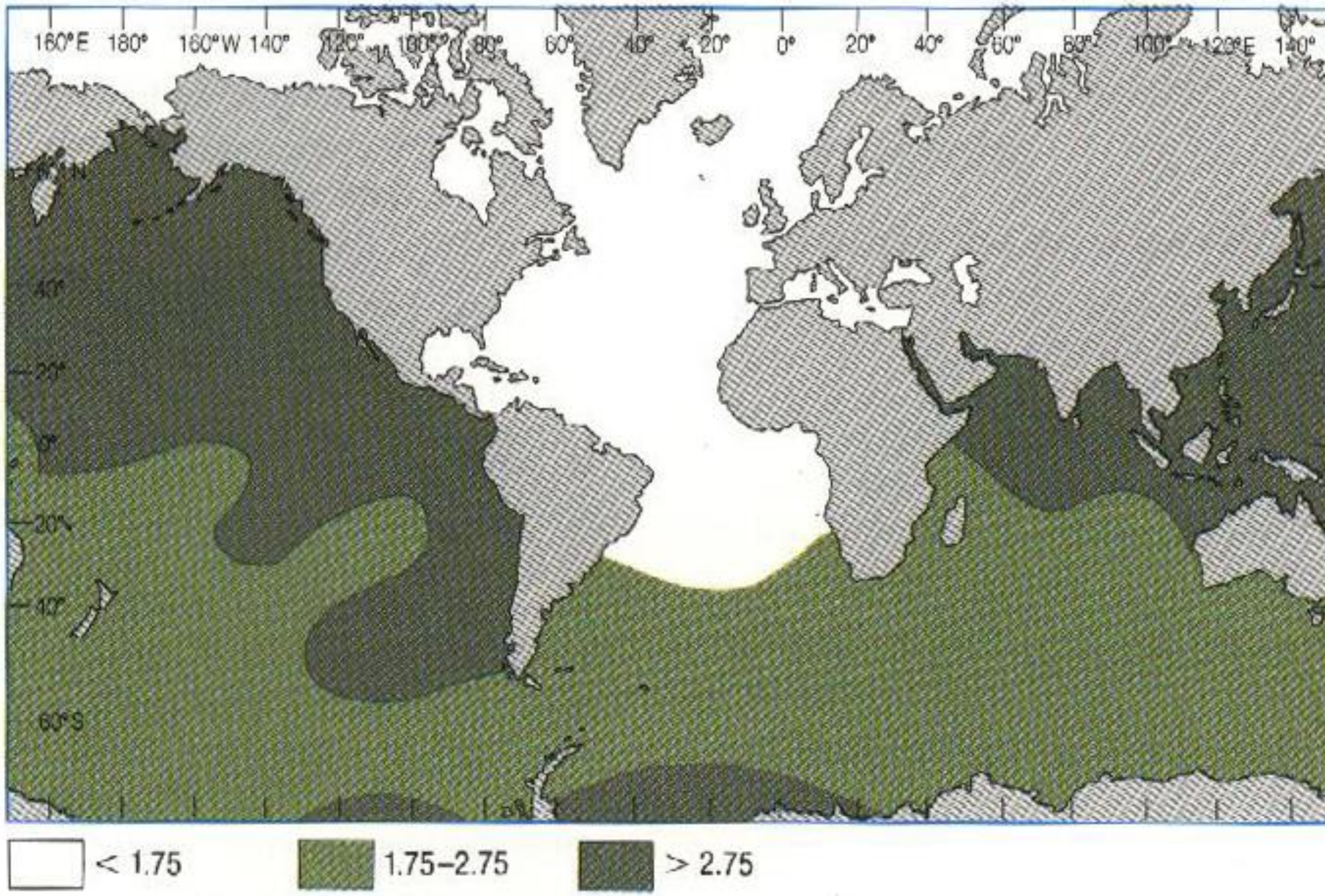


OCEAN CHEMISTRY

Nutrient Distributions

- More nutrients in deep Pacific *vs.* deep Atlantic

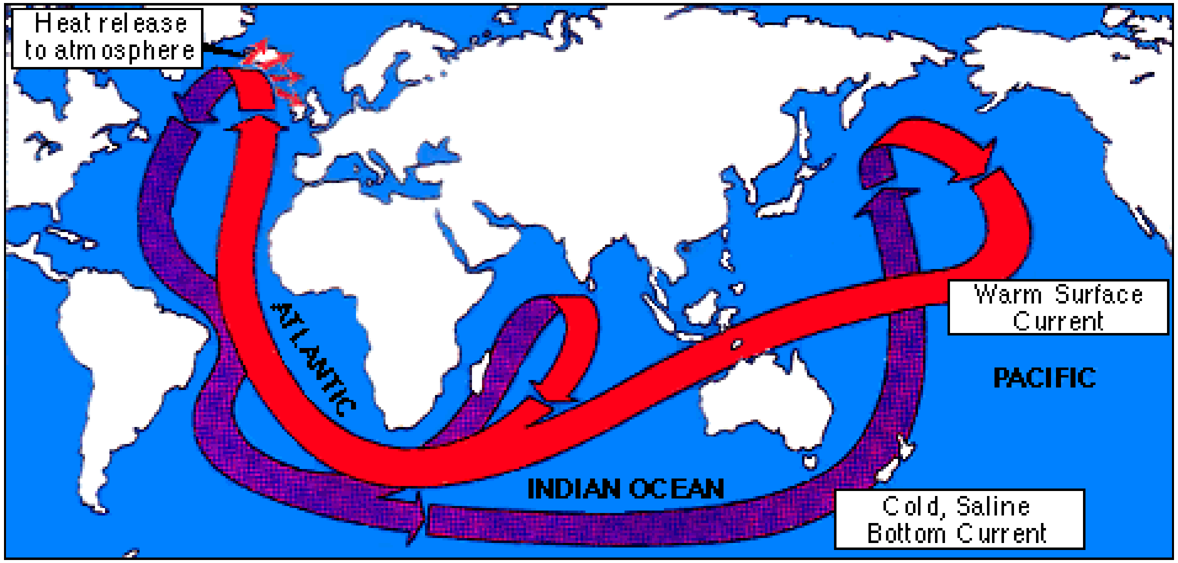
e.g., PO_4



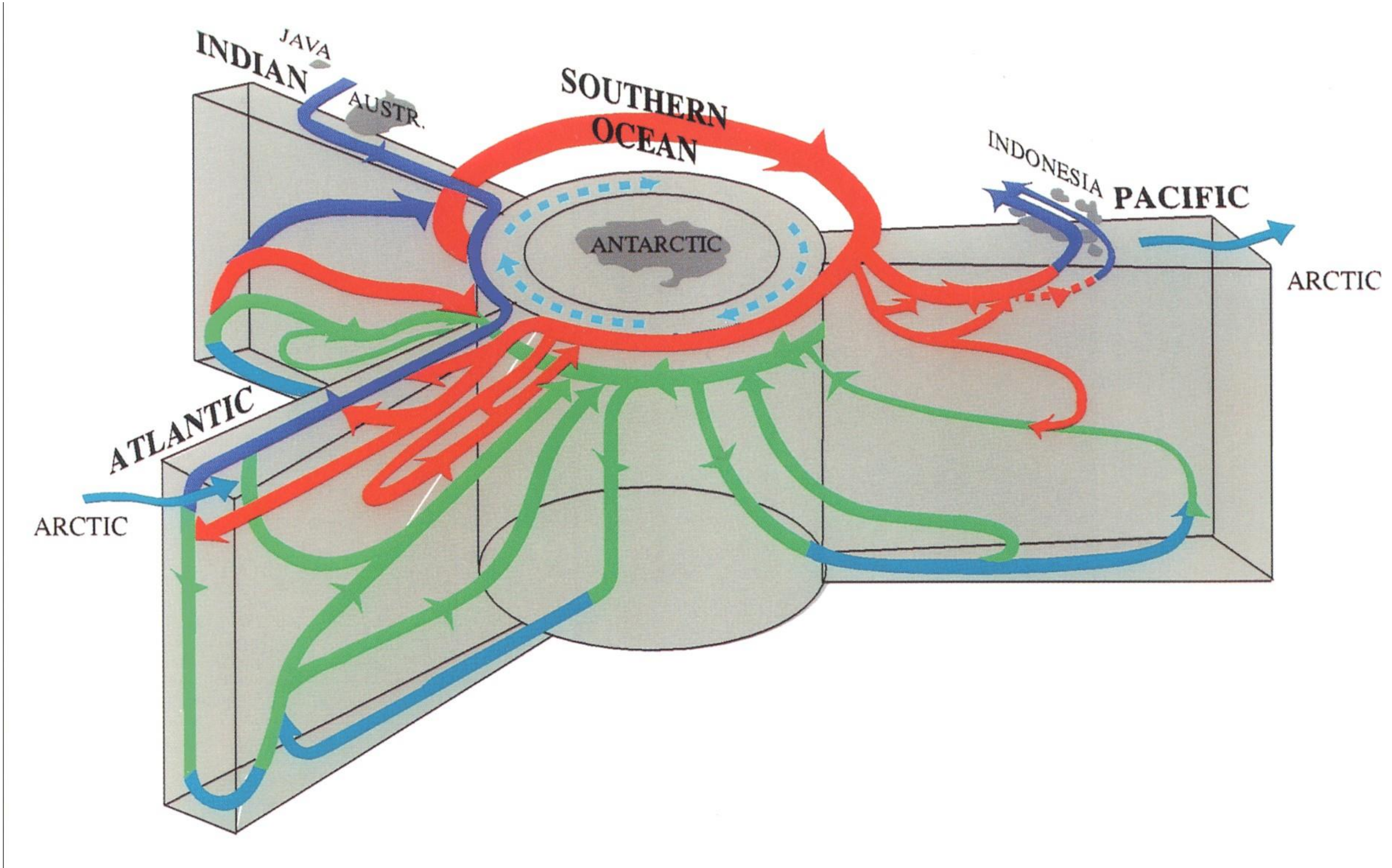
Distribution of phosphate in the oceans at 2000m depth.

Water mass movement through the deep ocean

- The "Ocean Conveyor belt"-physical oceanography
- Cold water sinks and moves through ocean basins; return via surface currents



The present large-scale ocean current system determines climate to a great extent. The huge "conveyor belt" reacts extremely sensitively to global temperature changes accompanying each increase and decrease in the content of carbon dioxide in the atmosphere. - Broecker


INDIAN
JAVA
AUSTR.
SOUTHERN OCEAN
ANTARCTIC
INDONESIA
PACIFIC
ARCTIC
ATLANTIC
ARCTIC

Remineralization of Organic Matter in Deep Ocean:

$(CH_2O)106(NH_3)16(H_3PO_4) + 138\ O_2$ (marine organic material. Particles.)

