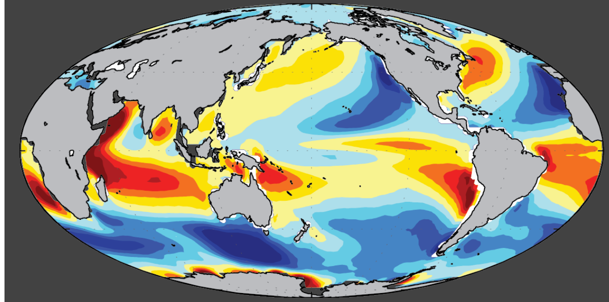
Introduction to Ocean Biogeochemical Processes and Modeling



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Ocean Biogeochemistry

The study of processes that control the distribution of elements in the sea—in terms of biological processes, chemical processes, and geological processes.

Q: Why do we care?
A: Impacts, on a range of spatial and temporal scales:

- eutrophication; harmful algal blooms

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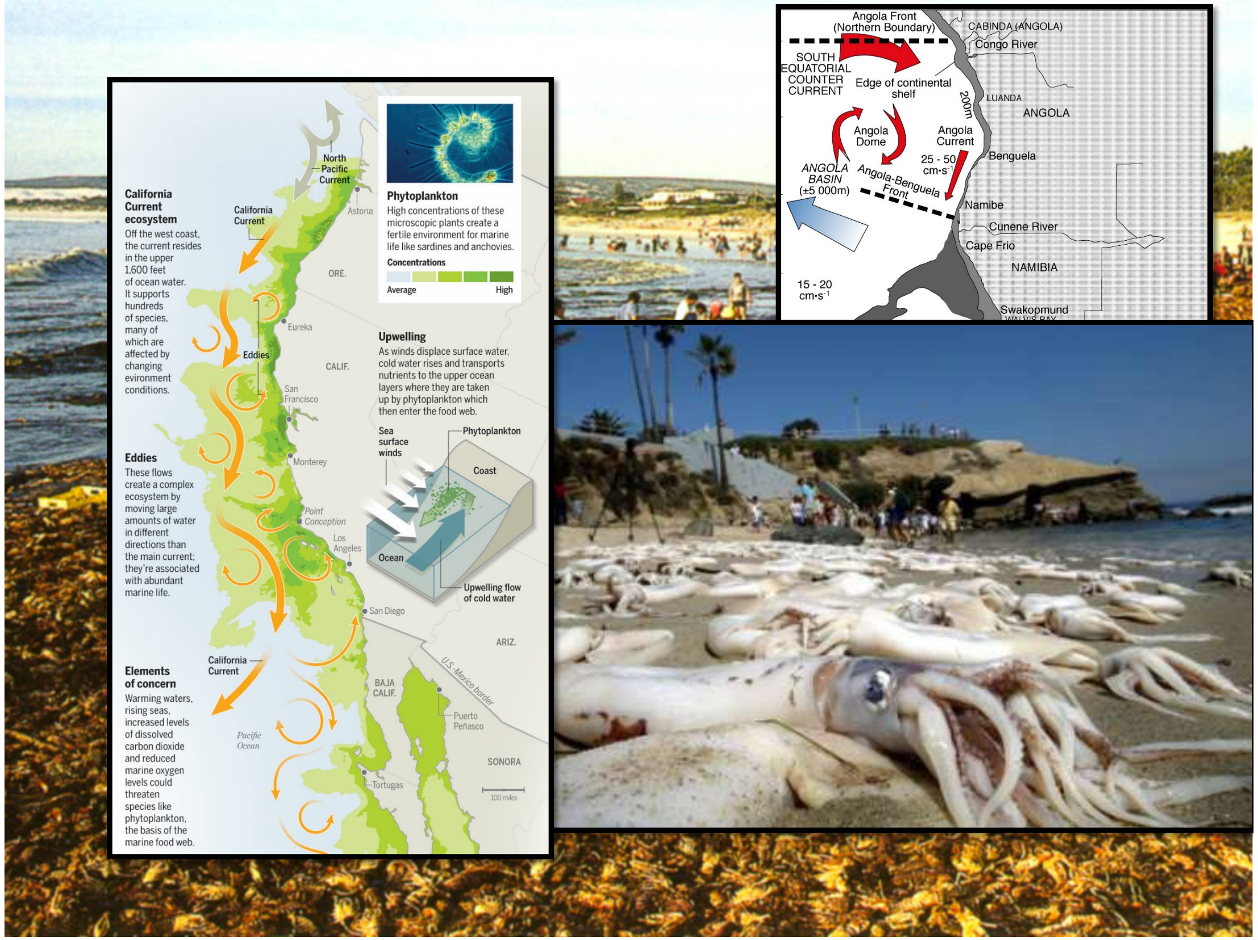
Periodically, the northeastern and less-frequently, western shores of Mobile bay will experience an event which the locals have termed a "Jubilee". During a Jubilee, many fish, crabs, and other wildlife will leave the deeper waters they usually inhabit and mass in large, dense shoals along the coastal areas indicated on this map.

