Lecture 23:
Marine Nitrogen Cycle

Karen Casciotti

Overview

- Why study the nitrogen cycle?
- Nitrogen pools, fluxes, and distributions
- Biogeochemical transformations
- Open questions
- Human impacts on the nitrogen cycle

Life Needs Nitrogen

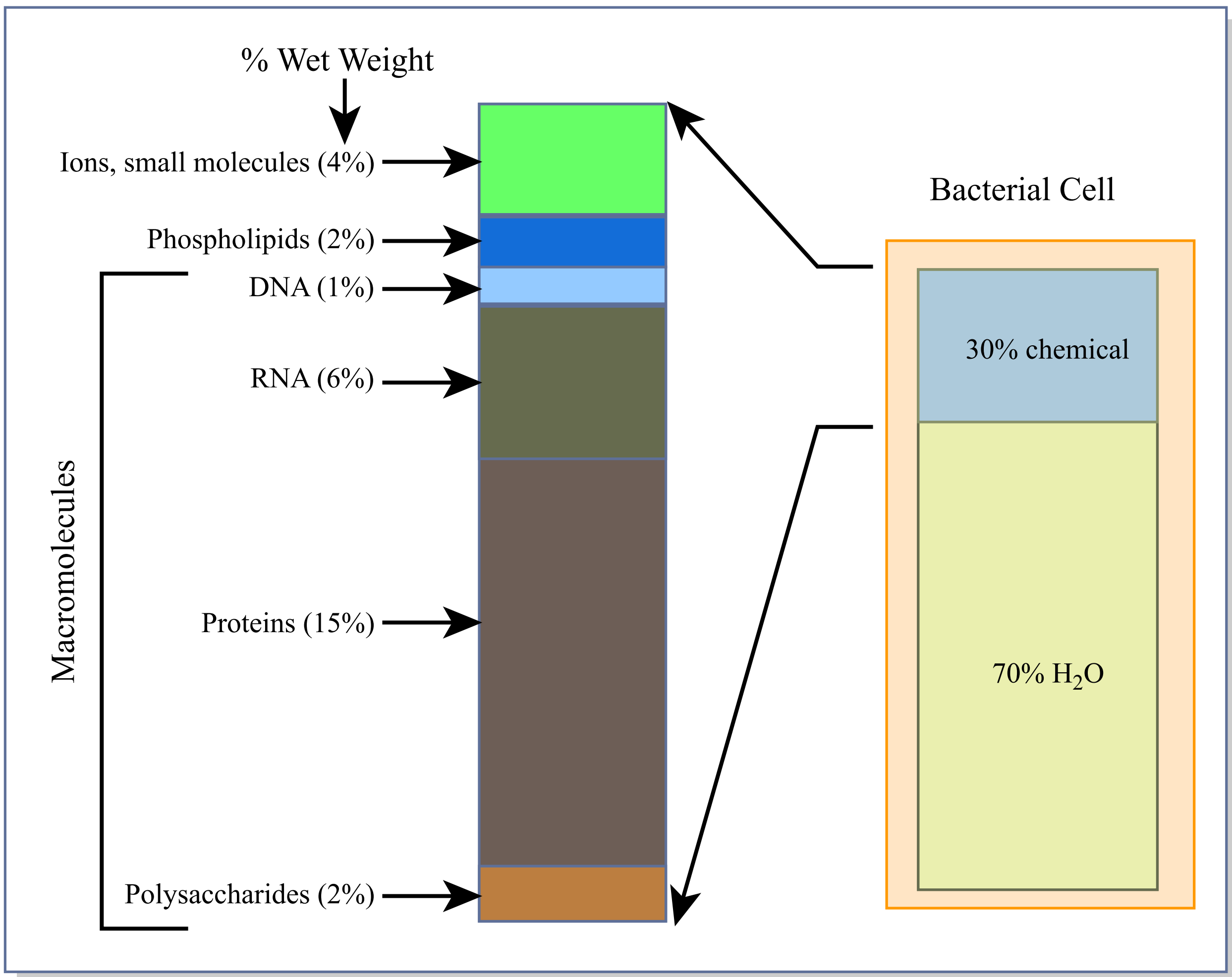


Figure by MIT OCW.

Overall Phytoplankton
C:N = 6.6
N:P= 16:1

* $C_{39}H_{53}O_{24}N_{15}P_4$

  C:N = 2.6

* $C_{61}H_{97}O_{20}N_{16}$

  C:N = 3.8

Nitrogen transformations

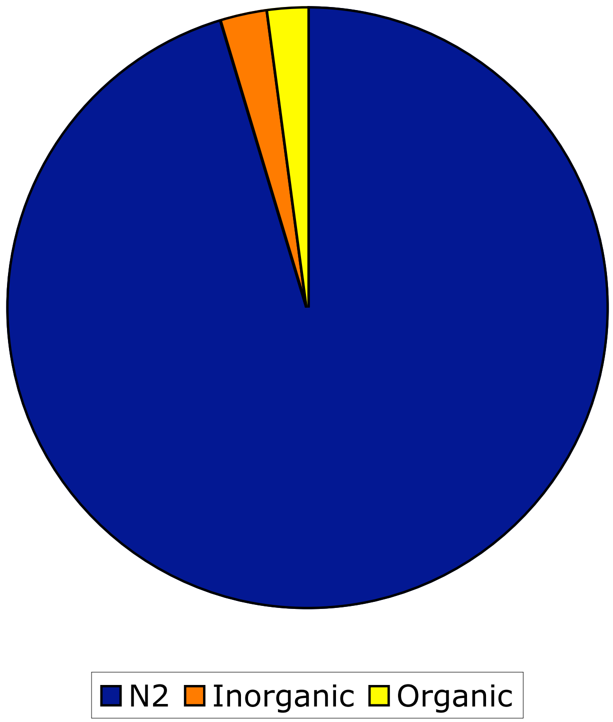
Chemical species	Oxidation state	
N_{org}, NH_4^+	-III	Reduced
NH_2OH	-I	↓
N_2	0	↓
N_2O	I	↓
NO	II	↓
NO_2^-	III	↓
NO_3^-	V	Oxidized

Marine Nitrogen Pools

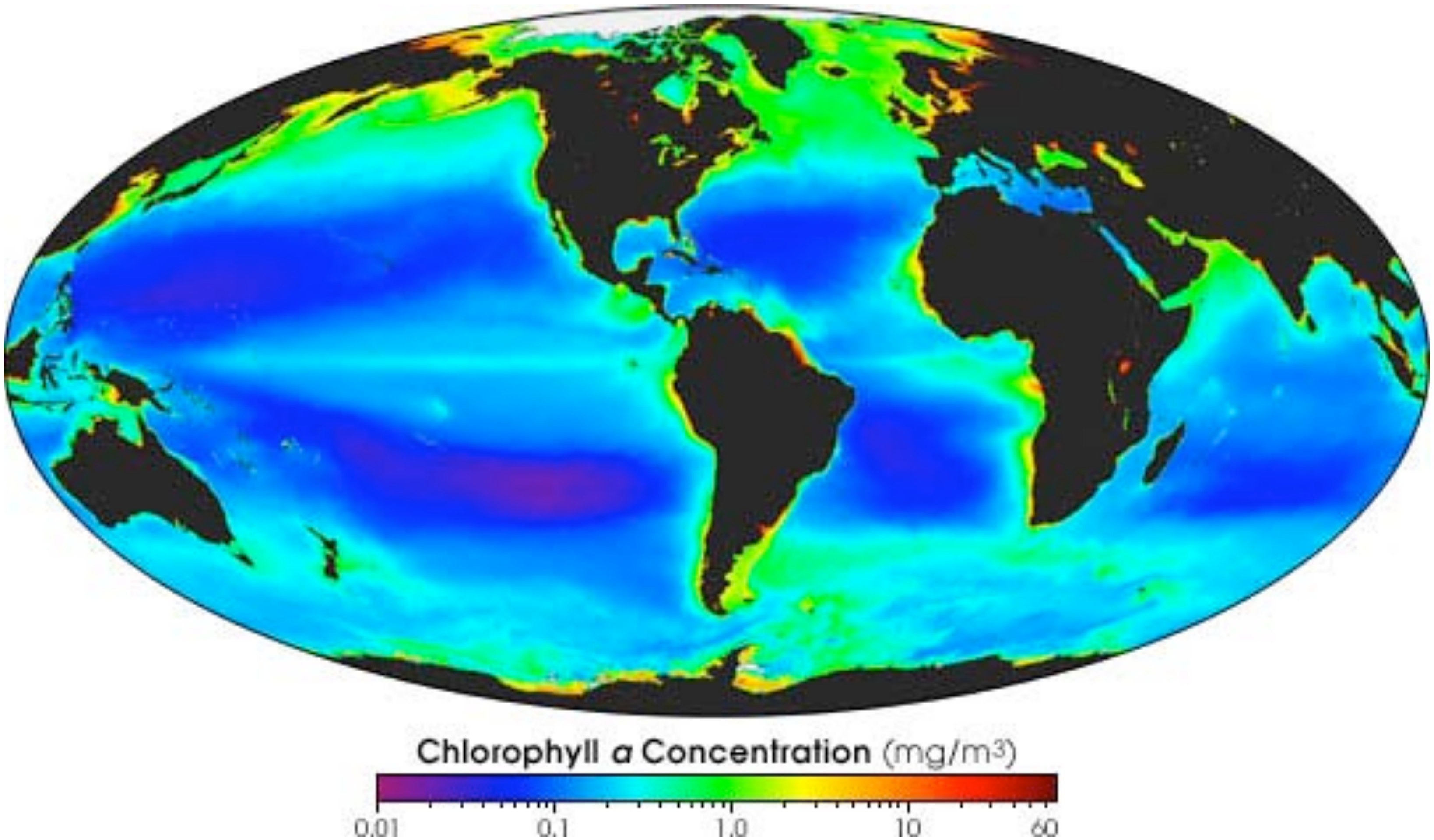
- **Nitrogen gas (N_2)** — **95.2 %**
  - Nitrous oxide (N_2O)
  - Nitric oxide (NO)

- "Fixed" Nitrogen
  - Inorganic nitrogen:
    - **Nitrate (NO_3^-)** — **2.5 %**
    - Nitrite (NO_2^-)
    - Ammonium (NH_4^+)

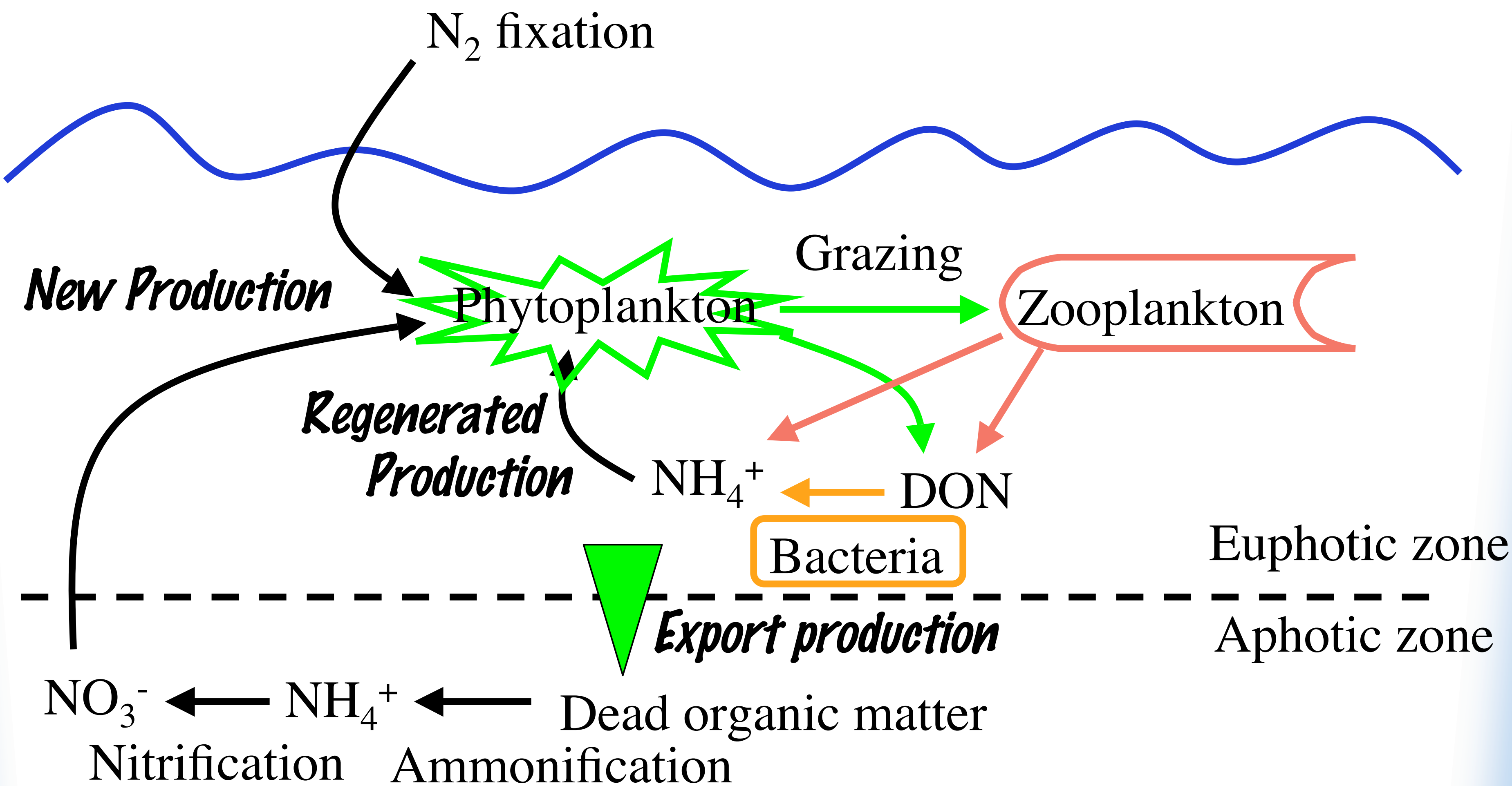
  - Organic nitrogen:
    - **Detritus** and Living biomass — **2.3%**
    - Dissolved organic matter
      - Proteins/Amino acids
      - Urea
      - Nucleic acids