$\downarrow$ (respiration)

$106\ CO_2 + 122\ H_2O + 16\ HNO_3 + H_3PO_4$ (release of inorg. C and nutrients)

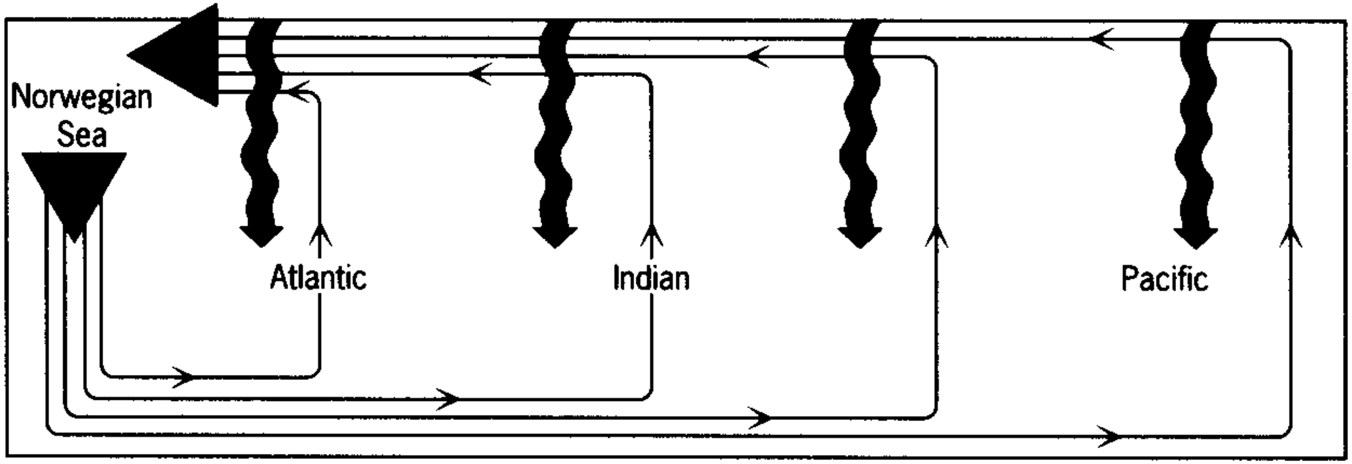
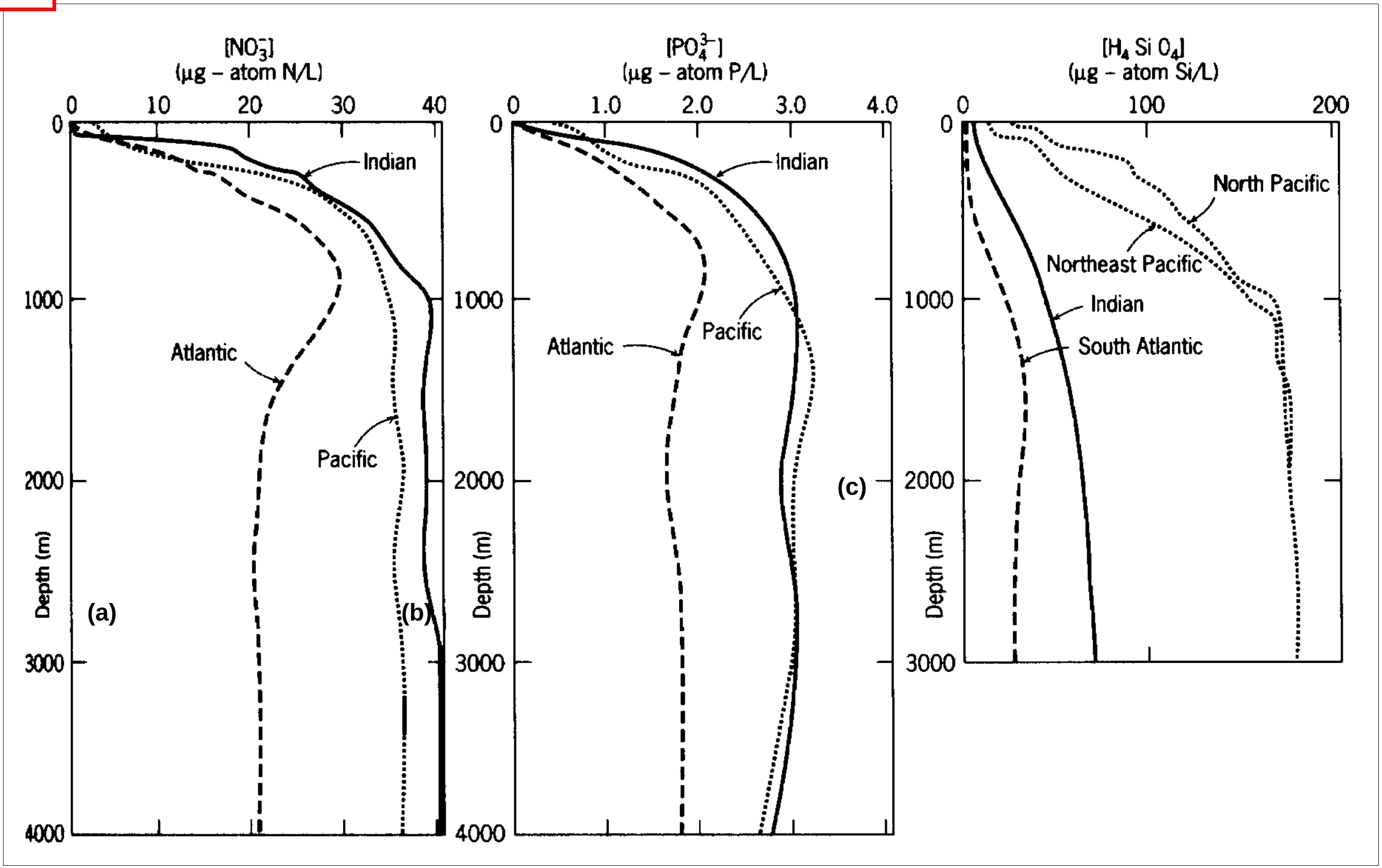


FIGURE 10.5. Idealized vertical section running from the North Atlantic to the North Pacific showing the major advective flow pattern (solid lines) and the rain of biogenic particles (wavy lines). *Source:* From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich, Publishers, Orlando, FL, p. 25. Reprinted by permission.

- Water sinks from the surface in restricted regions
- Deep Waters must return to the surface somewhere
- Where and how are still poorly known

- Major source of cold water in north Atlantic
- Other zones of deep water formation too (Antarctic)
- Time scale to move from deep Atlantic to deep Pacific is several hundred years!
- Whilst conveyor belt moves along water is continuously collecting dissolved nutrients from particle fallout from euphotic zone



For the deep ocean basins (ATLantic, INDian, PACific):

$[\text{nutrients}]_{ATL} < [\text{nutrients}]_{IND} < [\text{nutrients}]_{PAC}$

Distribution – Summary

The distributions of the nutrients in the oceans therefore are controlled by a combination of oceanic circulation and biological activity, and water column recycling processes.

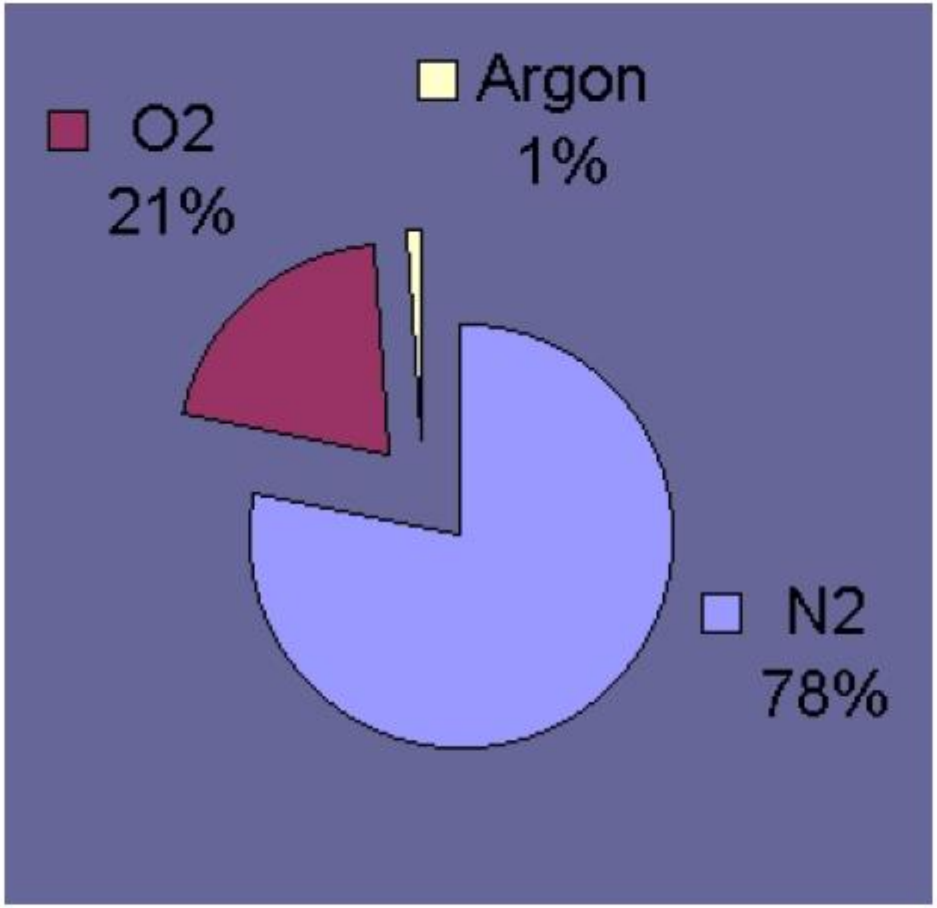
Average abundance of different N species in the sea.

Nitrogen Species	Chemical Formula	Concentration (μMol N kg^{-1})
Dinitrogen	N_2	1200
Nitrate	NO_3	30
Ammonium	NH_4	0.1
Nitrite	NO_2	< 0.1
Nitrous Oxide	N_2O	< 0.1
Dissolved Organic Nitrogen (DON)	various	10

'fixed nitrogen' = all species EXCEPT molecular N_2

Transformations of N dominated by REDOX and enzymatic reactions

Composition of the Atmosphere



How Total Global N is Split Between Different Reservoirs

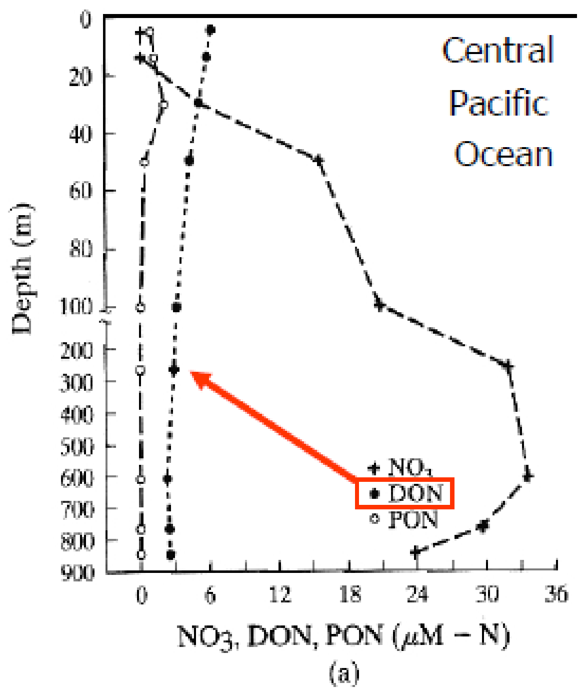
Table 2 N amounts in global reservoirs (Tg N yr^{-1}).