Locals look forward to this time and frequently plan large parties around the large amounts of easily-obtainable seafood that the bay produces during these Jubilees.

Written record of these events can be traced back to the late 19th century, but the first scholarly treatment came in 1960, when Harold Loesch, a marine biology professor at Texas A&M University published "Sporadic Mass Shoreward Migrations of Demersal Fish and Crustacea in Mobile Bay" which attributed the phenomenon to oxygen depletion events caused by decaying organic matter in the bay that, when conditions are perfect, drive the fish, crabs, and shrimp into shallower waters less affected by the oxygen shortage.



California Current ecosystem

Off the west coast, the current resides in the upper 1,600 feet of ocean water. It supports hundreds of species, many of which are affected by changing evironment conditions.

Phytoplankton

High concentrations of these microscopic plants create a fertile environment for marine life like sardines and anchovies.

Upwelling

As winds displace surface water, cold water rises and transports nutrients to the upper ocean layers where they are taken up by phytoplankton which then enter the food web.

Eddies

These flows create a complex ecosystem by moving large amounts of water in different directions than the main current; they're associated with abundant marine life.

Elements of concern

Warming waters, rising seas, increased levels of dissolved carbon dioxide and reduced marine oxygen levels could threaten species like phytoplankton, the basis of the marine food web.

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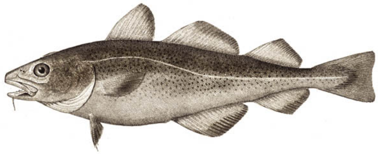
synoptic-to-seasonal scales
↓
decadal-to-centennial+ scales

- eutrophication; harmful algal blooms
- hypoxic events that can affect demersal resources, metal toxicity, and emissions of harmful gasses
- productivity and distribution of fisheries

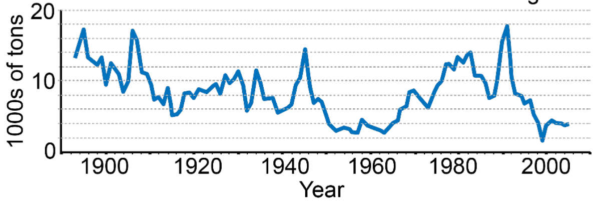
Fluctuations in living marine resources

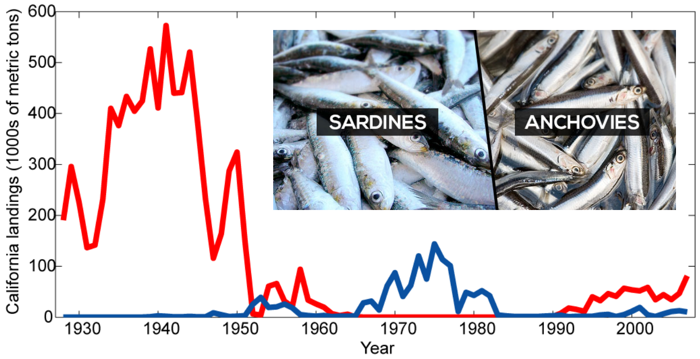
What drives changes in landings of commercial fish stocks?

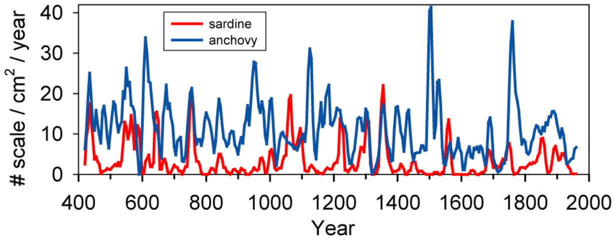
Overfishing or environmental variability?



Gulf of Maine Cod - Total Commercial Landings







Soutar and Isaacs (1969); Baumgartner et al. (1992)