Sea Surface Chlorophyll *a*



Dugdale and Goering, 1967: the New Production paradigm

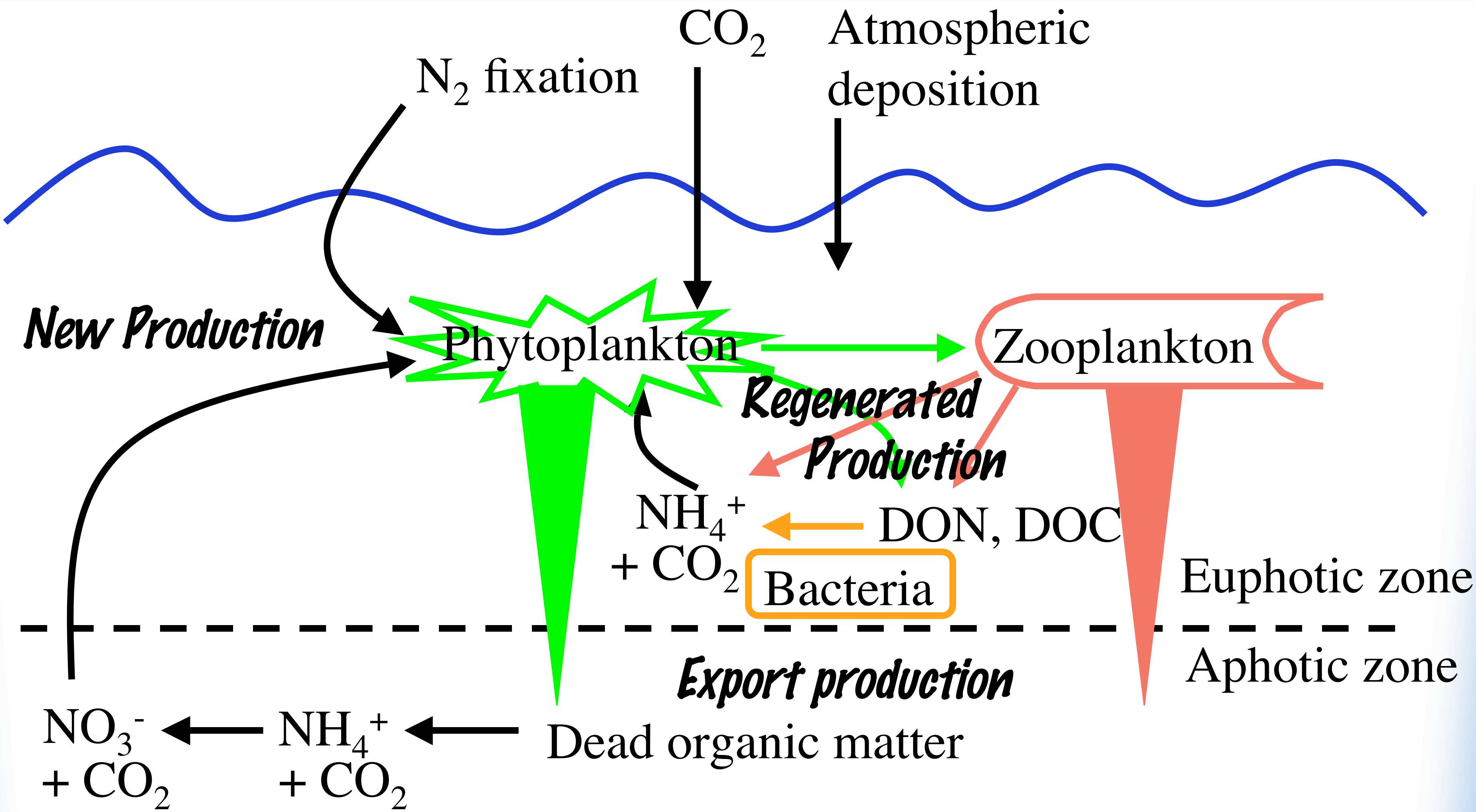


Dugdale and Goering, 1967: the New Production paradigm

- Introduced the concept of balanced new and export production
- Introduced the use of ^{15}N-labeled compounds to measure rates of new and regenerated production.

- “Ammonium is an important nitrogen source… but nitrate and nitrogen fixation are the most important parameters with respect to nitrogen limitation of primary productivity.”

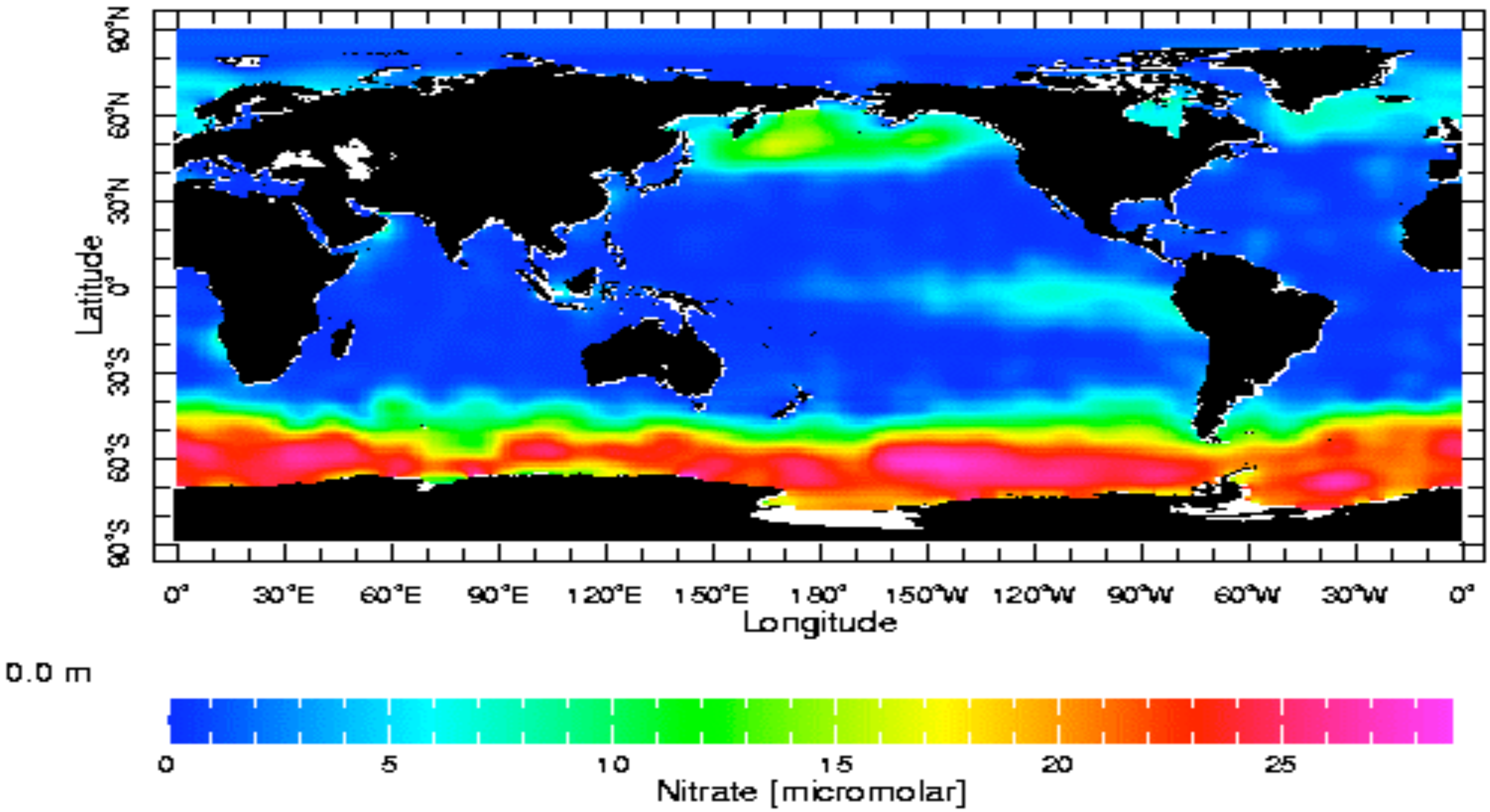
Eppley and Peterson. 1979:
Export Production and the "Biological Pump"



Eppley and Peterson, 1979

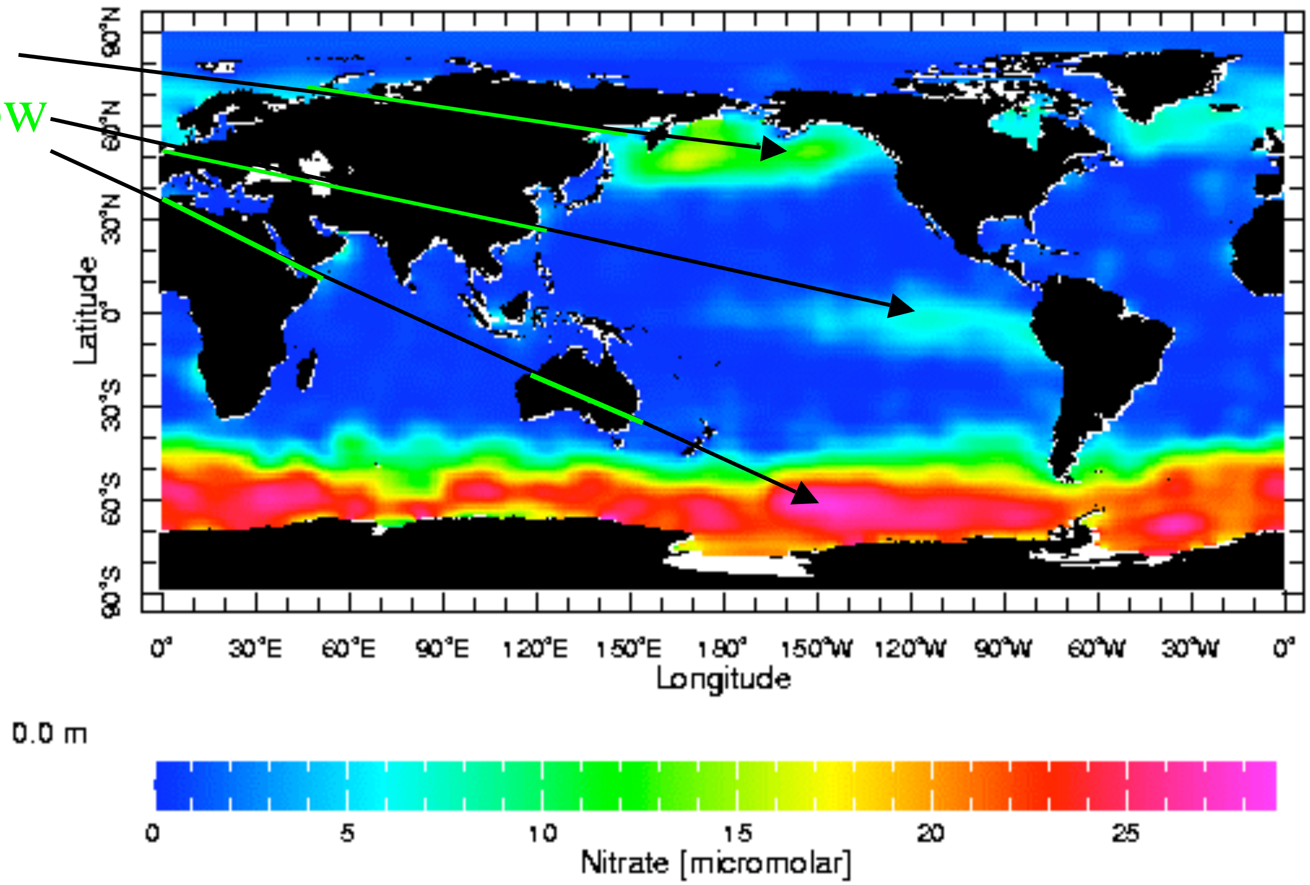
- "Only the sinking flux due to new production associated with N_2 fixation and atmospheric sources of N can be identified as… transport of atmospheric CO_2 to the deep ocean."
- Introduced "f ratio" as ratio of new/total production