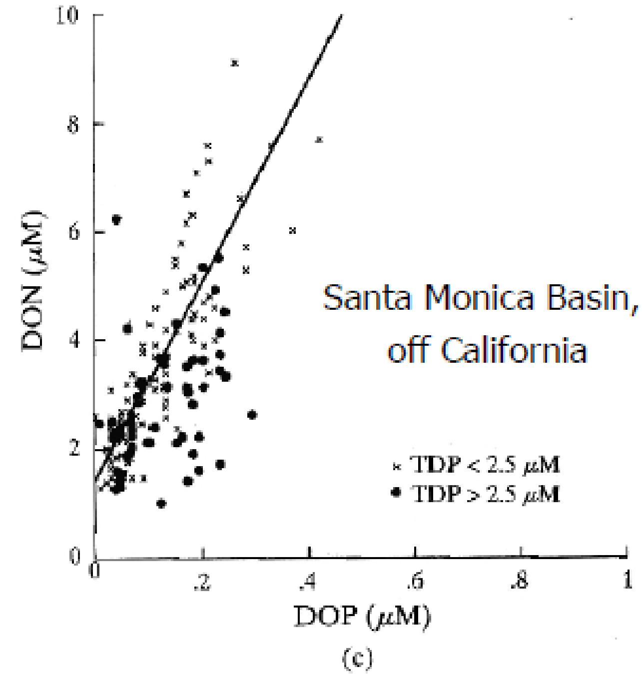
Reservoirs	*Amount*	*Percentage of total*
Atmosphere, N_2	3,950,000,000	79.5
Sedimentary rocks	999,600,000	20.1
Ocean		
N_2	20,000,000	0.4
NO_3^-	570,000	0.0
Soil organics	190,000	0.0
Land biota	10,000	0.0
Marine biota	500	0.0

Source: Mackenzie (1998) except ocean, N_2 from Schlesigner (1997).

(Galloway JN 2005, "The Global Nitrogen Cycle" in Biogeochemistry, vol 8 of *Treatise on Geochemistry*)

DON is more “refractory” (resistant to decay) than DOP





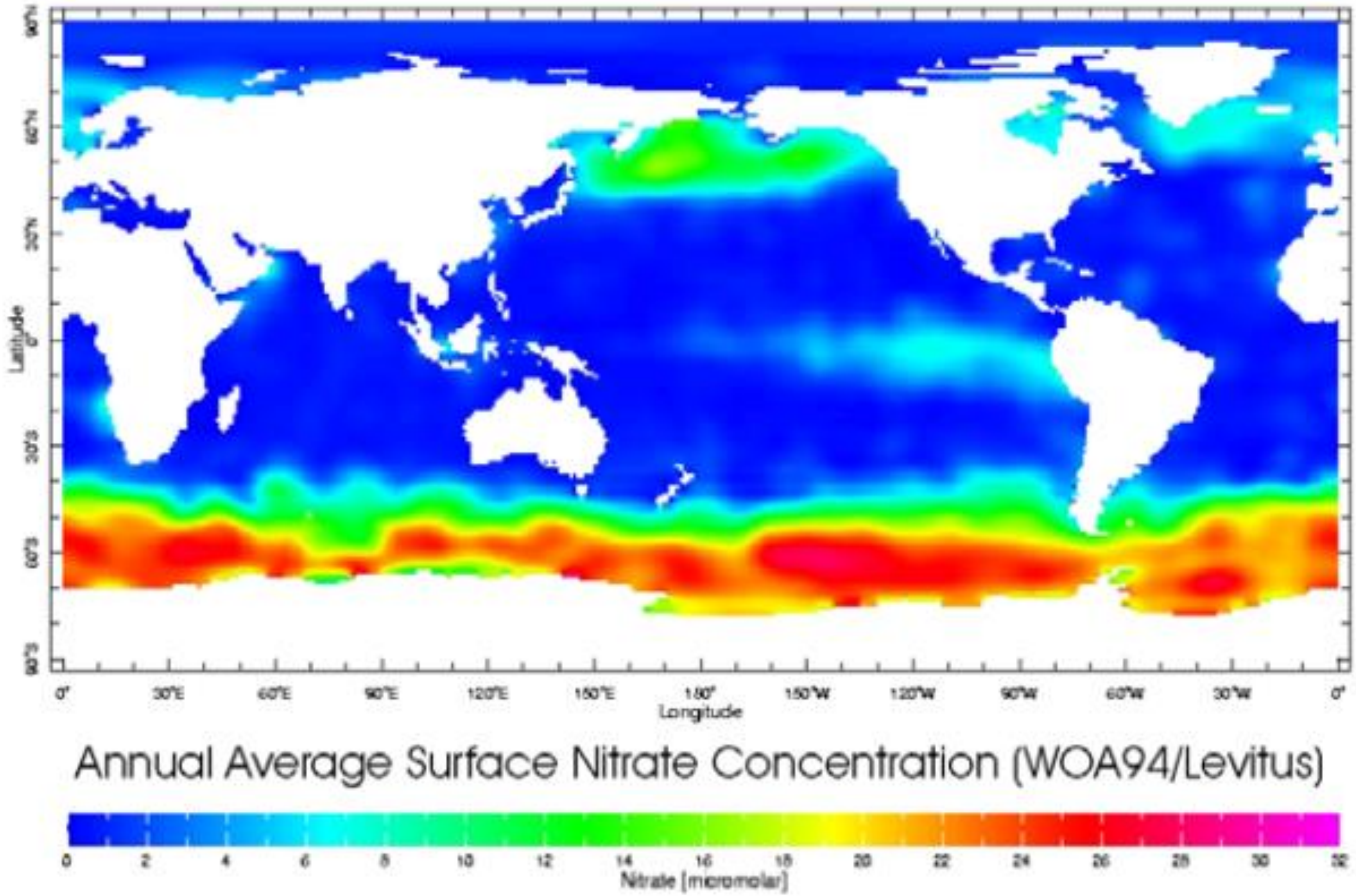
From: figure 8.8 of M.E.Q. Pilson “An Introduction to the Chemistry of the Sea”, Prentice Hall, 1998 (taken in turn from Jackson & Williams (1985) *Deep-Sea Res*. **32**: 223-235)
PON = Particulate Organic Nitrogen.

The Nitrogen Paradox.

The biosphere is bathed in very high concentrations of dinitrogen (N_2). But despite this nitrogen excess, nitrogen starvation is common thoughout the living world. Most organisms cannot utilise the vast amounts of dinitrogen but have to rely instead on the less abundant forms such as nitrate and ammonia. Only specialised micro-organisms (the nitrogen-fixers), or organisms in symbioses with them, can utilise the vast stores of dinitrogen. All other organisms (the large majority) are dependent on the availability of other forms of nitrogen.

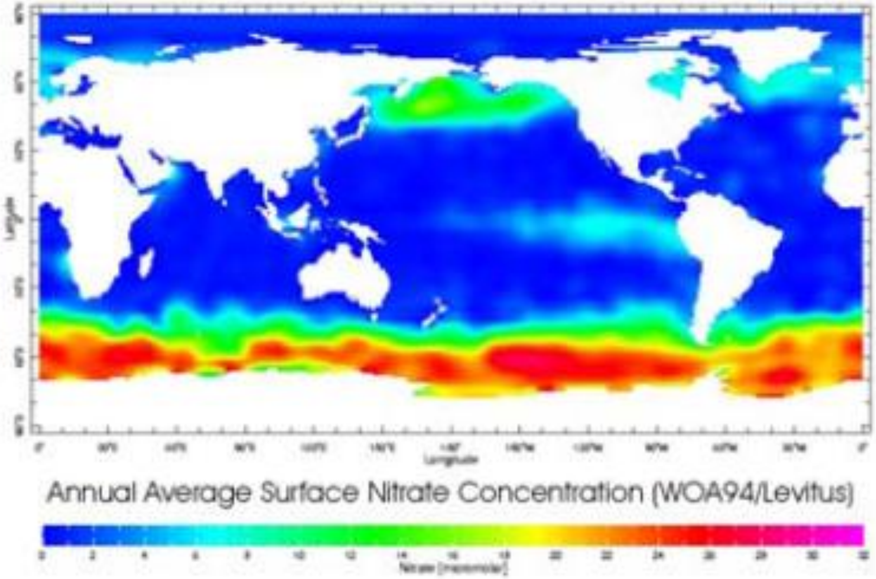
White, T.C.R. *The Inadequate Environment: nitrogen and the abundance of animals.* (Springer-Verlag, Berlin, 1993)

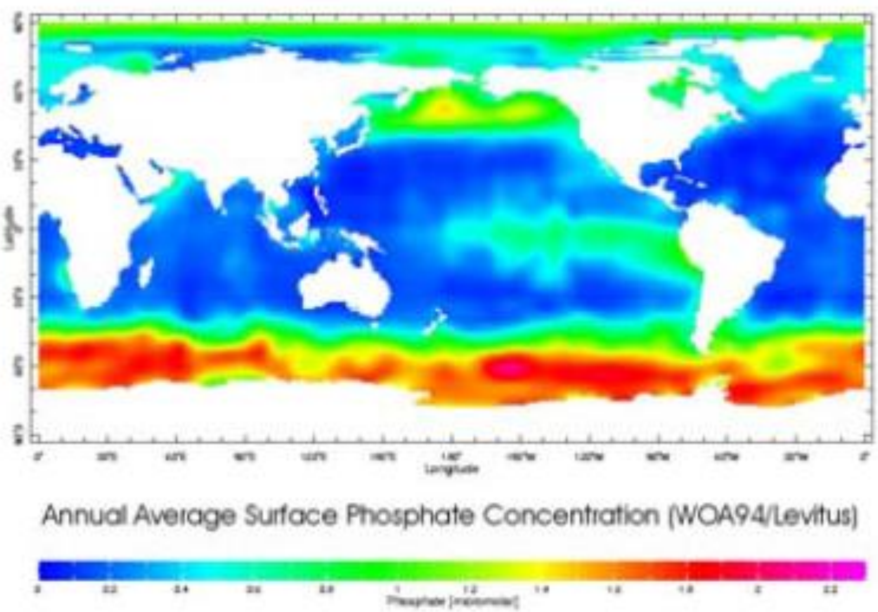
Surface Nitrate Concentration (World Ocean Atlas)



Annual Average Surface Nitrate Concentration (WOA94/Levitus)

Surface Nitrate and Phosphate Concentrations (World Ocean Atlas)