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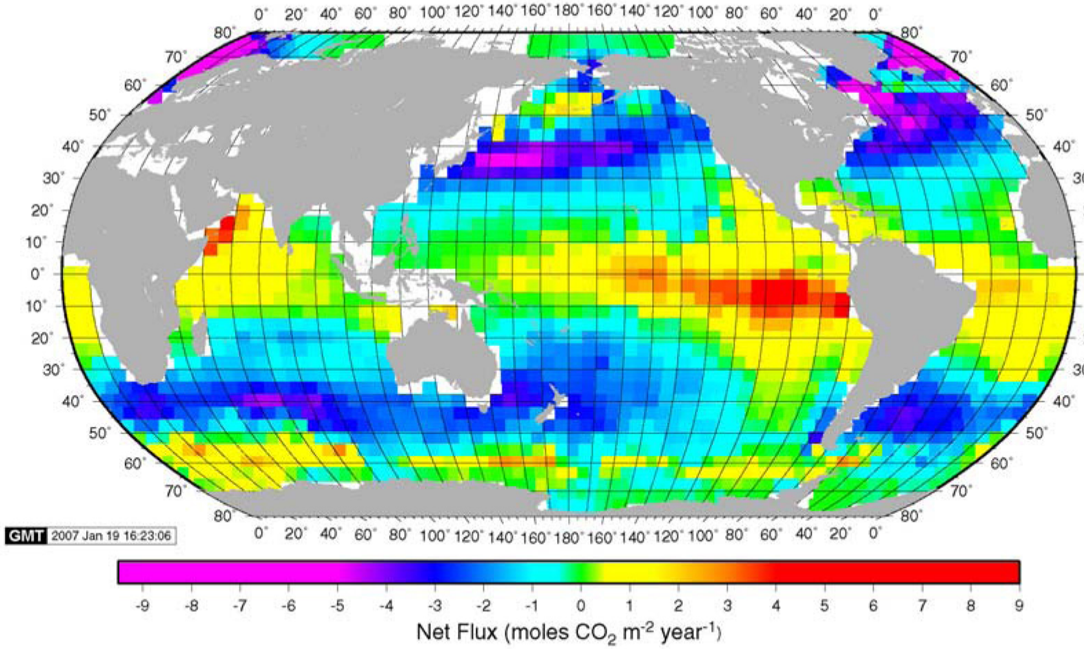
- productivity and distribution of fisheries
- flux of carbon between the