Sea Surface Nitrate Map



Sea Surface Nitrate Map

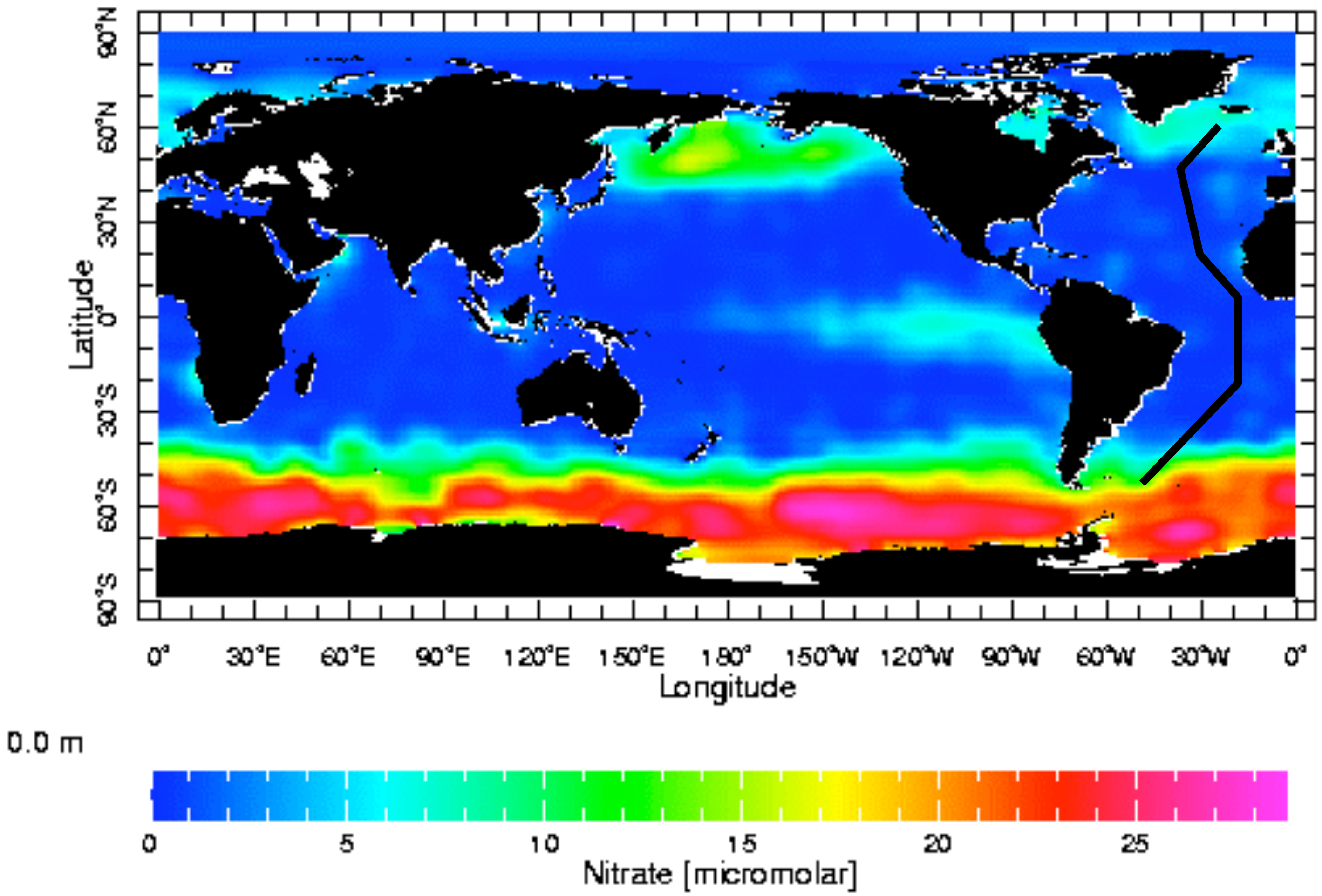
‘HNLC’ regions (high nutrient, low chlorophyll)



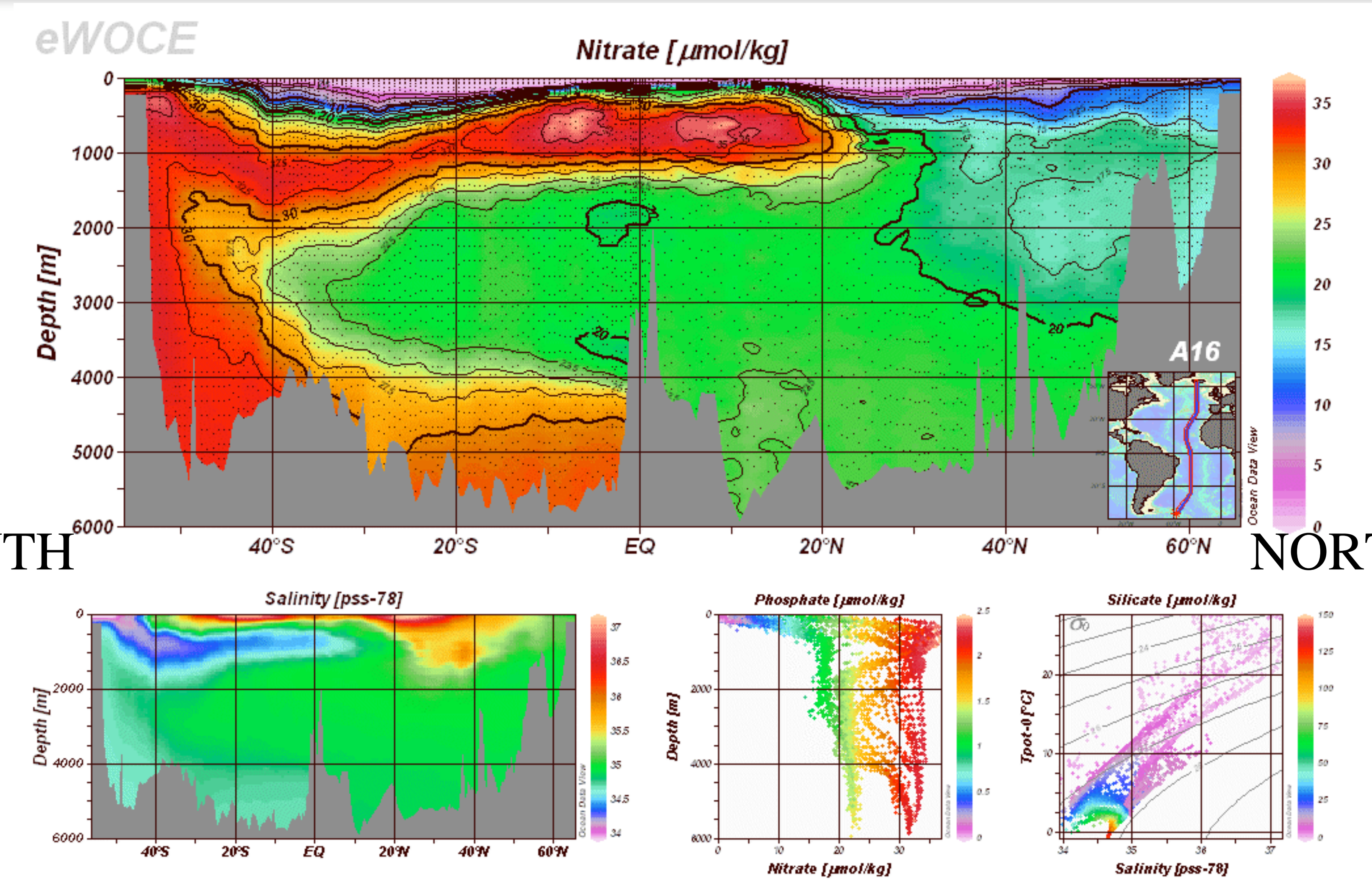
These regions are typically limited by other factors:

- Light
- Temperature
- Iron, micronutrients

Sea Surface Nitrate Map

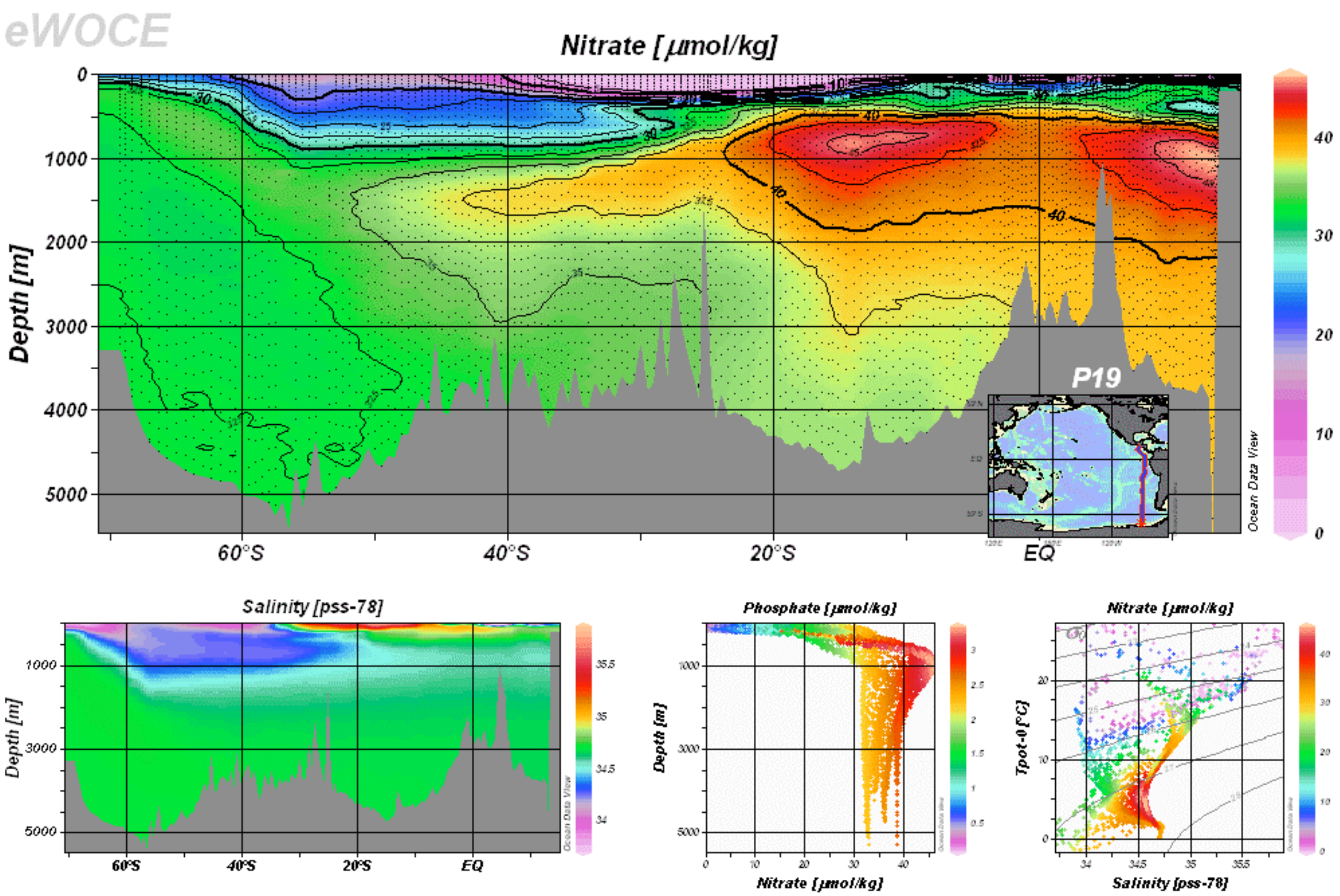


Distribution of Nitrate in Atlantic Ocean



SOUTH NORTH

Nitrate section through the ETP



Redfield Ratios and Remineralization

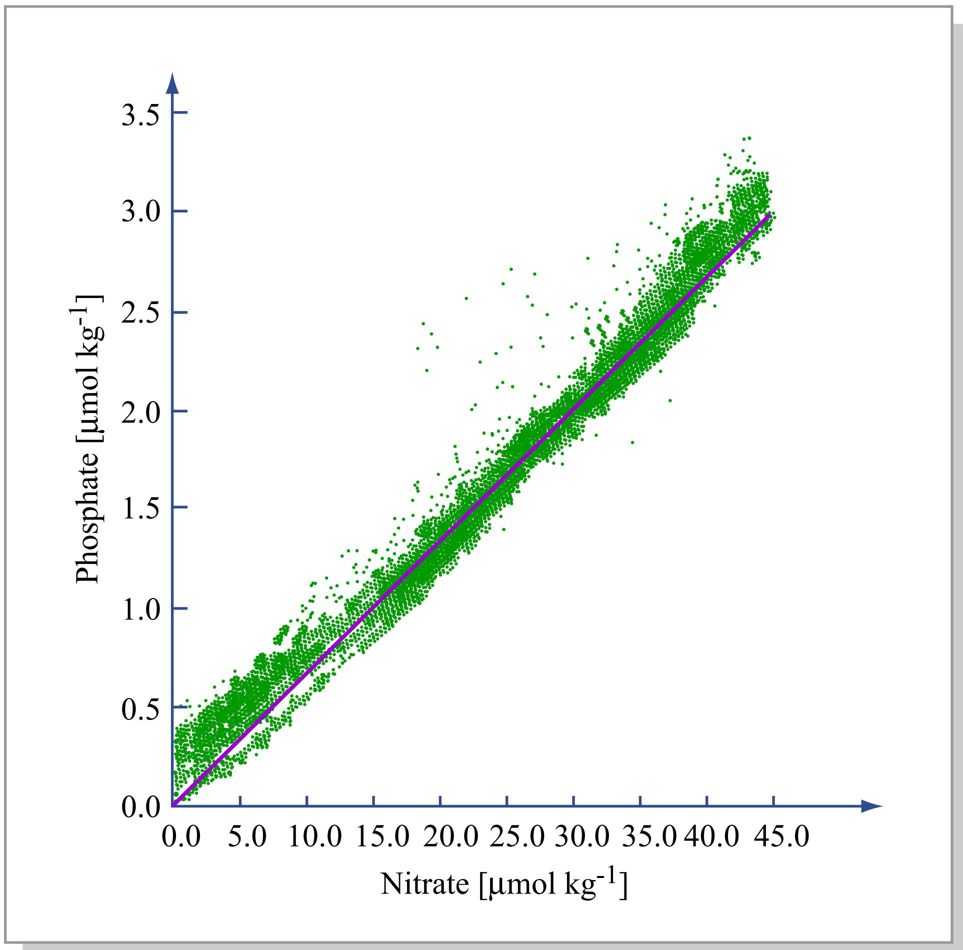


Figure by MIT OCW.

"Redfield Ratio": $C_{106}:N_{16}:P_1$
applies to both the average composition of phytoplankton biomass and the ratio of nitrate and phosphate generated from organic matter remineralization under oxic conditions

Remineralization of generalized organic matter:

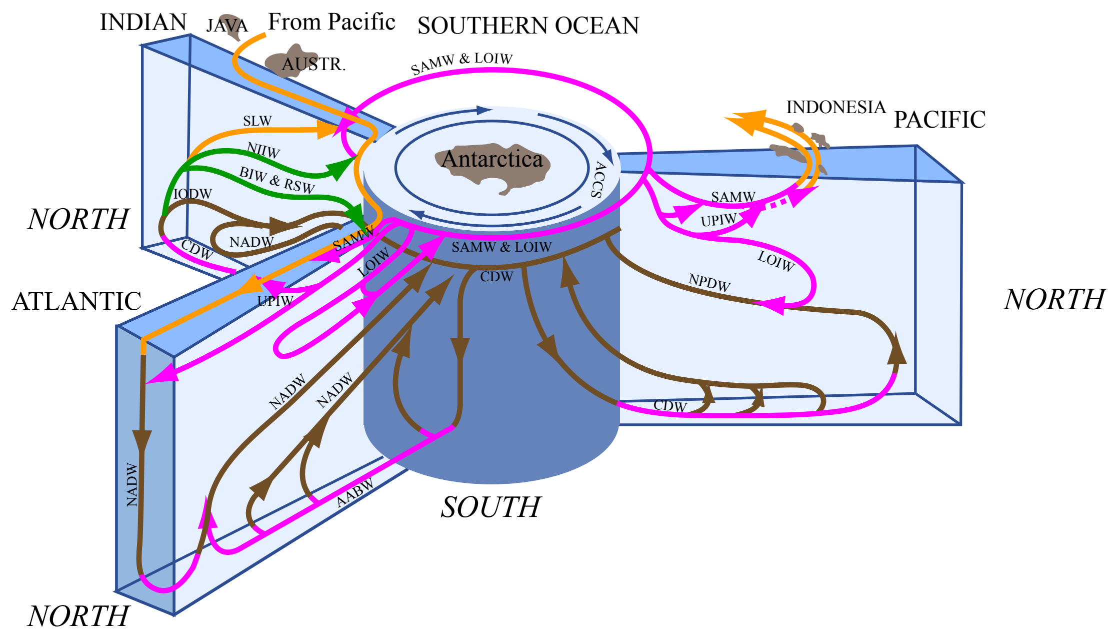
$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$$

$$\downarrow$$

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

$(106\ O_2)$ $(32\ O_2)$

Global Thermohaline Circulation



SLW	Surface layer water	NADW	North atlantic deep water
SAMW	Subantarctic mode water	UPIW	Upper intermediate water, $26.8 \leqslant \sigma_\theta \leqslant 27.2$
RSW	Red sea water	LOIW	Lower intermediate water, $27.2 \leqslant \sigma_\theta \leqslant 27.5$
AABW	Antarctic bottom water	IODW	Indian ocean deep water
NPDW	North pacific deep water	BIW	Banda intermediate water
ACCS	Antarctic circumpolar current system	NIIW	Northwest Indian intermediate water
CDW	Circumpolar deep water		

Figure by MIT OCW.

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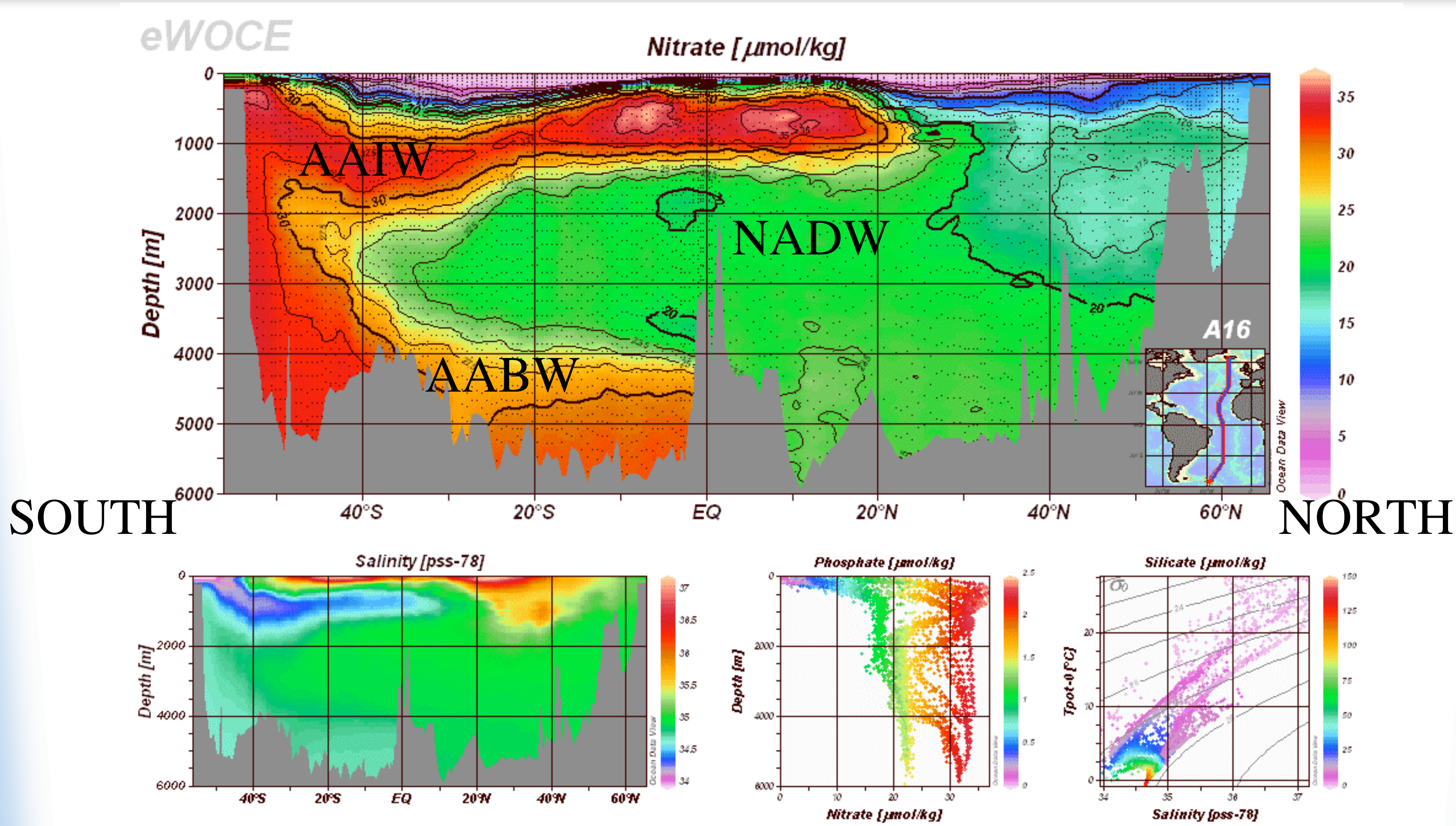