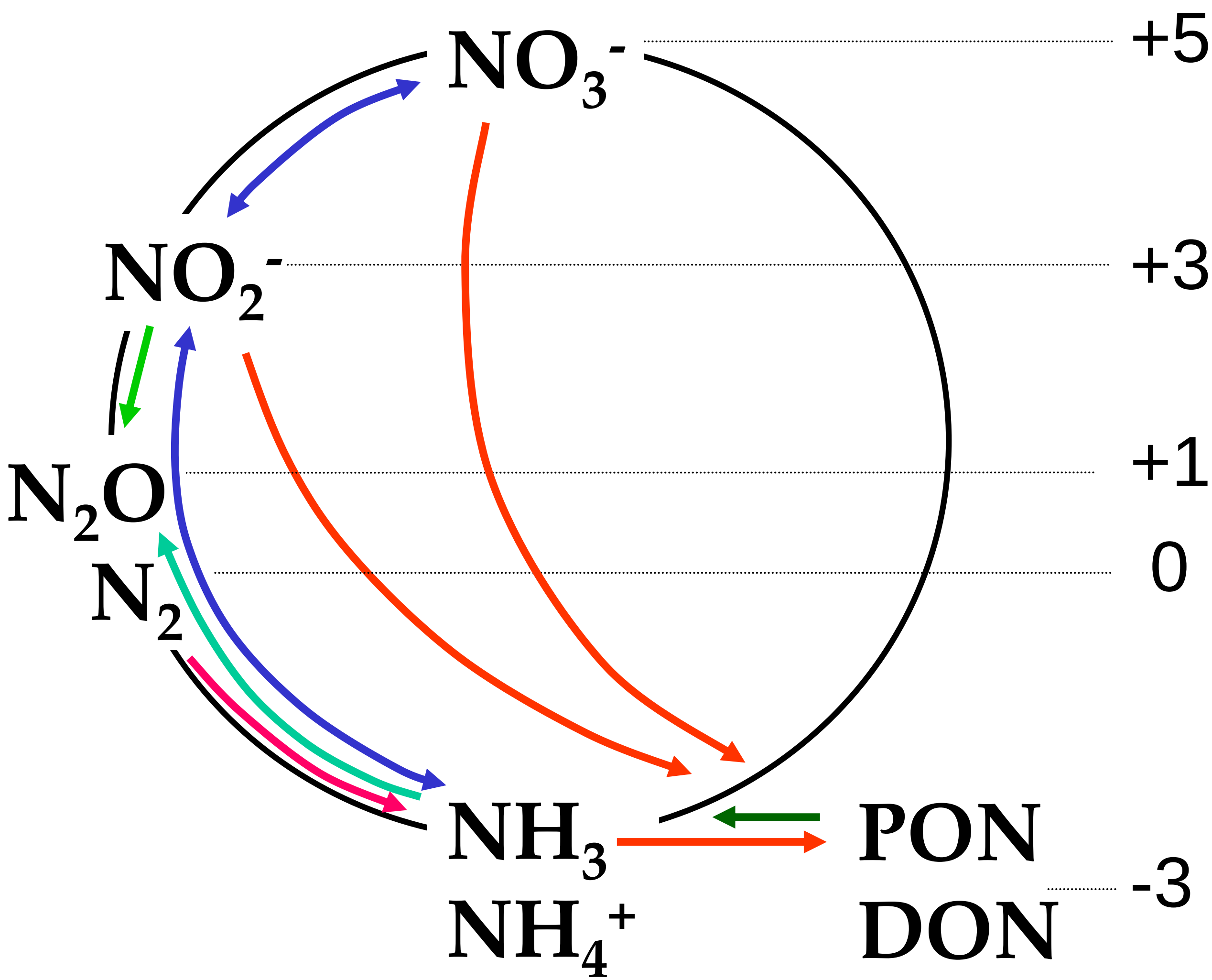


Speciation of N in seawater

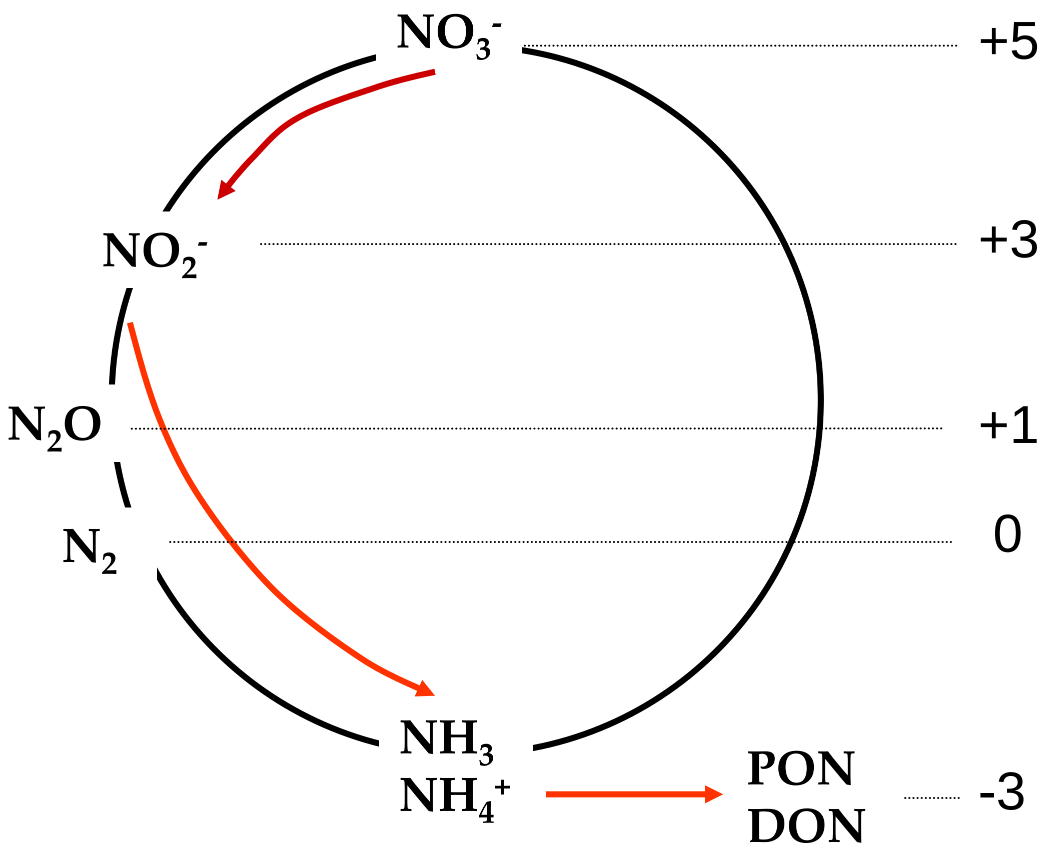
Species	Formula	OxidationNumber
Nitrate	NO_3^-	+5
Nitrite	NO_2^-	+3
Nitric oxide (g)	NO	+2
Nitrous oxide (g)	N_2O	+1
Nitrogen (g)	N_2	0
Ammonia (g)	NH_3	-3
Ammonium	NH_4^+	-3
Organic amine	RNH_2	-3

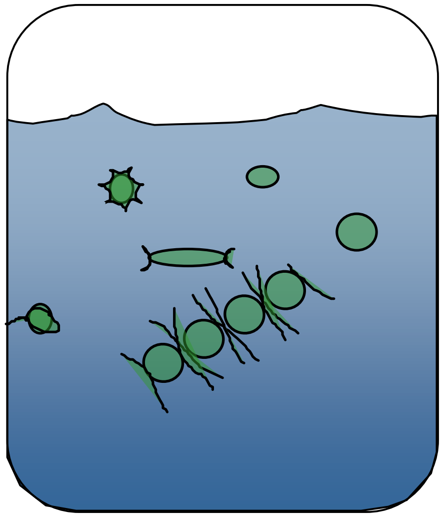
N_2 is the most abundant form in ocean.
Generally unusable by organisms because N≡N bond is difficult to break
In Ocean: most ‘fixed’ N is dissolved NO_3 (stable species in oxic seawater)
On Land: most ‘fixed’ N is stored in plant biomass

Biological Nitrogen Transformation



Nitrogen Assimilation





- Yields nutrient
- Under oxic conditions

Uptake/ Assimilation of N

> Major pathways in Sea

External Environment

NO_3^- NO_2^- NH_4^+ glutamine glutamate

↓ ↓ ↓ ↓ ↓ ***Transport***

Cell ↓ ↓ ↓ ↓ ↓

NO_3^- → NO_2^- → NH_4^+ → glutamine → glutamate → →

1a 1b 2a 2b

|---------------- *Assimilation* ---------------------------|

NO_3^- Uptake: Algae, bacteria, fungi, plants

1a. Nitrate reductase (NaR)

1b. Nitrite reductase (NiR)

NH_4^+ Uptake: Algae, bacteria, fungi, plants

2a. Glutamine synthetase (GS)

2b. Glutamate synthase (GOGAT)

Assimilatory Nitrate Reduction (e.g. by phytoplankton)

$$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$$

$$2\,NO_2^- + 4H^+ + 4e^- \rightarrow N_2O_2^{2-} + 2\,H_2O$$

$$N_2O_2^{2-} + 6H^+ + 4e^- \rightarrow 2\,NH_2OH$$

$$NH_2OH + 2H^+ + 2e^- \rightarrow NH_3 + H_2O$$

- *Reduction of N*
- *This requires energy!*
- *NH_2OH is hydroxylamine*
- *$N_2O_2^{2-}$ is hyponitrite*

- The NH_3 can then be synthesized through reaction with carboxylic acids (R-COOH) into various amino acids without further change in oxidation number.
- Some phytoplankton have transport systems which favour the uptake of reduced N-species (e.g. NH_4^+, $(NH_2)_2CO$ (urea))
- These species are generally removed most rapidly from seawater
- Some phytoplankton cannot assimilate NO_3^-

What happens to the assimilated N?

1. Plants die in surface layers where there is light

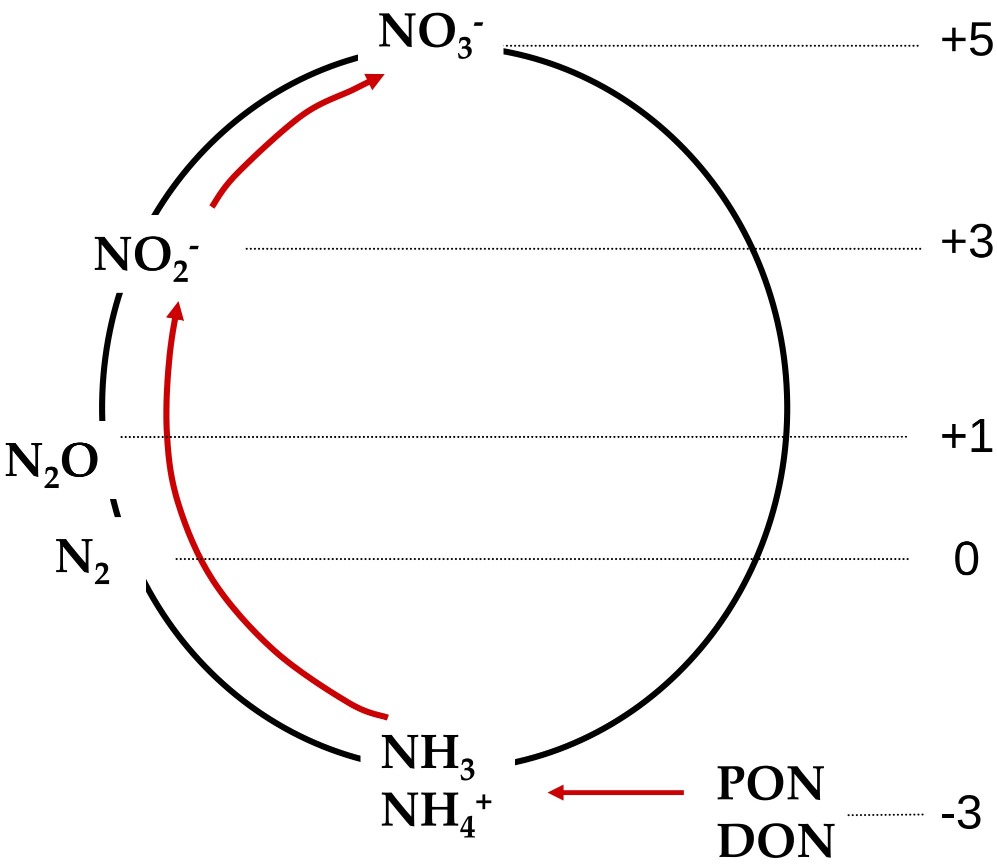
2. Plants get eaten in surface layer by grazers (Protozoa, zooplankton) → reduced forms of N are excreted (NH_3, urea)