atmosphere and deep ocean and sediment; closing the carbon cycle

Modeled air-sea CO_2 flux



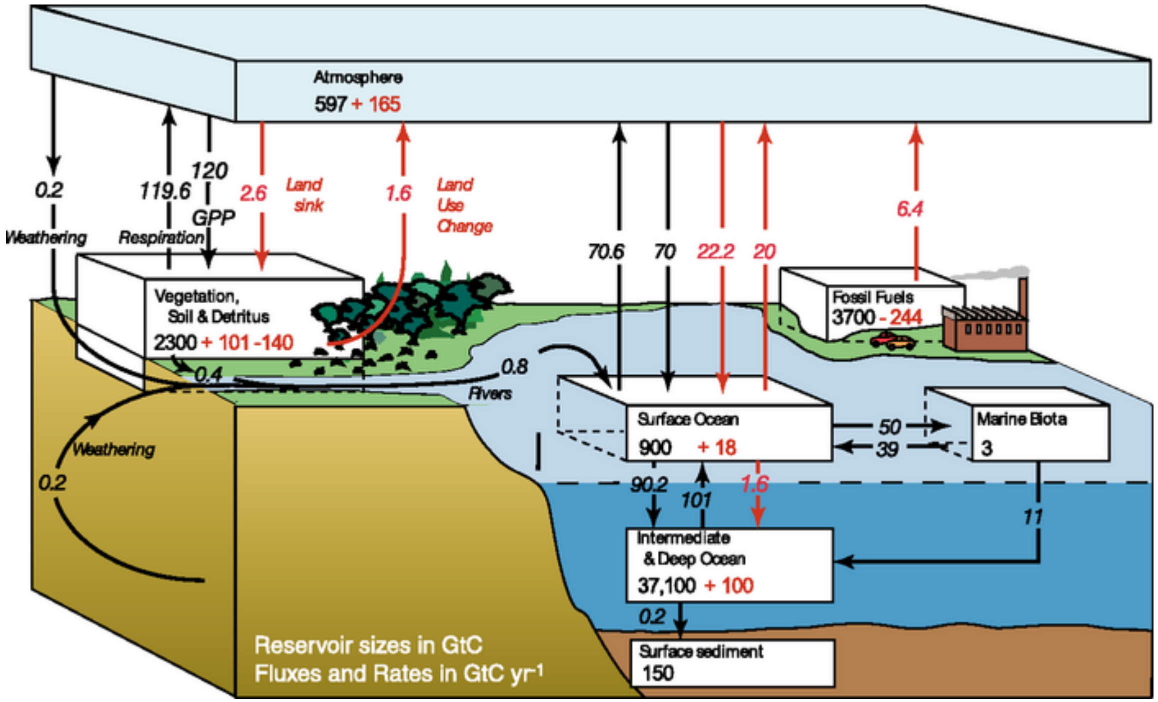
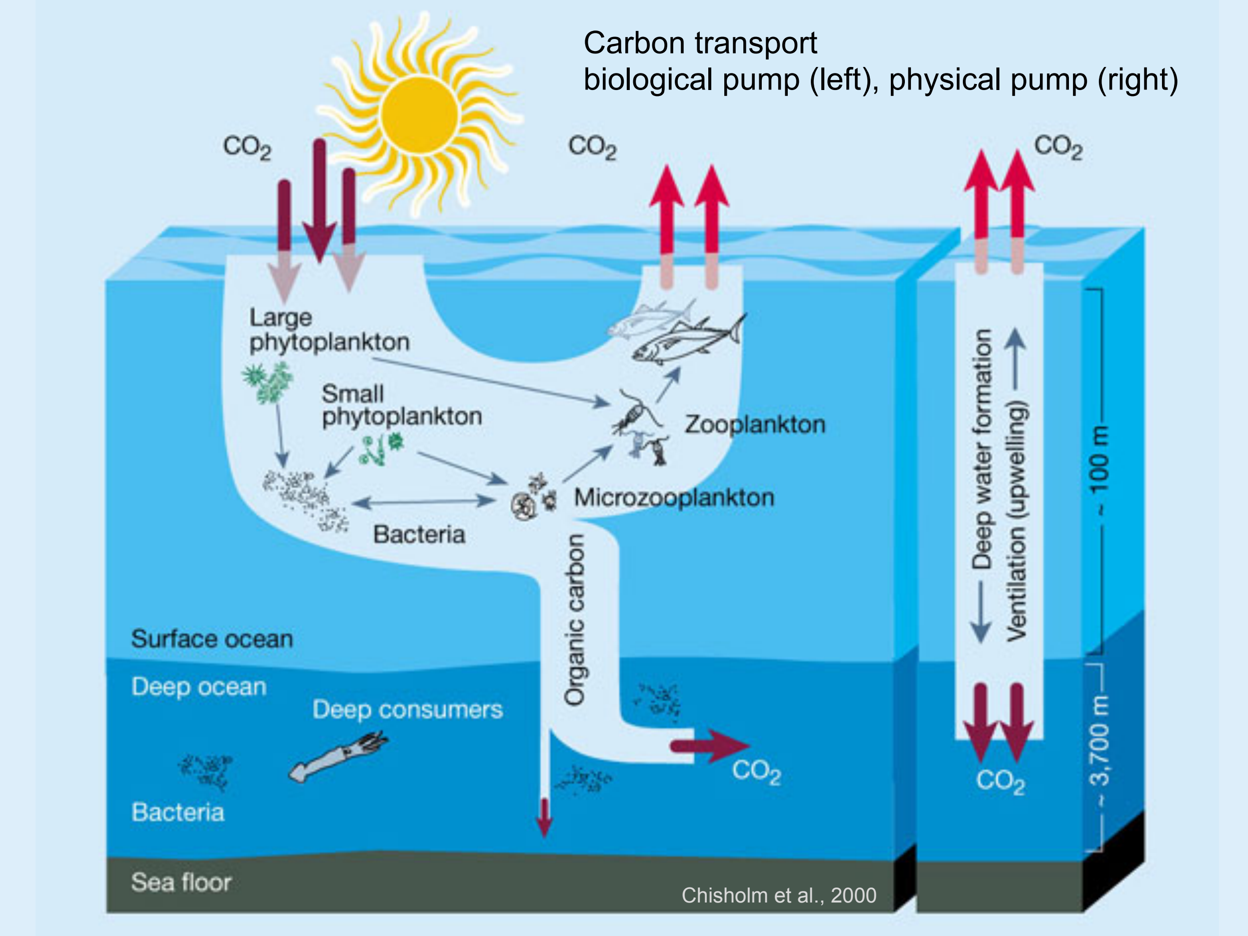