Overview

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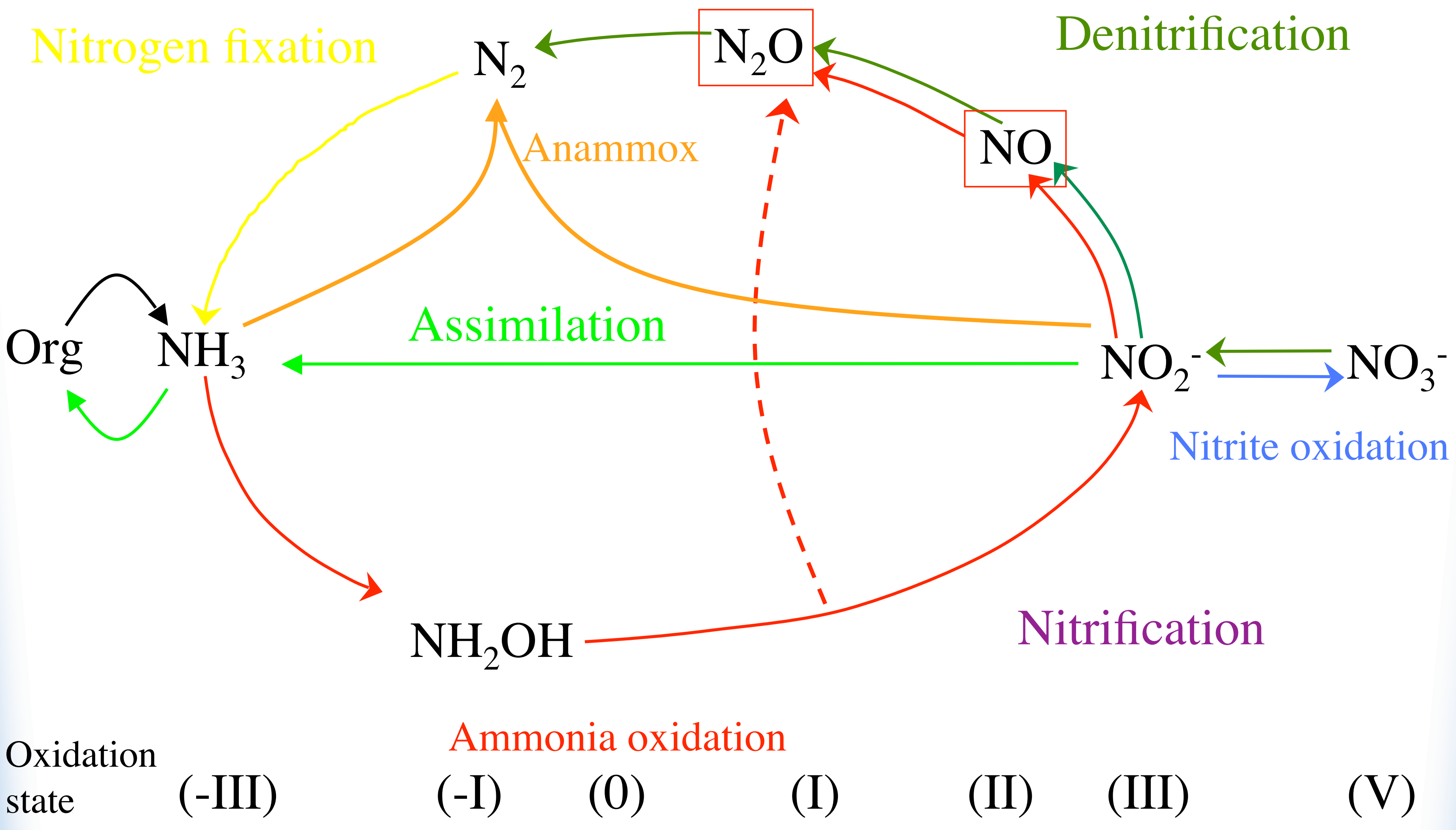
- Biogeochemical transformations
- Open questions
- Human impacts on the nitrogen cycle

Microbial Nitrogen Cycle



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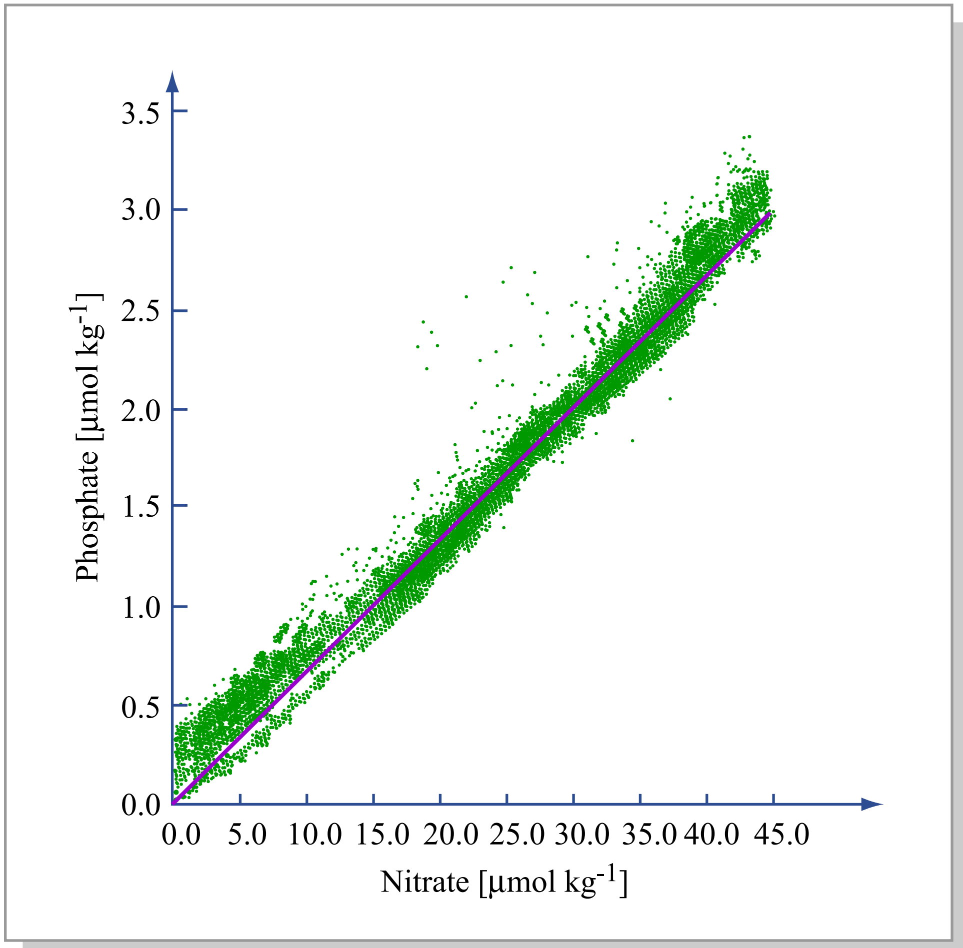

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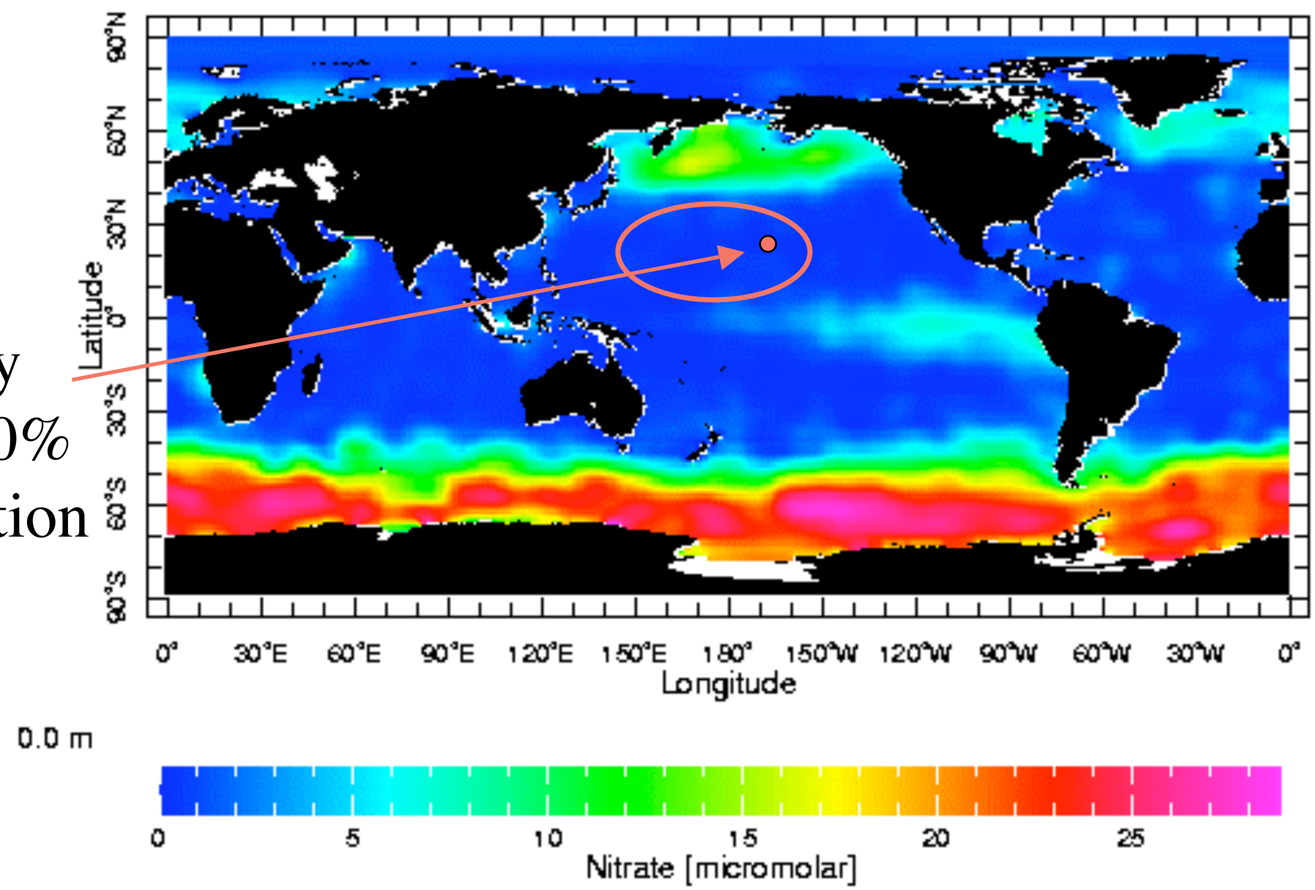
$$\uparrow \qquad\qquad \uparrow$$

$$(106\ O_2) \qquad (32\ O_2)$$

Sea Surface Nitrate Map

HOTS:
N_2 fixation may account for 30-50% of export production



Evidence for N_2 Fixation

- Occurrence of nitrogen fixing species, such as *Trichodesmium spp.*
- Low $\delta^{15}N$ of sinking organic matter suggestive of significant N_2 fixation
- Acetylene reduction or $^{15}N_2$ incorporation rate estimates

Oceanic Diazotroph Diversity

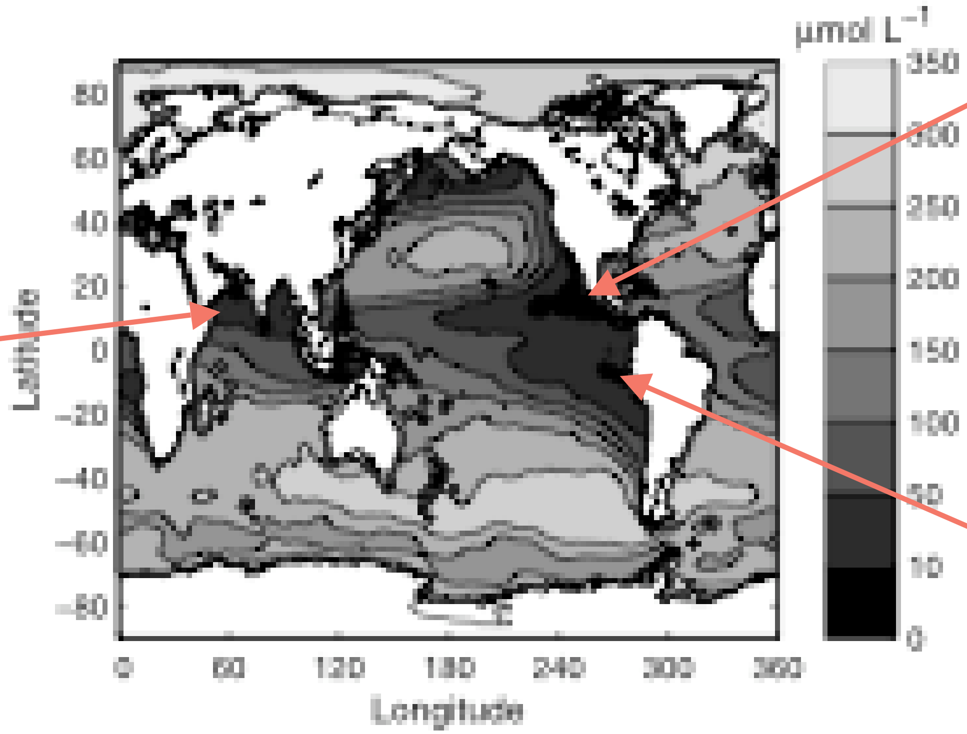
Zehr, 2000
Trends in Microbiology

Image removed due to copyright restrictions.