3. Or plants sink and die, or die and sink, or animals die and sink, etc… that is, PON sinks into deeper water below euphotic zone

$$\mathrm{PON} \xrightarrow{\text{cell lysis}} \mathrm{DON} \xrightarrow{\text{ammonification}} \mathrm{NH_3} \qquad \textit{FAST}$$

$$\mathrm{NH_3} \xrightarrow{\text{oxidation by Nitrosomonas}} \mathrm{NO_2^-} \xrightarrow{\text{oxidation by Nitrobacter}} \mathrm{NO_3^-} \qquad \textit{SLOW}$$

Nitrification (Bacterial)



- Yields energy (autotrophic: used to synthesize ATP = energy for biomass formation)
- Oxic conditions

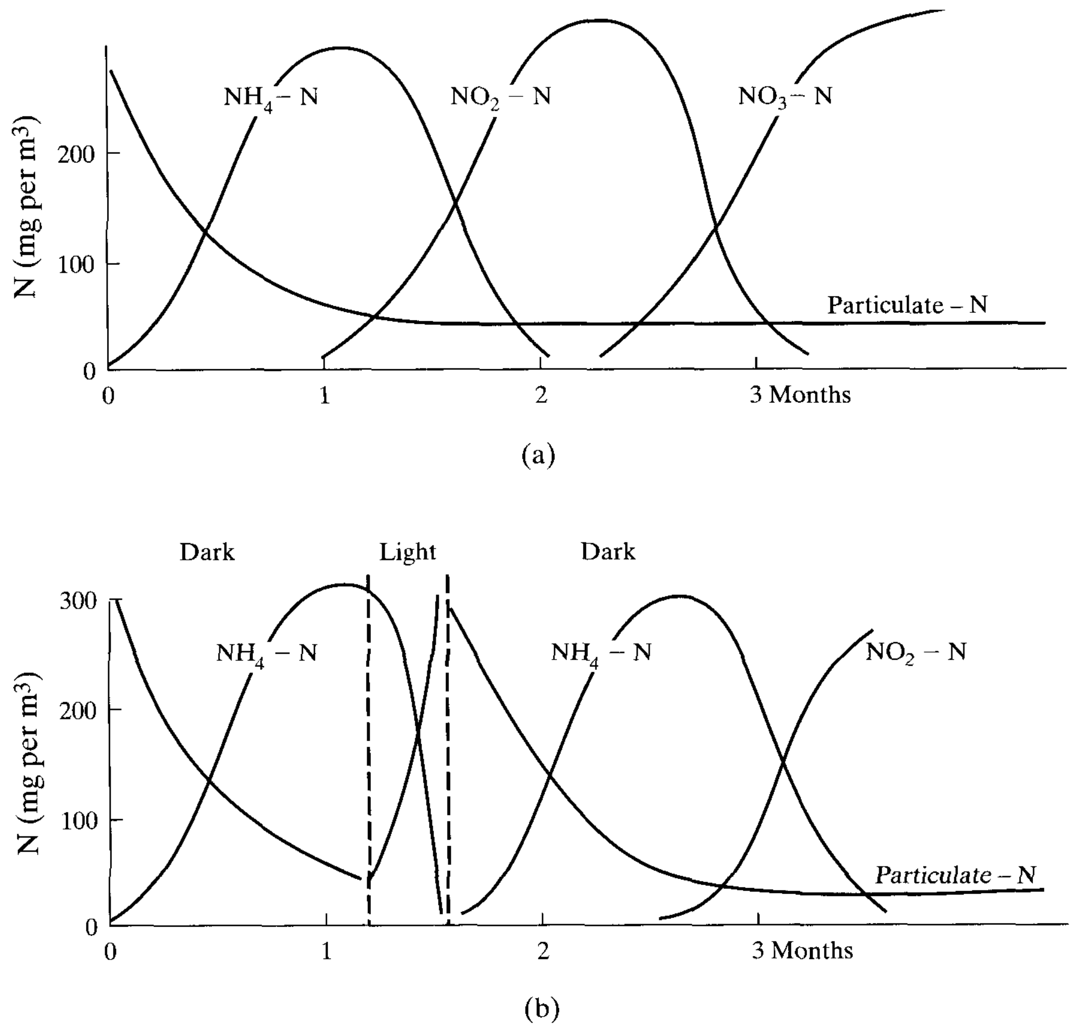
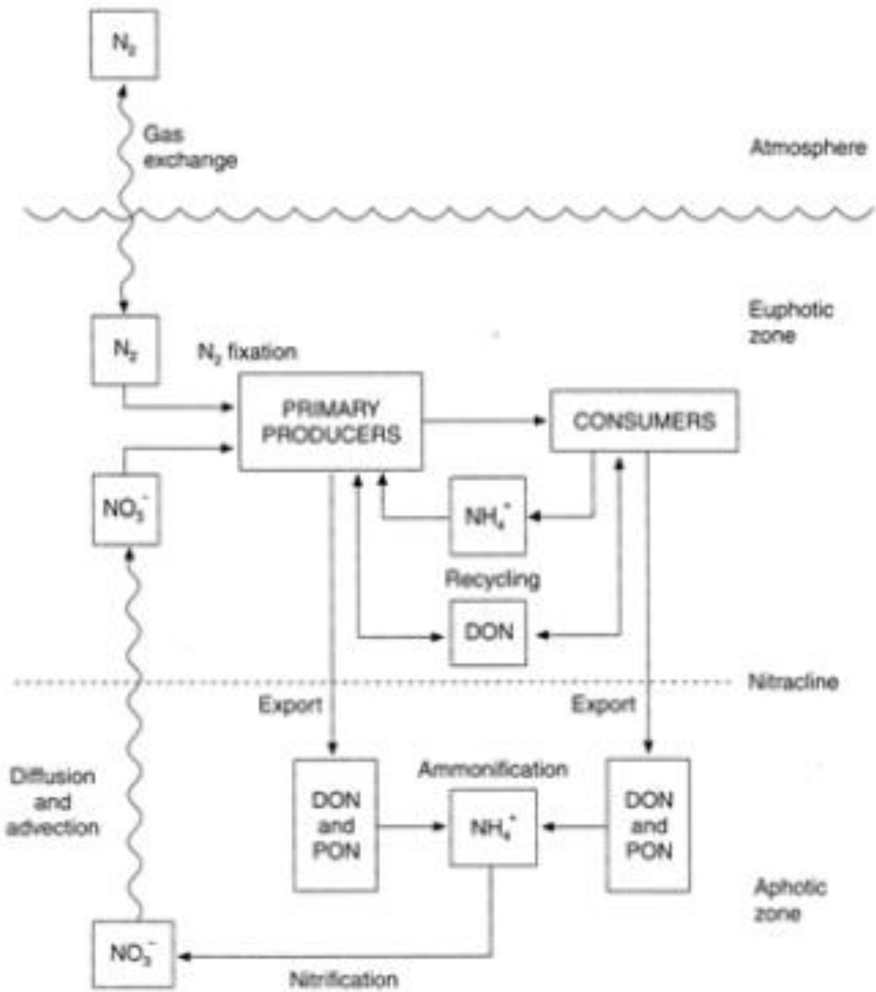


Figure 8.7 *In a series of experiments during the 1930s, Von Brand and Rakestraw stored suspensions of diatoms in seawater in the dark and observed the production of ammonia and its conversion to nitrite and finally to nitrate (a). If the processes were interrupted by placing the experimental carboys in a lighted window, ammonia was taken up during the formation of organic matter as diatoms regrew to their original density. When placed back in the dark, the sequence began as before (b).* (Reprinted with permission from Harvey (1957). Copyright by Cambridge University Press..)

In deeper water, below Euphotic Zone...

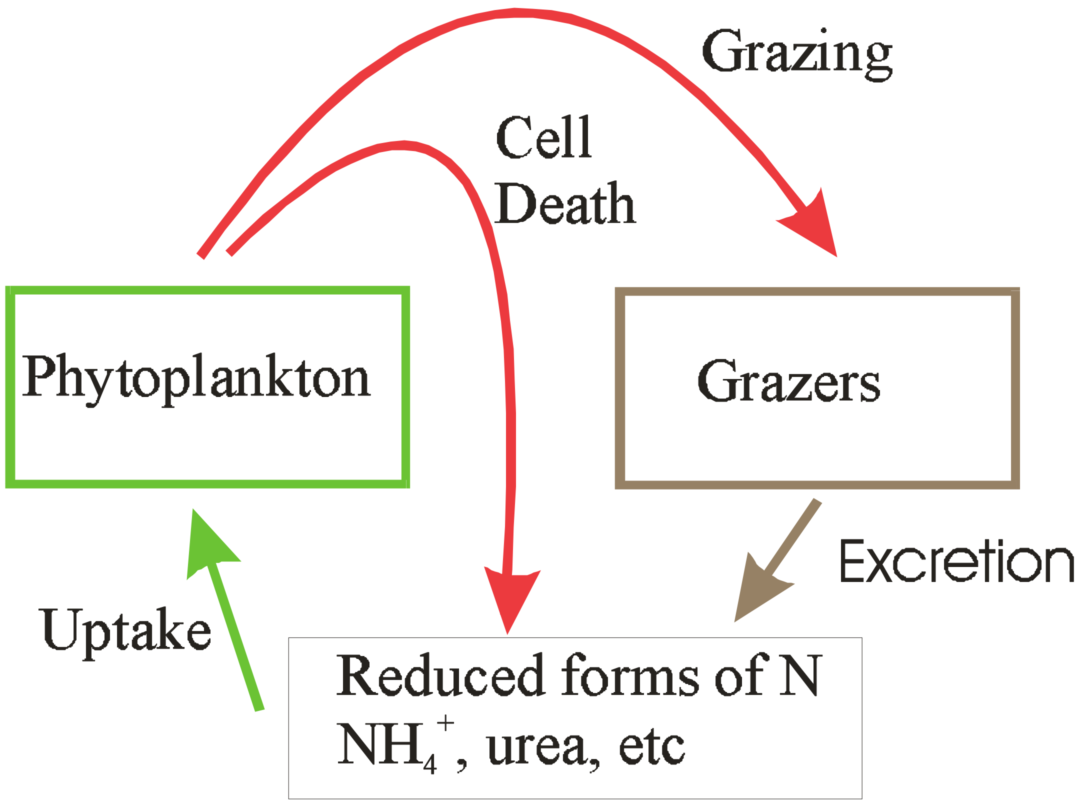
- Nitrification of NH_3 takes place in the presence of O_2 (SLOW, takes months)
- Mediated by two groups of bacteria
- NO_3 is the thermo-dynamically stable form of N

Nitrogen Cycle of the Open-Ocean (Surface Waters)