Figure 7.3. The global carbon cycle for the 1990s, showing the main annual fluxes in GtC yr^{-1}: pre-industrial 'natural' fluxes in black and 'anthropogenic' fluxes in red (modified from Sarmiento and Gruber, 2006, with changes in pool sizes from Sabine et al., 2004a).

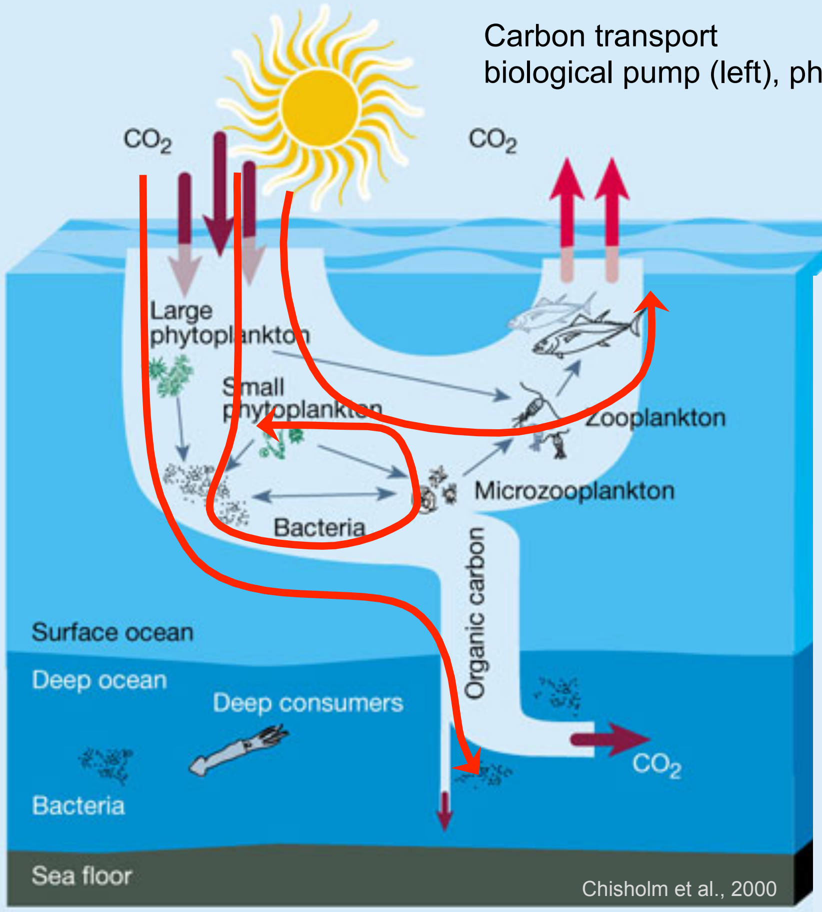
IPCC AR4, Ch 7



Carbon transport
biological pump (left), physical pump (right)

Chisholm et al., 2000

Carbon transport
biological pump (left), physical pump (right)



Chisholm et al., 2000

Note 3 pathways of organic matter cycling:

1. microbial loop
2. classical food chain
3. export to deep ocean

(These are *not distinctly separate* in the real ocean!)

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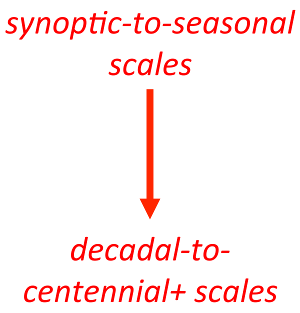

synoptic-to-seasonal scales

decadal-to-centennial+ scales

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- productivity and distribution of fisheries
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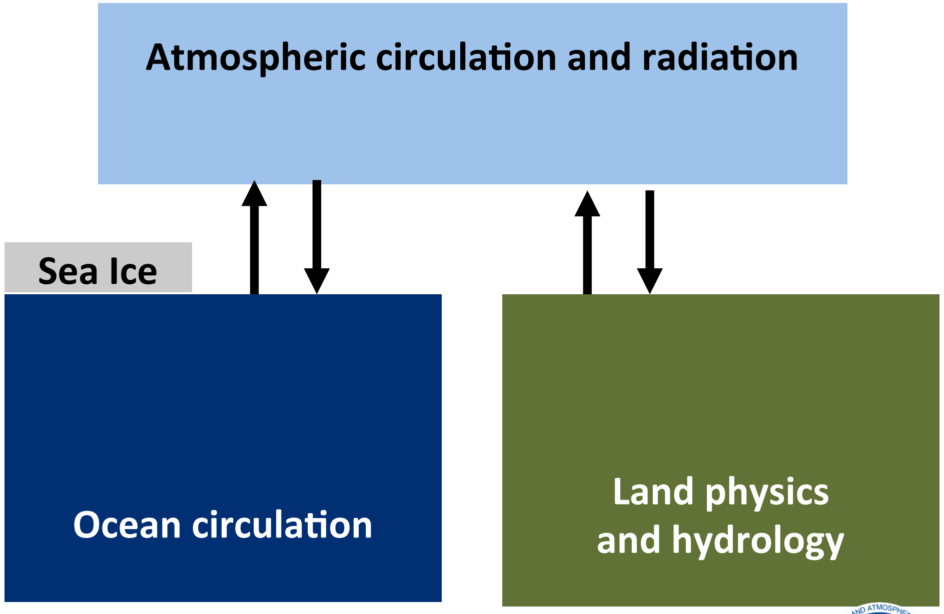
Modeling aims and components – *How can this be done?*

Biogeochemical and ecosystem models are included as components of both global and regional models, typically with a targeted goal in mind. Goals direct model type and complexity.

Higher trophic-level organisms (e.g., food webs and humans) are additional model components.