Water Column Denitrification Zones

Arabian Sea

Eastern Tropical North Pacific



Eastern Tropical South Pacific

Figure 7. Dissolved O_2 (μmol/L) at 400 m from the World Ocean Atlas [*Levitus and Boyer*, 1998].

Overview

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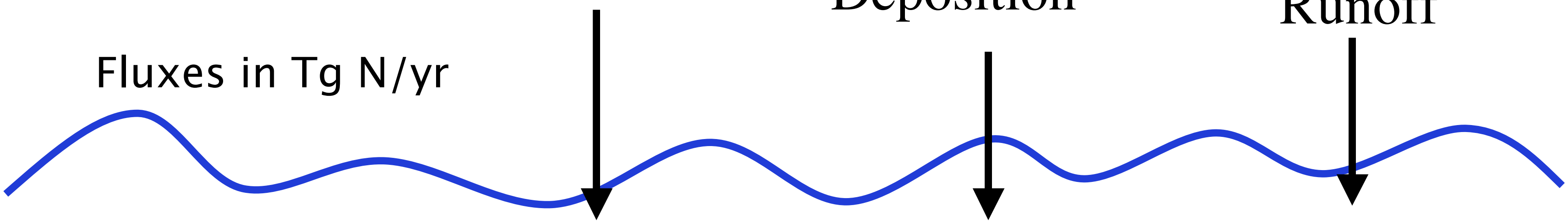
Major Questions in Marine N Cycling

- Is the nitrogen cycle in balance?
- How does the N cycle vary on glacial/interglacial timescales?
- How is N_2O produced in the ocean?
- By what mechanism is 'extra excess N_2' formed?

Nitrogen Inputs to the Ocean

Fluxes in Tg N/yr



	Nitrogen Fixation	Atmospheric Deposition	Continental Runoff
Codispoti and Christensen [1985]	25	24	25
Gruber and Sarmiento [1997] (preindustrial)	125 ± 50	15 ± 5	41 ± 20
Gruber and Sarmiento [1997] (postindustrial)	125 ± 50	30 ± 5	76 ± 20
Codispoti et al [2001]	Same as G&S	86 (includes DON)	Same as G&S

Nitrogen Exports from the Ocean

Fluxes in Tg N/yr

	Organic Burial	Sedimentary Denitrification	Water column Denitrification	Anammox
Codispoti and Christensen [1985]	21	60	60	?
Gruber and Sarmiento [1997] (preindustrial)	15 ± 5	85 ± 20	80 ± 20	?
Gruber and Sarmiento [1997] (postindustrial)	25 ± 10	95 ± 20	80 ± 20	?
Codispoti et al [2001]	25 ± 10	300	150	?

Nitrogen Budgets

	Codispoti and Christensen [1985]	Gruber and Sarmiento [1997]		Codispoti et al [2001]
Total sources	74	181 ±44	231 ±44	287
Total sinks	142	184 ±29	204 ±30	481
Residence time of N in the ocean	5,000 years	3,500 years		1,500 years

Is the N cycle in balance? Maybe not!
Is it a moving target?
What are the consequences?

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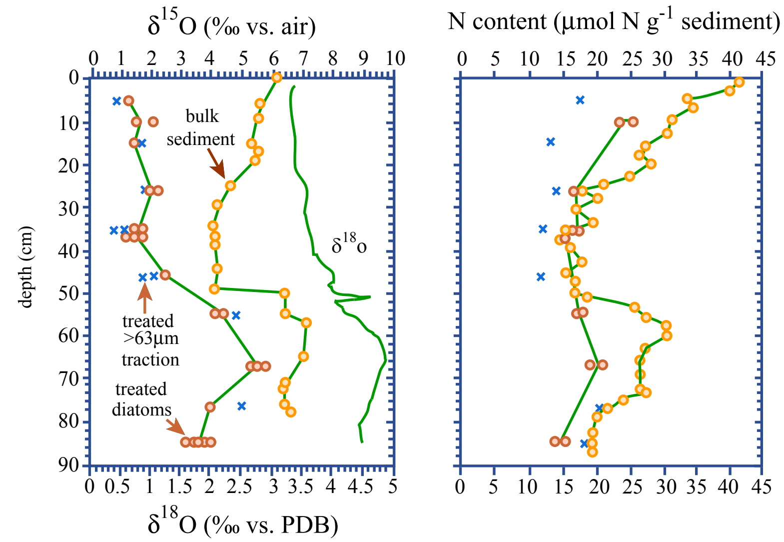
Southern ocean nitrate utilization changes

Higher $\delta^{15}N$ in diatom-bound organic matter suggests higher degree of nitrate utilization in the Antarctic zone during glacial times.



Depth profiles in gravity core All 107-22 (Antarctic Zone, Atlantic Sector, 55°S, 3°W, 2768 mi of (a) $\delta^{13}N$ and (b) N content of bulk N (open circles), diatom N (solid circles), and the perchloric acid-treated >63 µm fraction (crosses). which is composed of large diatoms, radiolaria and some detrital gains, Replicate analyses are shown for the cleaned diatom and >63 µm fraction with solid line connecting the mean value of diatoms N analysis. The N content of the builk sediment is in some cases lower than that of diatorn fraction because of the presence of dense detrital grains in the bulk sediment the planktonic focaminiferal δ^{13} stratigraphy [from keigwin and Boyle, 1989] suggested that sediment from the last Glacial maximum is at 65 cm depth.

Figure by MIT OCW.

Sigman et al., 1999

Southern ocean nitrate utilization changes

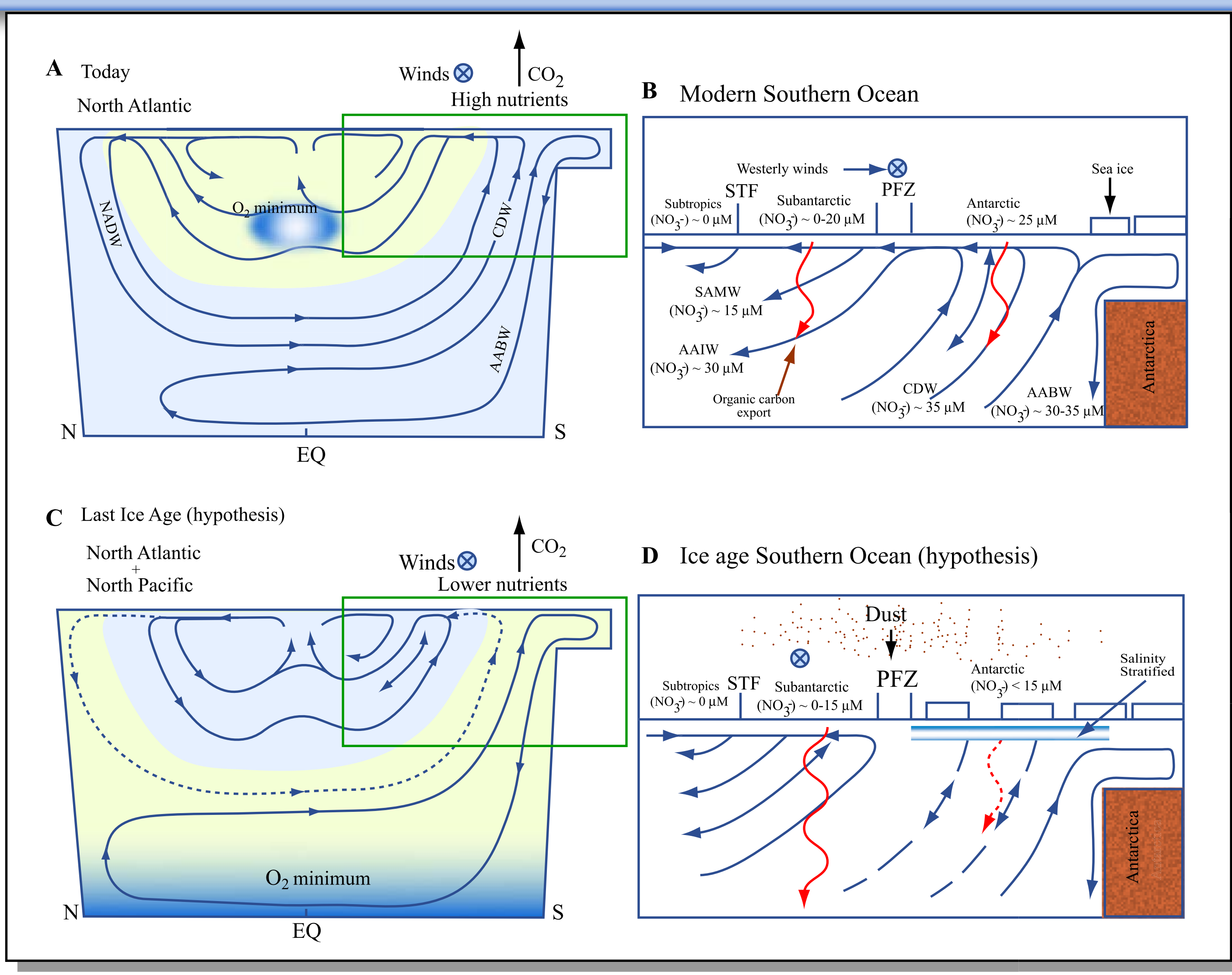


Figure by MIT OCW.

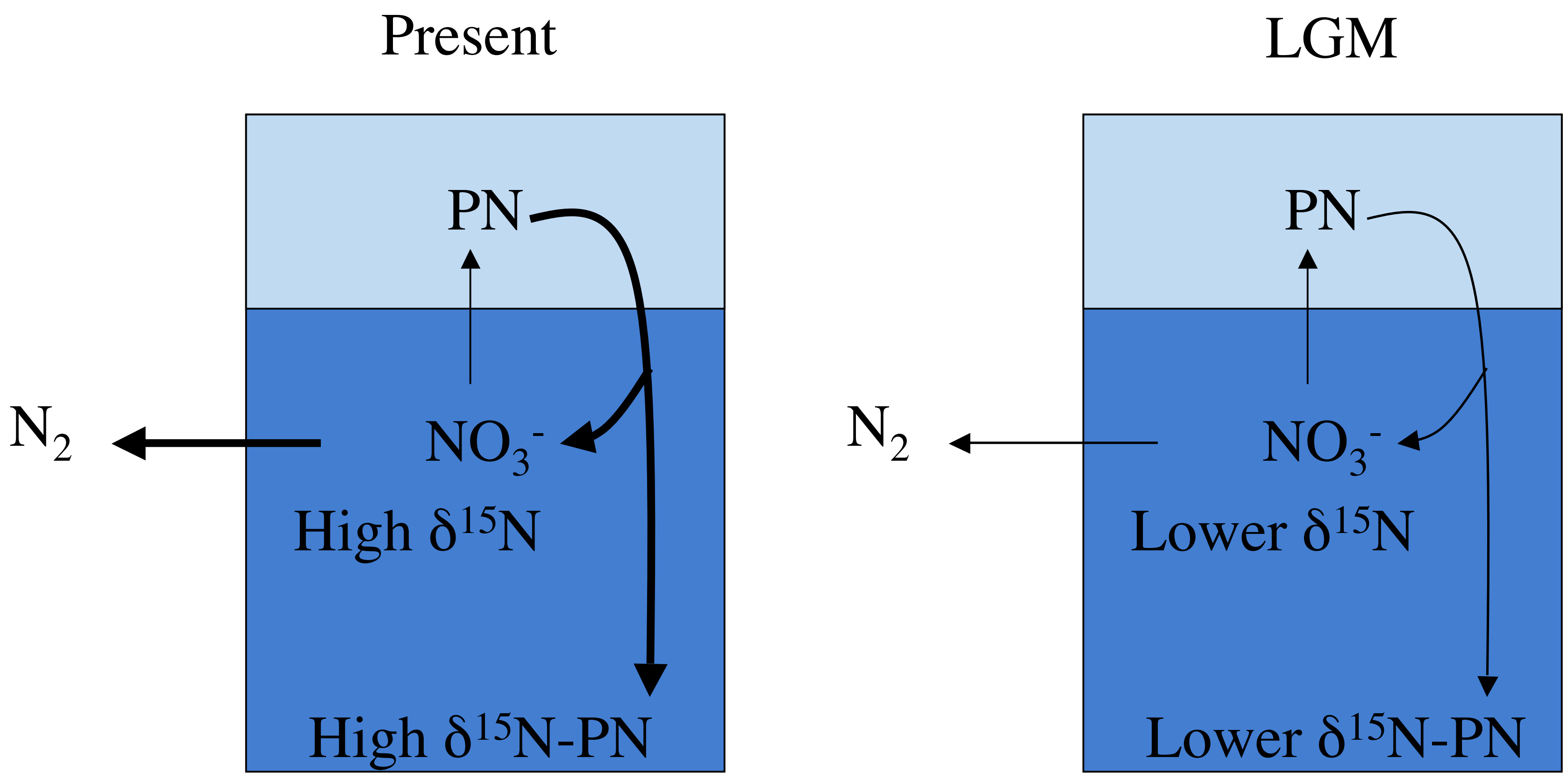
Sigman and Boyle, 2000

Changes in Denitrification

Sedimentary $\delta^{15}N$ changes from the ETNP

Chart removed due to copyright restrictions.
Ganeshram, R., et al. "Glacial-interglacial Variability in Denitrification in the World's Oceans: Causes and Consequences." *Paleoceanography* 15, no. 4 (2000): 361–376.