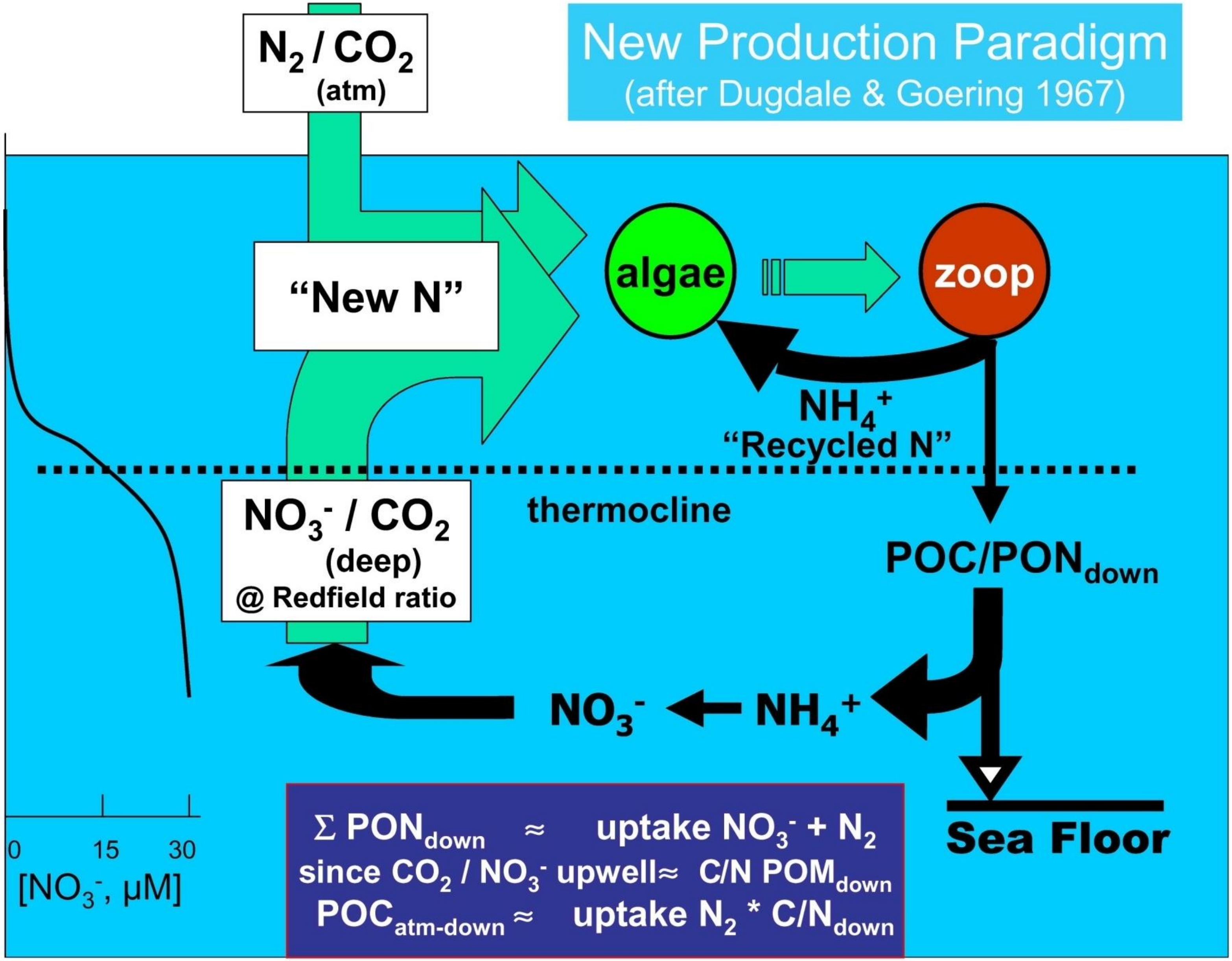


(Karl DM, 2001, Nitrogen Cycle, In: *Encyclopedia of Ocean Sciences*, Academic Press)

Surface Ocean Nitrogen Recycling



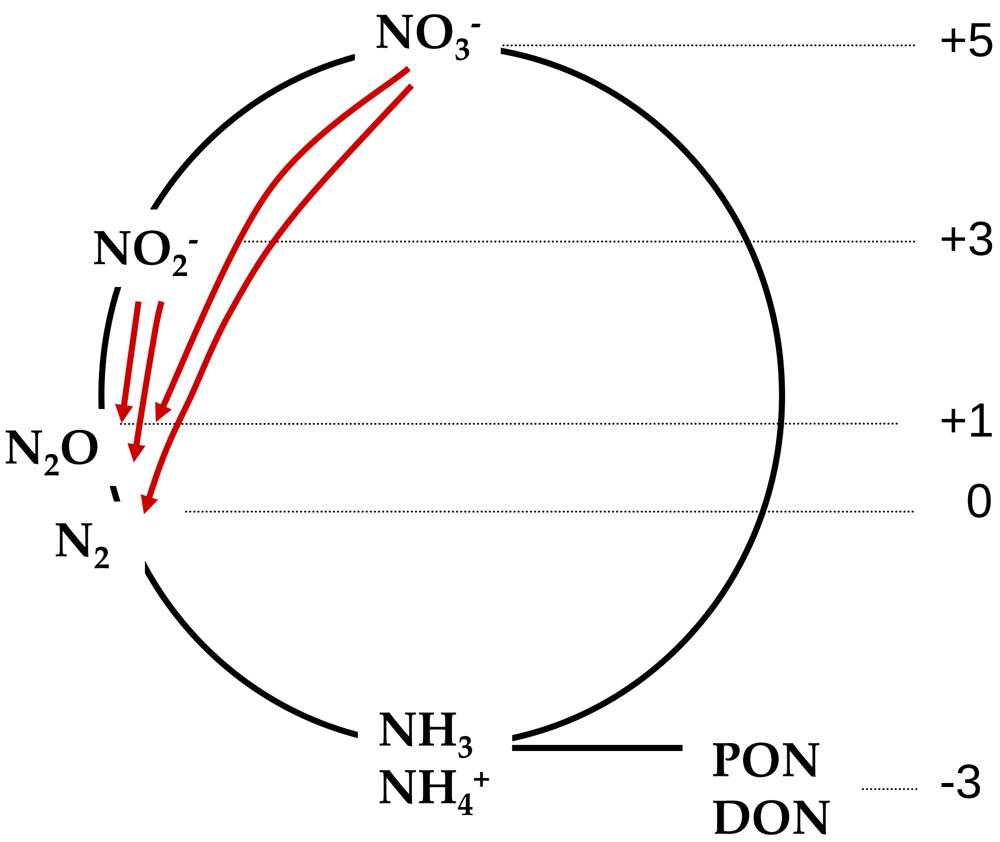
- Recycling of reduced forms of N in the ocean surface layer is fast and efficient.
- Production supported by this 'recycled' N is called 'regenerated production'

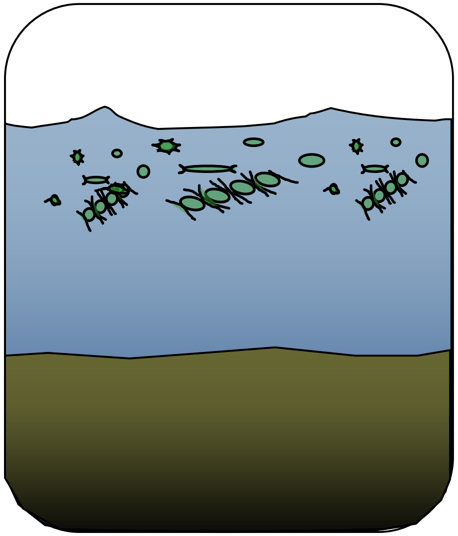

New Production Paradigm
(after Dugdale & Goering 1967)
N_2 / CO_2
(atm)
"New N"
algae
zoop
NH_4^+
"Recycled N"
thermocline
NO_3^- / CO_2
(deep)
@ Redfield ratio
POC/PON_{down}
NO_3^-
NH_4^+
Sea Floor
0
15
30
[NO_3^-, μM]
$\Sigma\ PON_{down}$ ≈ uptake NO_3^- + N_2
since CO_2 / NO_3^- upwell ≈ C/N POM_{down}
$POC_{atm\text{-}down}$ ≈ uptake N_2 * C/N_{down}

Sources and Sinks of Fixed Nitrogen

- In seawater containing O_2, NO_3^- is the thermodynamically stable form (not N_2)
- Most N is in the form of N_2 because of kinetic limitations (energy required to break N-triple bond)
- When seawater is anoxic, $[O_2] \approx 0$, then NO_3^- is the next most favoured oxidising agent

Denitrification (dissimilatory pathway)





- NO_3^- used as electron acceptor (in place of oxygen) →heterotrophic
- Anoxic conditions in Oxygen minimum zones or sediments

Denitrification or Anammox?

Anammox stands for Anaerobic Ammonium Oxidation

- Process first observed in waste-treatment plants, now also in the Black Sea, Gulfo Dulce (off Costa Rica), Benguela, etc

- Which of denitrification or anammox destroys most DIN in the oceans?

Dalsgaard *et al.* (2003) *Nature,* **422**, 606-608; Kuypers *et al.* (2003) *Nature,* **422**, 608-611; Kuypers et al. (2005) *PNAS,* **102**, 6478-6483

Denitrification

... + PO**N** + **N**O3 → **N2** + ...

Annamox

... + **N**O2 + **N**H4 → **N2** + ...

How to tell which is removing DIN?

- spike with $^{15}NH_4$ and see if $^{15}N^{14}N$ is produced
- spike with $^{15}NO_3$ and see if $^{15}N^{14}N$ is produced