Modeling aims and components – *How can this be done?*



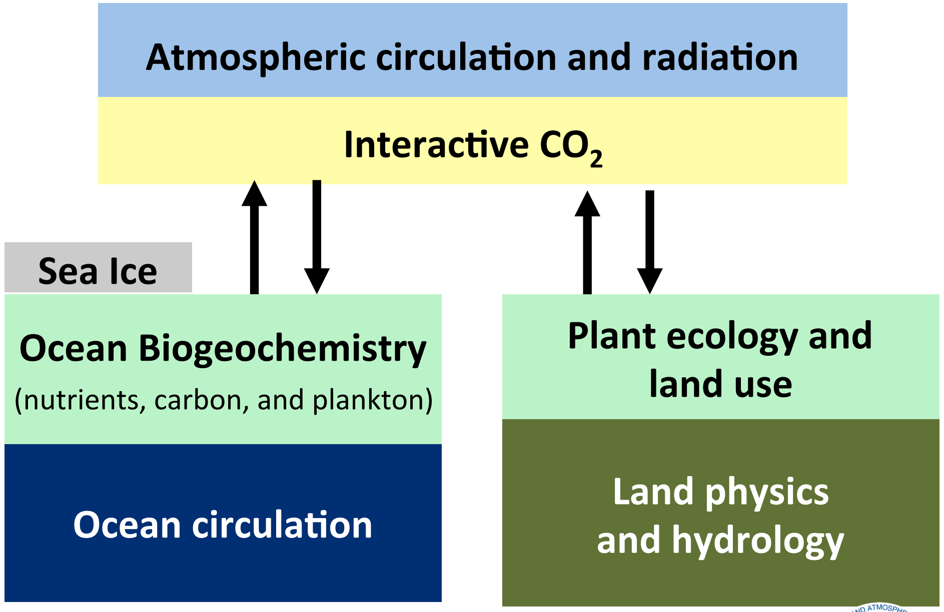
Atmospheric circulation and radiation

Sea Ice

Ocean circulation

Land physics
and hydrology

Modeling aims and components – *How can this be done?*



Atmospheric circulation and radiation

Interactive CO_2

Sea Ice

Ocean Biogeochemistry

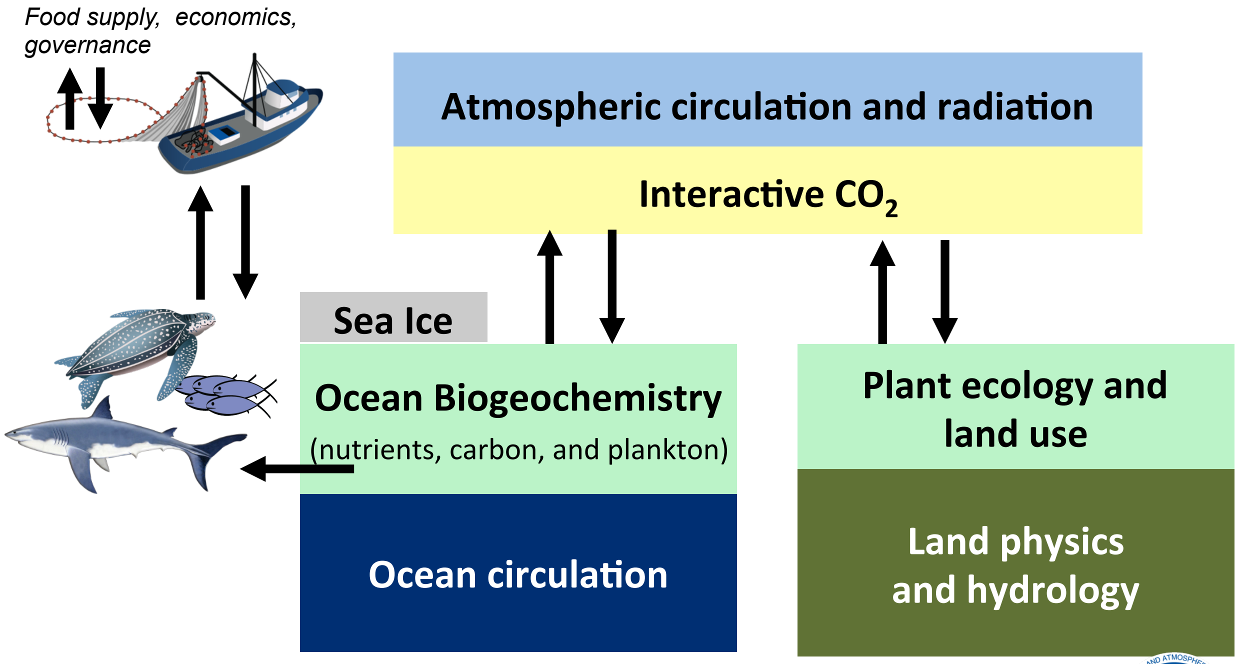
(nutrients, carbon, and plankton)

Ocean circulation

Plant ecology and land use

Land physics and hydrology

Modeling aims and components – *How can this be done?*



Food supply, economics, governance

Atmospheric circulation and radiation

Interactive CO_2

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(nutrients, carbon, and plankton)