Changes in Denitrification



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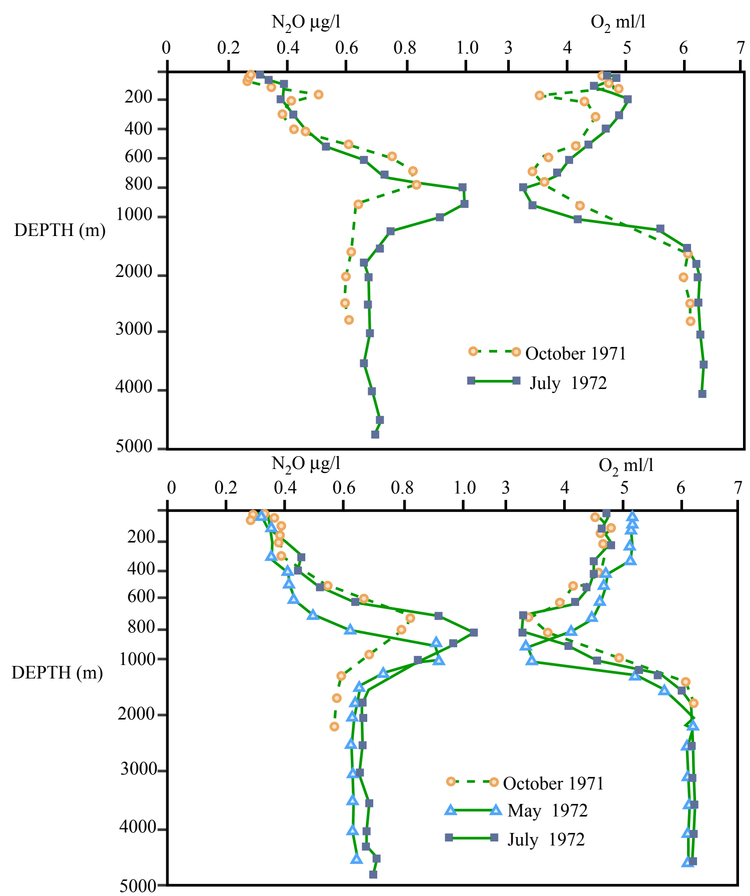
N_2O vs. AOU

Anticorrelation of N_2O and O_2 concentrations suggests N_2O is produced during organic matter remineralization (nitrification)



Vertical NO2 and O2 profiles at three different atations in the western North Atlantic, a, slope water of f Nova Scotia (42° 18' N, 61° 24' W); b, Gulf Stream (39° 07' N, 62° 21' W); c, Sargasso Sea (35° 52' N, 63° 44' W)

Figure by MIT OCW.

Yoshinari, 1976

Nitrification

Ammonia-oxidizing nitrifiers:

Nitrosomonas, Nitrosospira, Nitrosococcus

$$NH_3 + 3/2\ O_2 \longrightarrow NO_2^- + H_2O + 2\ H^+$$

Nitrite-oxidizing nitrifiers:

Nitrobacter, Nitrospira, Nitrospina

$$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^-$$

$$NH_3 + 2\ O_2 \longrightarrow NO_3^- + H_2O + 2\ H^+ \qquad \text{Overall}$$

Rates and Distributions

Chart removed due to copyright restrictions.
Dore, J. E., B. N. Popp, D. M. Karl, and F. J. Sansone. "A Large Source of Atmospheric Nitrous Oxide from Subtropical North Pacific Surface Waters." *Nature* 396, 63-66.

Denitrification and N_2O

Chart removed due to copyright restrictions.
Yoshinari, T., et al. "Nitrogen and Oxygen Isotopic Composition of N2O from Suboxic Waters of the Eastern Tropical North Pacific and the Arabian Sea—Measurement by Continuous-Flow Isotope-ratio Monitoring." *Marine Chemistry* 56 (1997): 253-264.

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Nitrate deficits

"N*" based on Redfield relationship of NO_3^- and PO_4^{3-}:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 138\ O_2$$
$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 119\ H_2O$$

$$N^* = [NO_3^-] - 16\ [PO_4^{3-}] + \text{constant}$$

Denitrification: N* ↓ (lower $[NO_3^-]$, unchanged $[PO_4^{3-}]$)
Also, higher N_2/Ar because of N_2 production from nitrate
production/accumulation of N_2 yields "excess N_2"

But, there's more N_2 than expected from nitrate deficits!!
this phenomenon has been termed "extra excess N_2"

"Extra Excess N "

What is it?

• Discrepancy between N deficit based on N:P ratios and N_2 excess from N_2/Ar ratios

How could it be explained?

• Remineralization of organic matter with high N:P ratio
• Lateral mixing of N_2 from sedimentary denitrification
• Anammox

Anammox

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

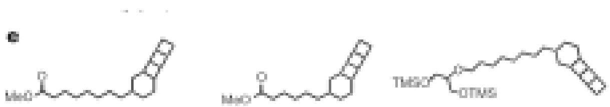
Who: Bacteria in the order *Planctomycetales*
What: anaerobically combine NH_4^+ and NO_2^- to form N_2
Where: anoxic sediments and watercolumns; Black Sea; Gulfo Dulce, Chile; Benguela Upwelling System
When: ??
Why: ??
How: Anammoxosome; enzymology known incompletely, but genome sequencing is providing targets for biochemical analysis.

Measurement of Anammox

Anammox

Organic geochemistry:

unique ladderane lipids



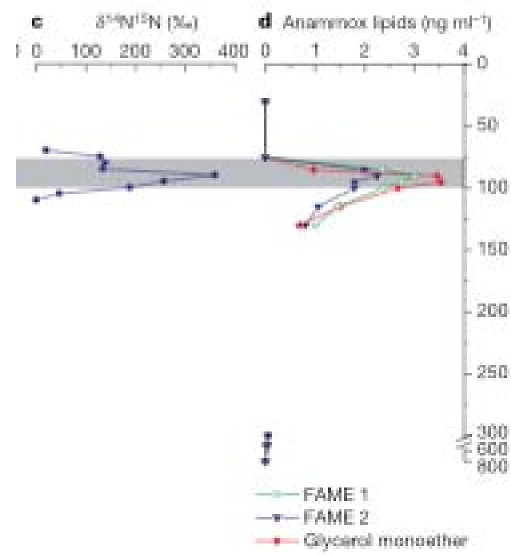
Molecular biology:

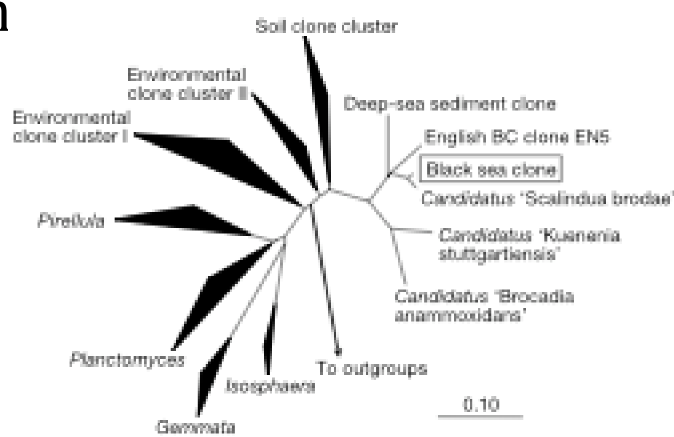
Detection of anamm

16S rRNA genes

Isotopic tracers:

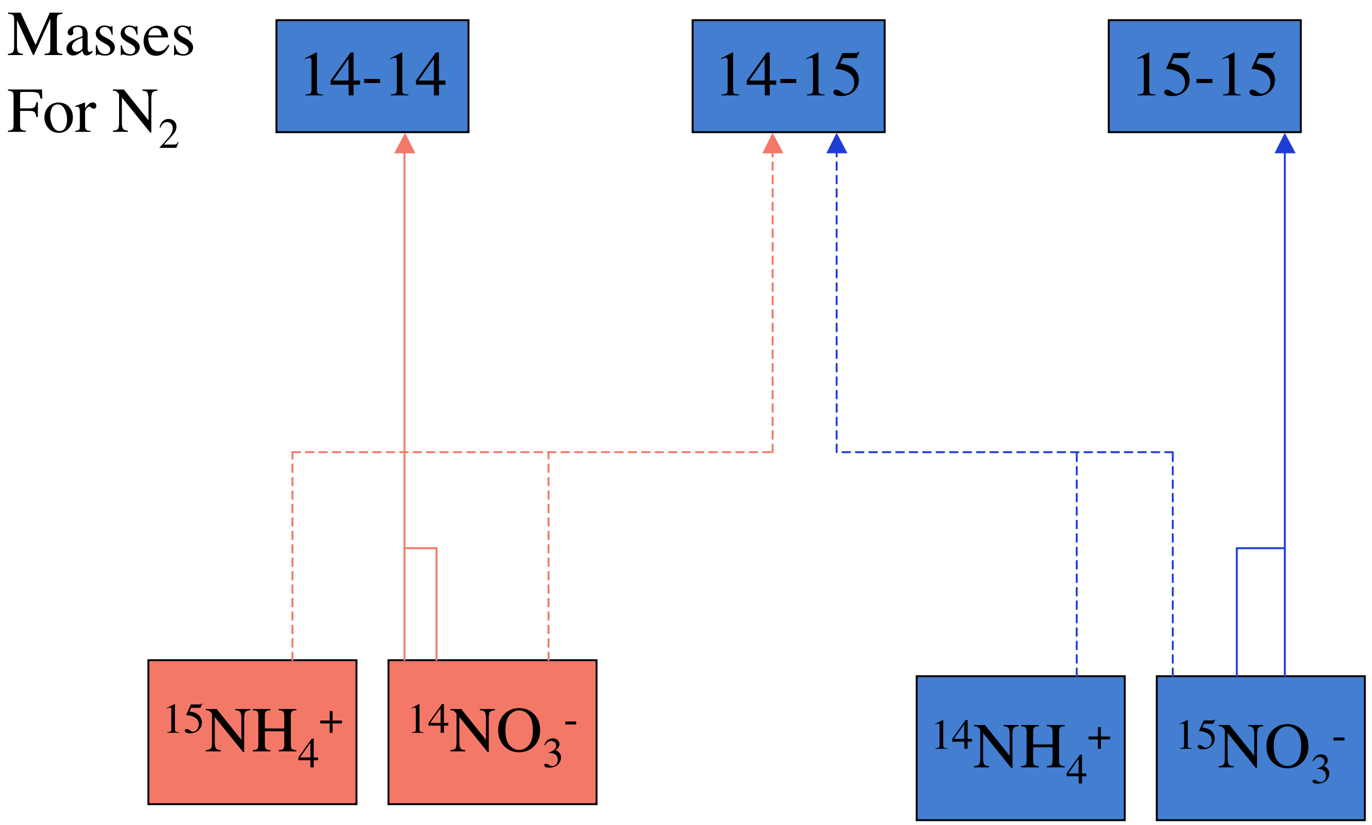
$^{15}NH_4^+ + {}^{14}NO_2^- \longrightarrow {}^{15}N^{14}N$