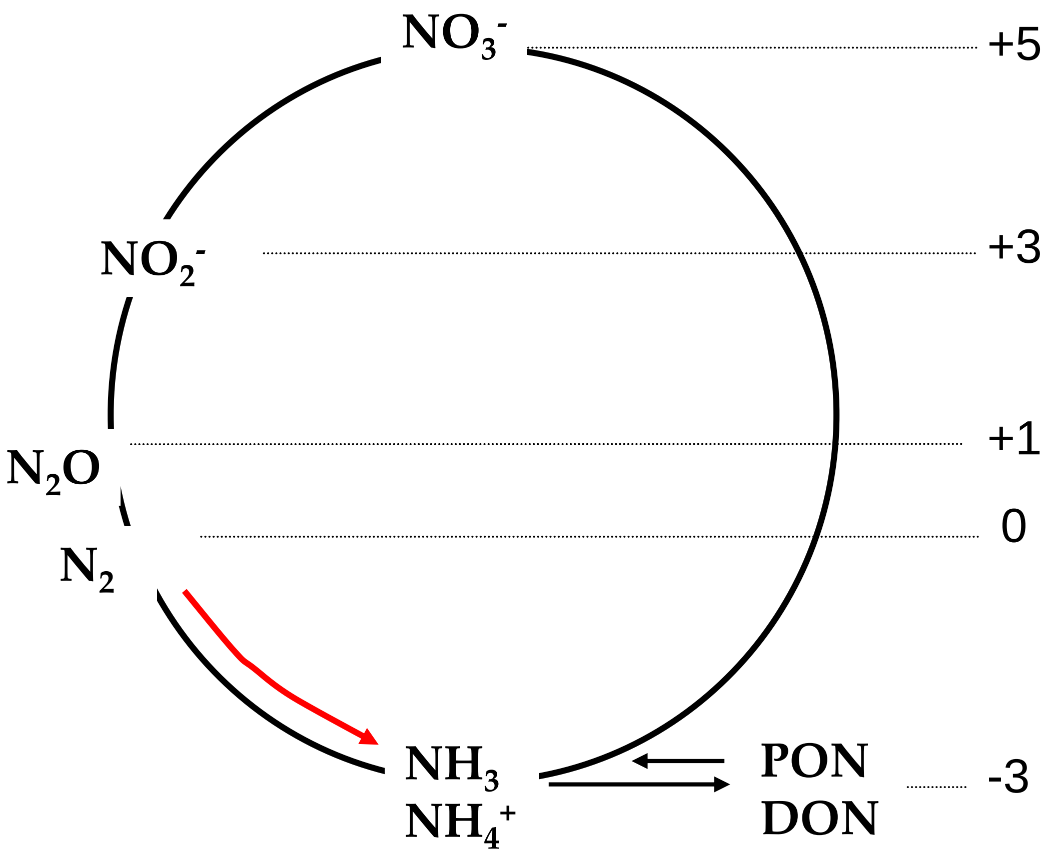
Nitrogen Fixation

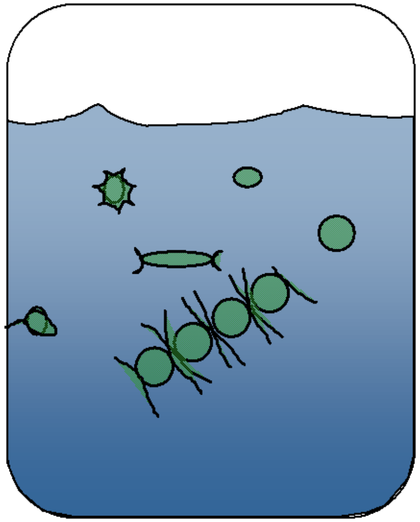
- $N \equiv N \rightarrow$ organic-N compounds
- requires significant energy
- relatively few species can do the job

In open ocean:

- restricted to photosynthetic cyanobacteria found most often in tropical coastal water (plus some heterotrophs)
- Requires Nitrogenase enzyme!!!
- North Atlantic sub-tropics and tropics seem to be regions of net N-fixation
- Most other oceanic N-fixers are benthic, symbiotic and/or heterotrophic. Live in shallow systems, salt marshes, etc.