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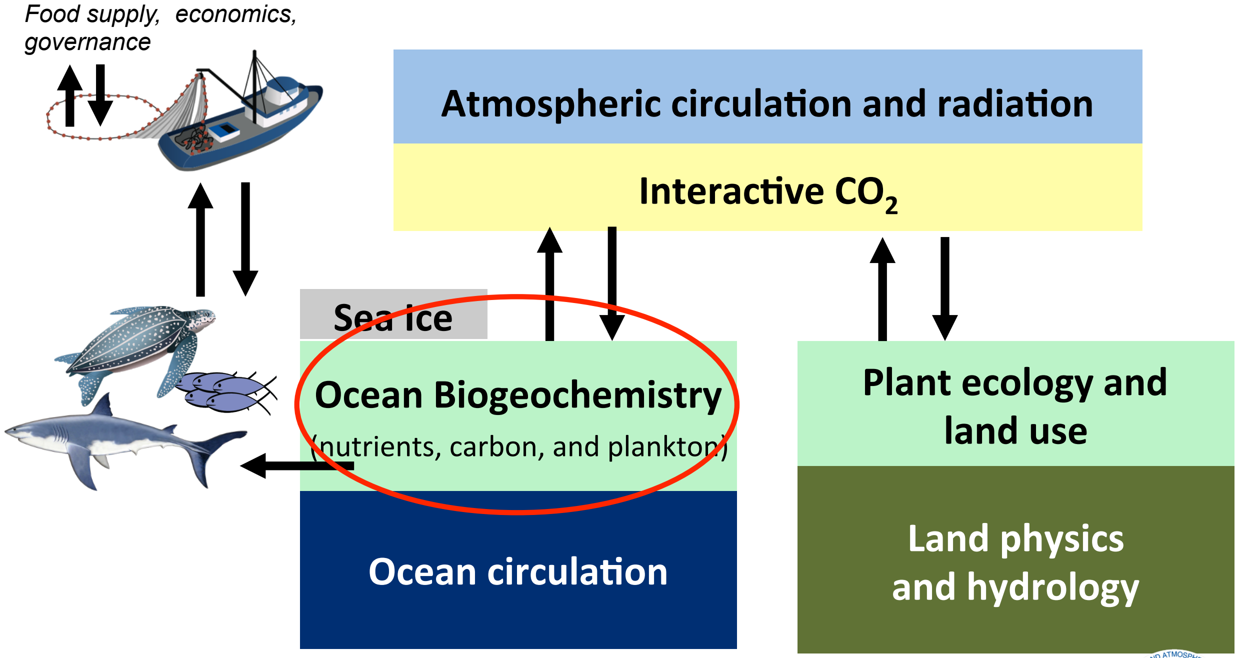

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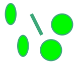
Outline

1. Mass balance in marine biogeochemistry
2. What types of organisms are we concerned with?
3. An example of a global marine biogeochemical model – COBALT.
   Stock et al., 2014 (*Progress in Oceanography*)

Mass Balance in Marine Biogeochemistry

(a simplified view)

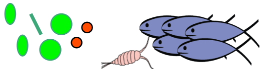
Photosynthesis



(Phytoplankton do this.)

$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 78\ H_2O \xrightarrow[\text{light chlorophyll}]{} C_{106}H_{175}O_{42}PN_{16} + 150\ O_2$$

Oxic Respiration



(All organisms do this—phytoplankton, heterotrophic and autotrophic bacteria, zooplankton, fish, etc.)

$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 78\ H_2O \longleftarrow C_{106}H_{175}O_{42}PN_{16} + 150\ O_2$$

Photosynthesis uses inorganic molecules (CO_2 and nutrients) to build organic matter using energy from the sun.

Oxic respiration (or remineralization) breaks down this organic matter (in the presence of dissolved oxygen) to release energy while returning the nutrients and C to their inorganic forms.

Mass Balance in Marine Biogeochemistry

(a simplified view)

$$106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 78\ H_2O \underset{\text{respiration}}{\overset{\text{photosynthesis}}{\rightleftharpoons}} C_{106}H_{175}O_{42}P + 150\ O_2$$

In addition to the elements above, phytoplankton require

In large amounts:	(Si)
In smaller amounts:	S, K, Na, Ca, Mg, Cl
In trace quantities:	Fe, Mn, Mb, Cu, Co, Zn, B, Va

Modelers typically focus on N, P, Si and Fe (as these are most often limiting to phytoplankton growth) and C (as it is a common unit of biomass, critical to atmospheric CO_2, and ocean carbonate cycle—acidification).

Inorganic nutrients are required for phytoplankton growth

Element	**Forms in Ocean**	**Major Biogeochem Role**
Carbon	CO_2, HCO_3^-, CO_3^{2-}	energy storage, structure, everything
Nitrogen	NO_3^-, NO_2^-, NH_4^+	proteins
Phosphorous	PO_4^{3-}	nucleic acids, membrane lipids
Silicon	$Si(OH)_4$	diatom frustules
Iron	$Fe(OH)_x$, Fe_{org}	photosynthetic and respiratory proteins
Other metals: Zn, Co, Mn, Cu		various proteins

"macronutrients"

"micronutrients"

Elements in organic matter

These two processes are the main sources and sinks for C, O, P, and N, and organic matter itself is a major reservoir for these elements.

As a consequence, the molar concentrations of these key biologically elements vary in stoichiometric ratios.