Kuypers et al., Nature 2003

Isotopic Tracers of Anammox



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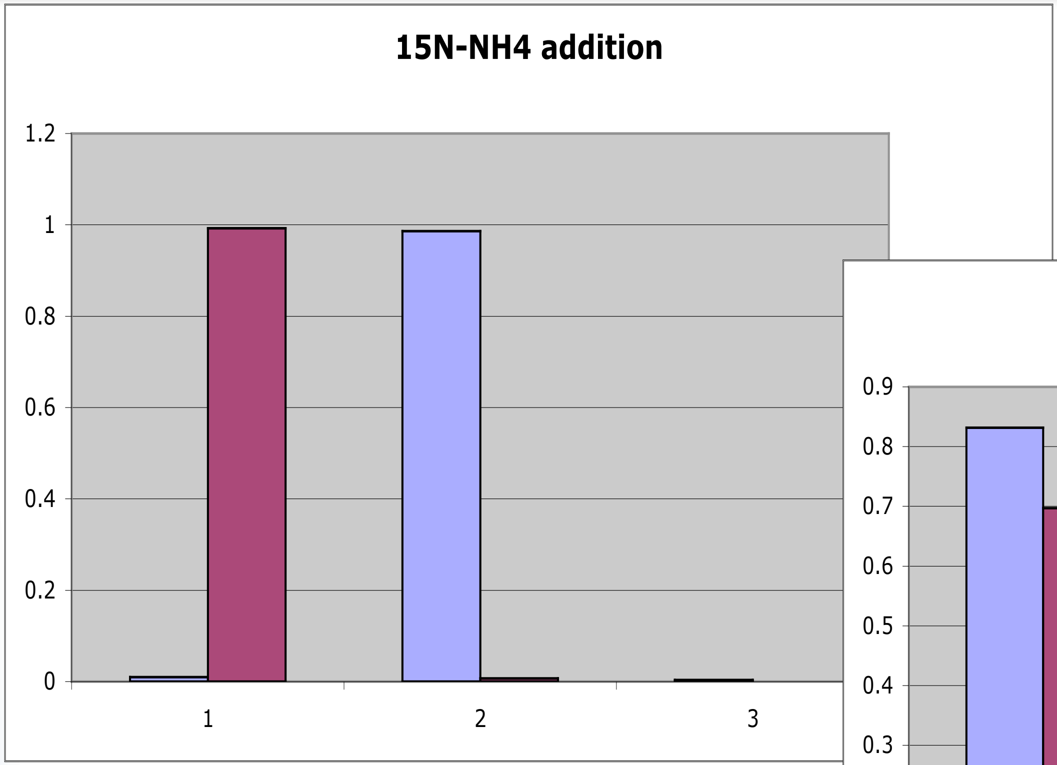
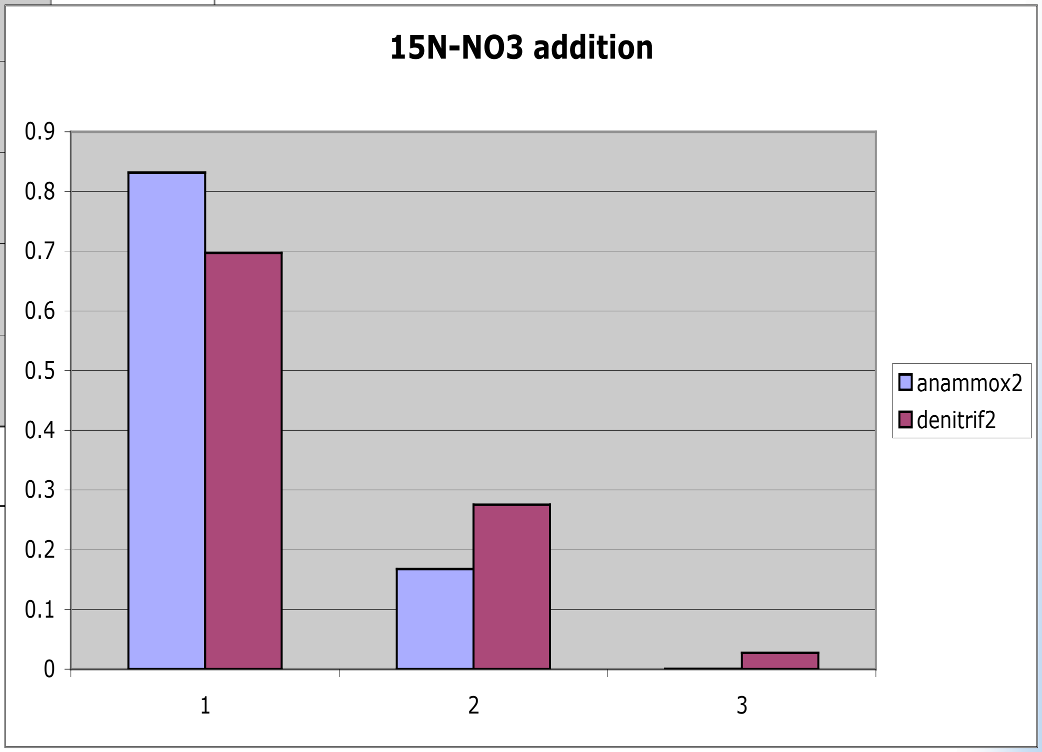


14-14 14-15 15-15



14-14 14-15 15-15

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Human perturbation of the N cycle

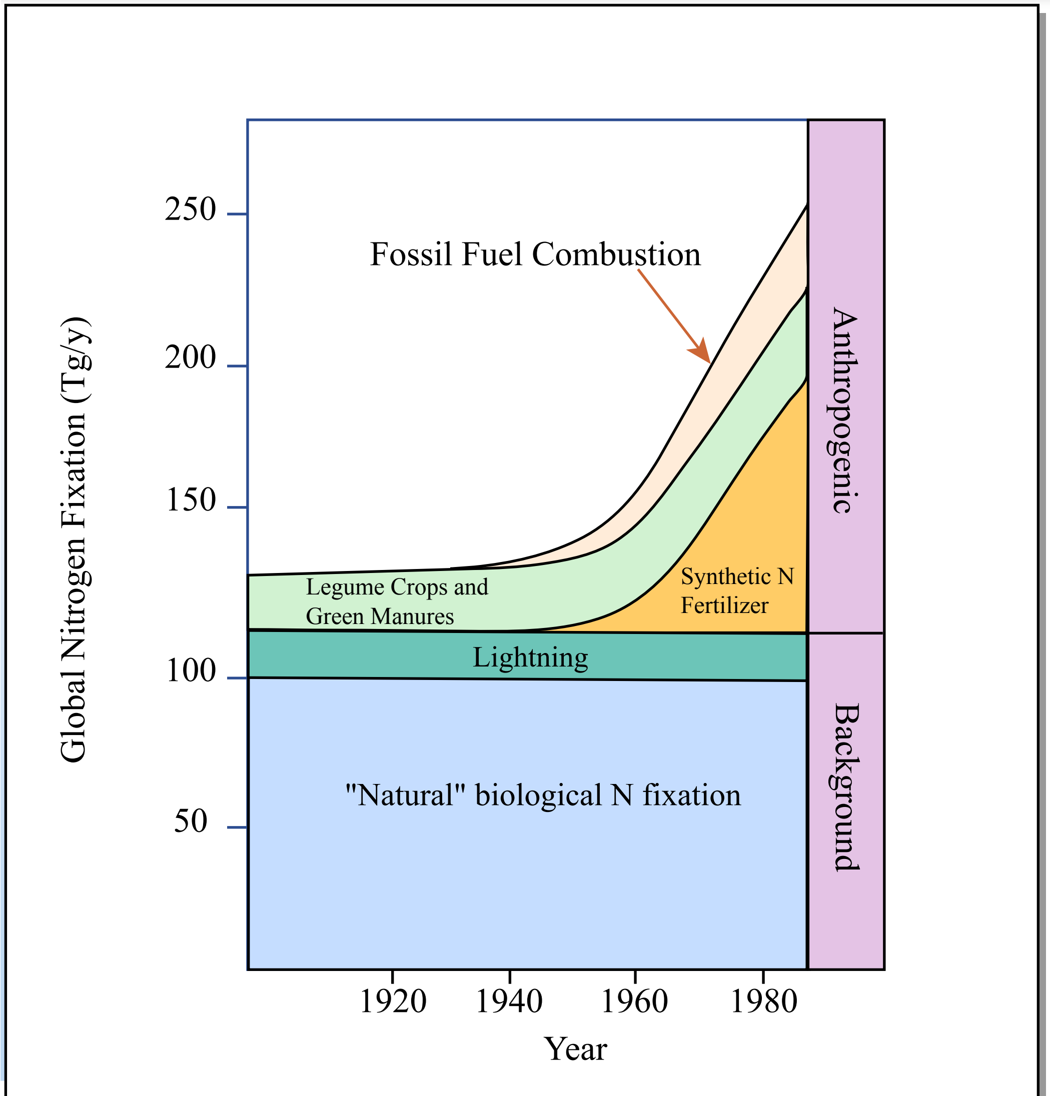


Figure by MIT OCW.

Nitrogen fixation by humans is now equivalent to natural terrestrial nitrogen fixation (~140 Tg N/yr).

The amount of human-produced N entering the oceans is not well known, but is on the order of 20-40 Tg N/yr

Eutrophication and Anoxia

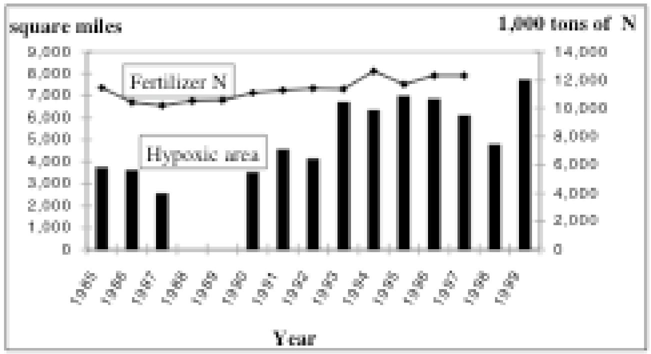
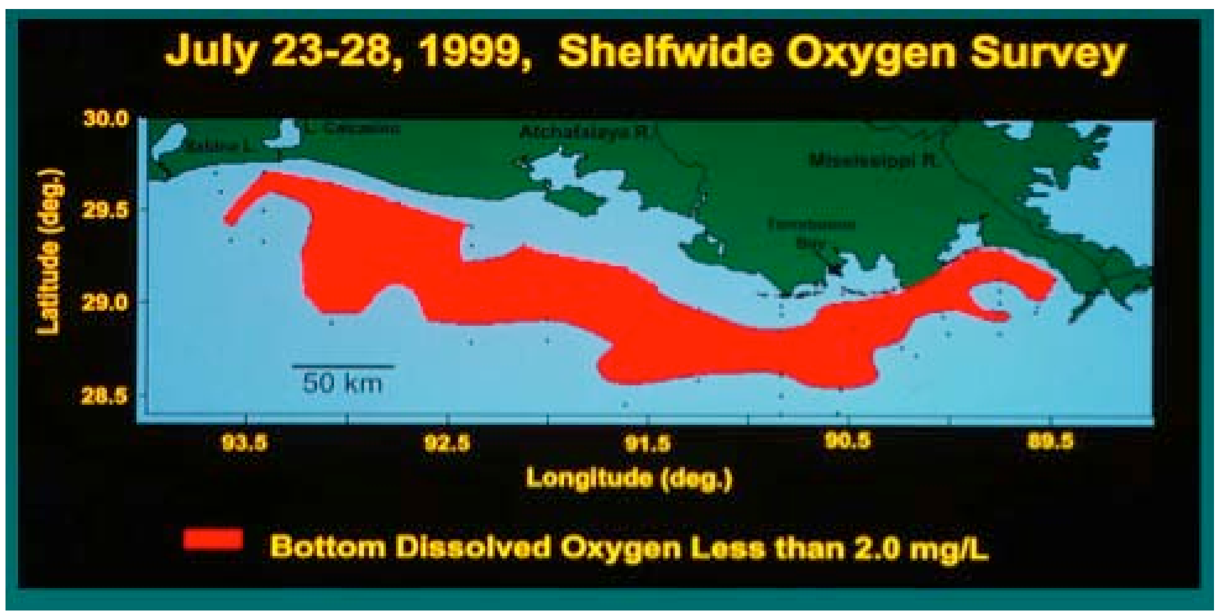


Figure 3. Hypoxic area in the Gulf of Mexico vs. fertilizer N use in the U.S.

Mississippi River nitrate loads and Gulf of Mexico Hypoxia



Sea Surface Chlorophyll *a*