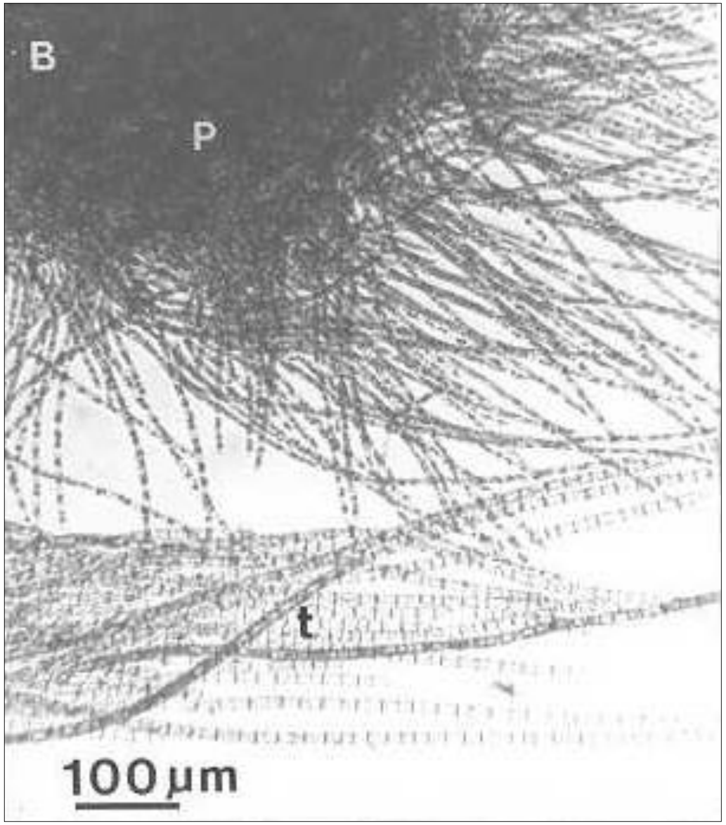
Biological N fixation



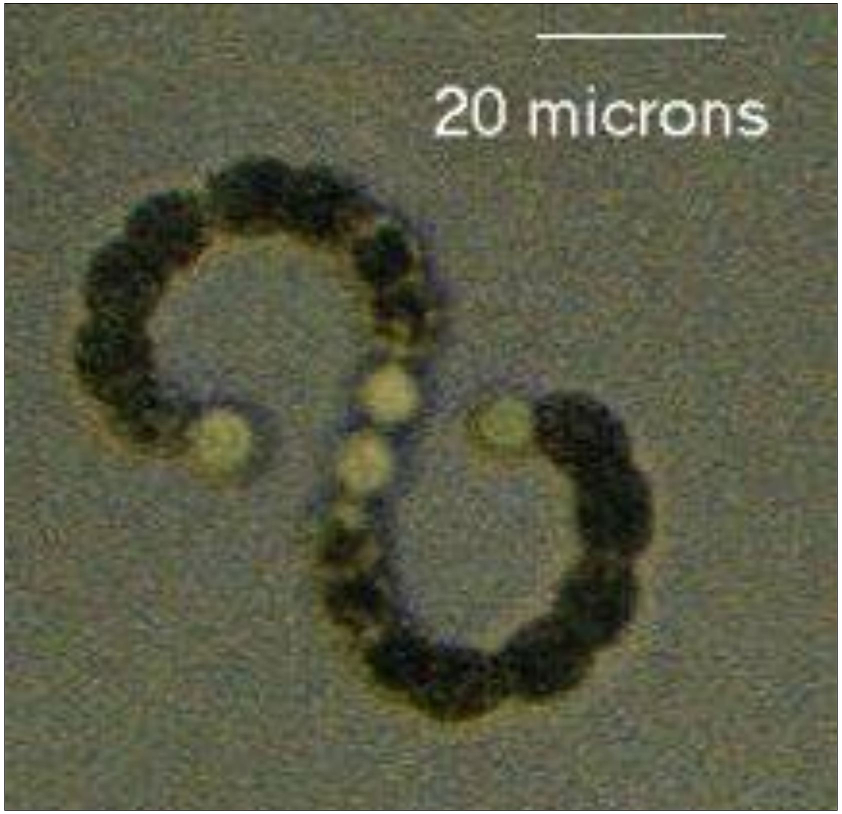


- Yields nutrient
- Locally anoxic conditions

Nitrogen-Fixers

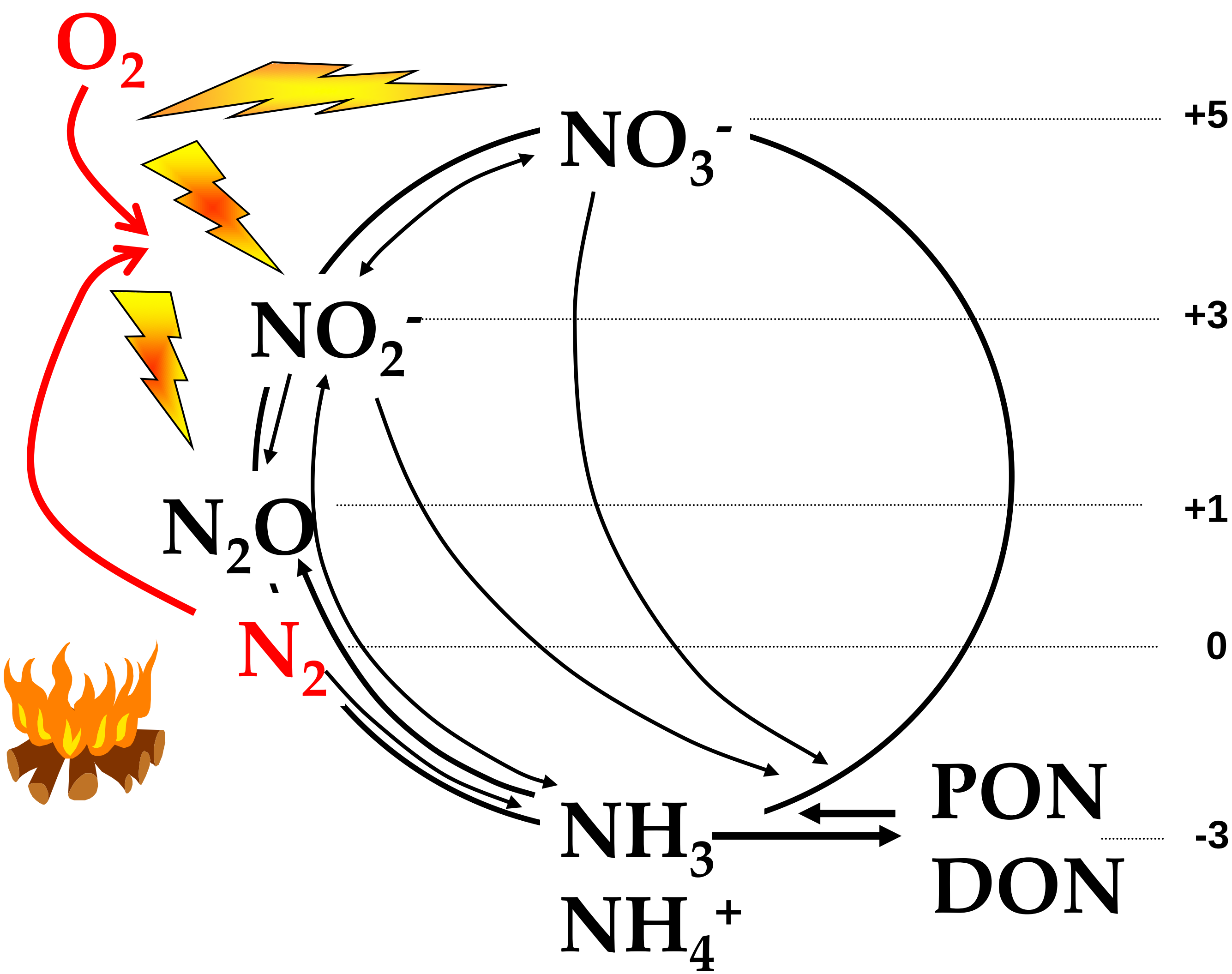


A puff (p) form of *Trichodesmium sp.* and a tuft (t) form of *T. thiebautii*

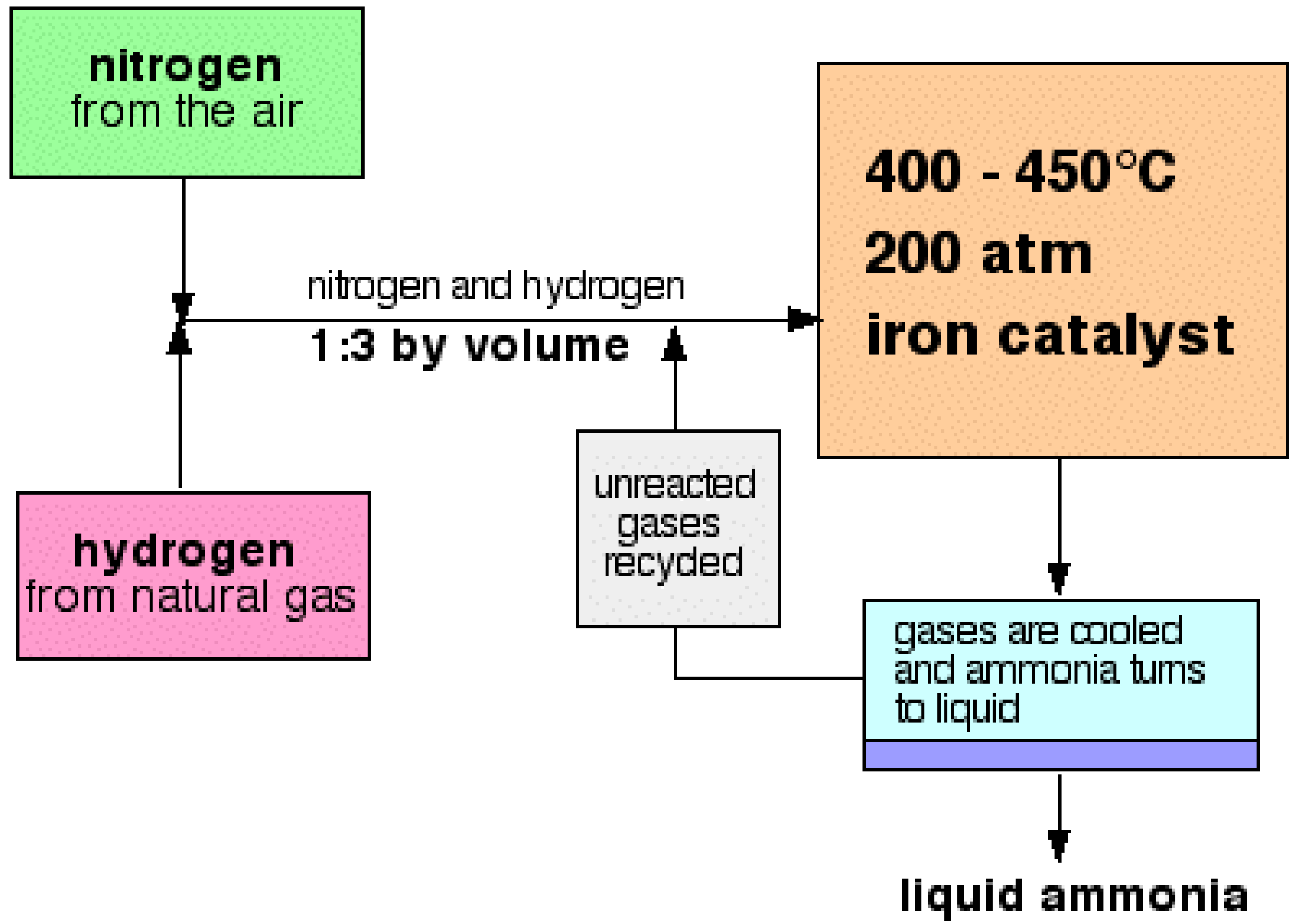


Anabaenopsis circularis and developing pair of heterocysts

Inorganic Nitrogen Fixation



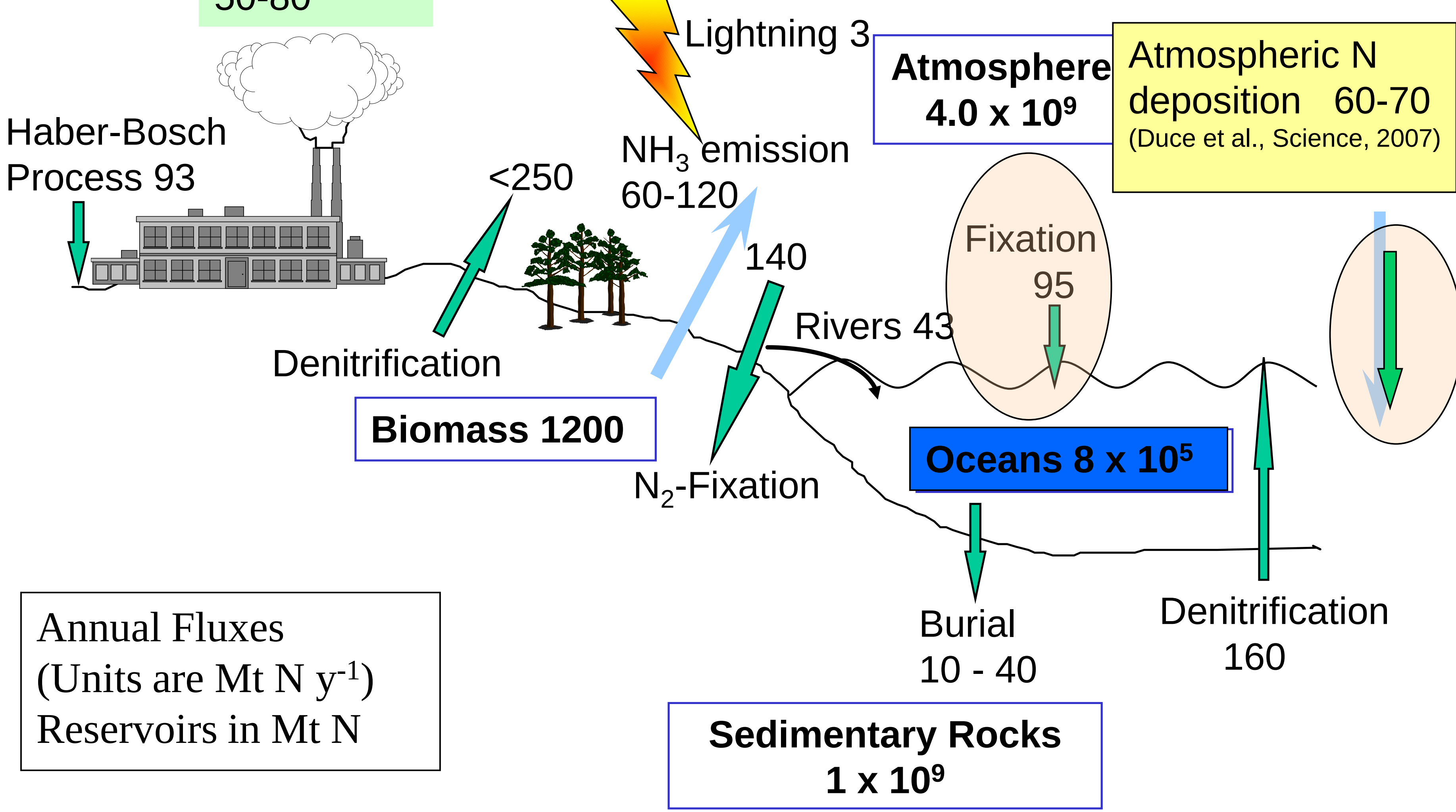
Industrial Nitrogen Fixation



$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \qquad \Delta H = -92\ \text{kJ mol}^{-1}$$

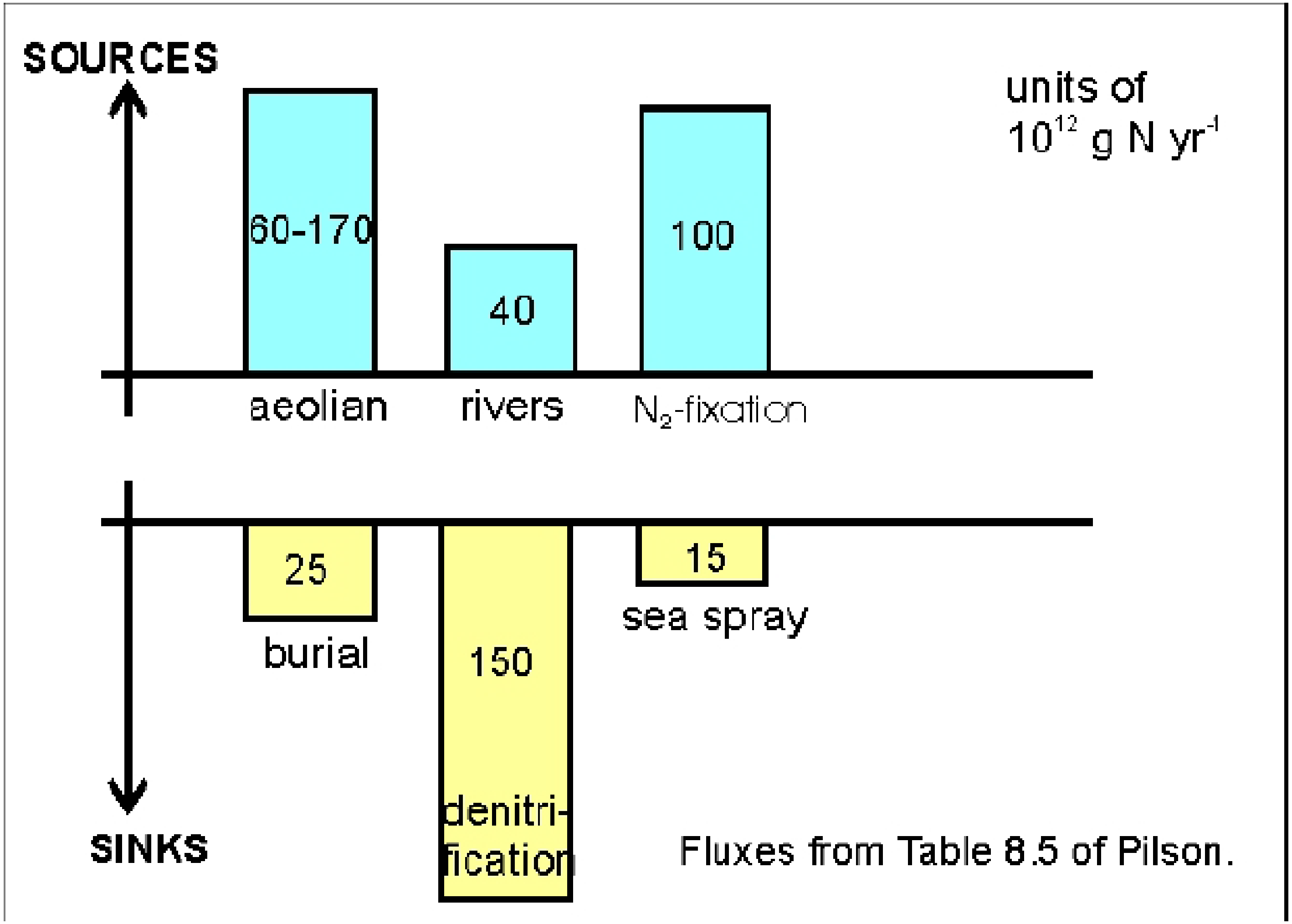
Global Nitrogen Cycle

Oceanic N_2-Fixation:
Current estimates: 100-200
Recent estimates (1990's): 10-20



Annual Fluxes
(Units are Mt N y^{-1})
Reservoirs in Mt N

Magnitude of N fluxes in the ocean.



** But the size of most fluxes is not accurately known **