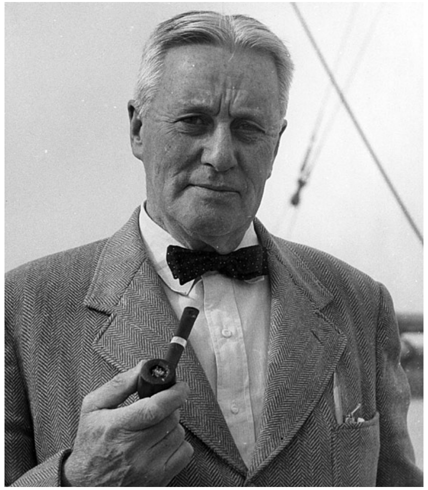
The average macronutrient molar composition of organic matter and the biologically active forms of these elements is

$$C:N:P:O_2 = 106:16:1:-150$$

The average micronutrient (minor elements) composition of organic matter is

$$P:Fe:Zn:(Cu, Mn, Ni, \& Cd) = 1 : 0.005 : 0.002 : 0.0004$$

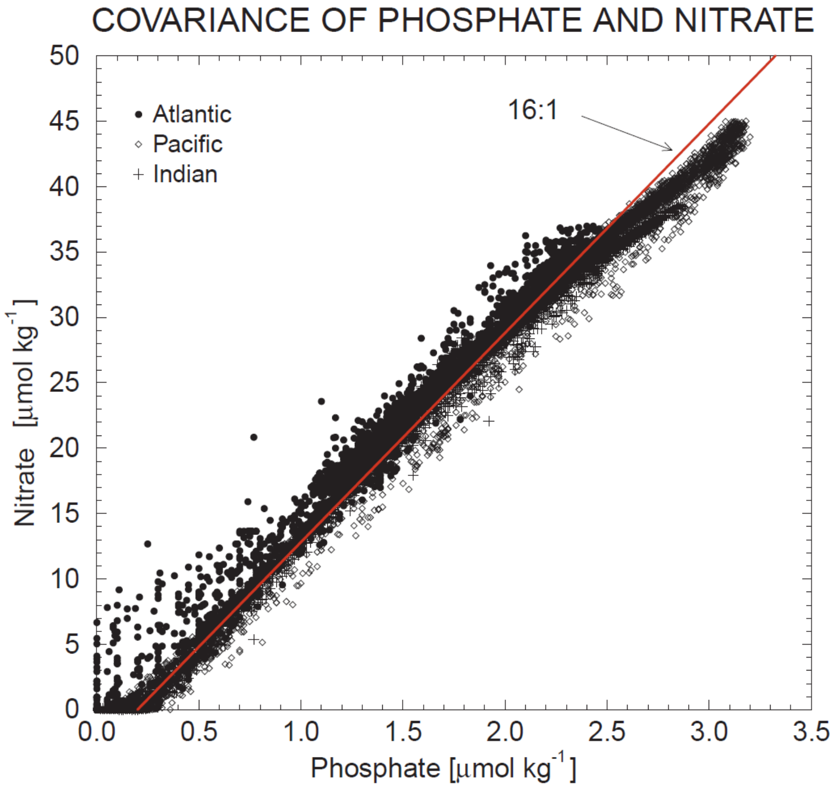
Elements in organic matter



Redfield (1890 – 1983); WHOI

This ratio of macronutrient concentrations, 106:16:1:-150, is called the Redfield ratio or Redfield stoichiometry after Alfred Redfield…

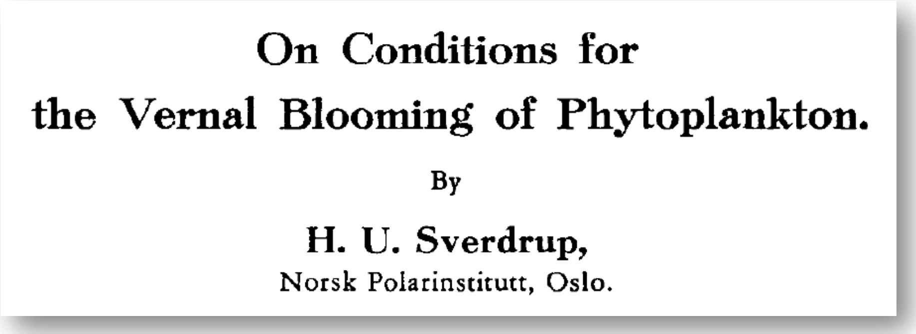
who was among the first to quantify the **consistency by which these element rations varied and proposed a hypothesis to explain the observation.**


COVARIANCE OF PHOSPHATE AND NITRATE
Atlantic
Pacific
Indian
16:1
Nitrate [μmol kg^{-1}]
Phosphate [μmol kg^{-1}]
0
5
10
15
20
25
30
35
40
45
50
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5

Factors limiting primary production: nutrients, light, and temperature

Just about everywhere, primary production in summer is limited by the *lack of nutrients* (exceptions being enclosed basins subject to eutrophication).

However, the factor limiting primary production in and subpolar and polar regions is the *lack of light*.

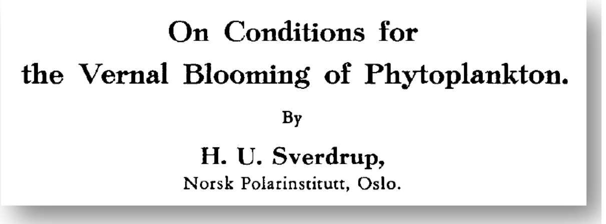


On Conditions for
the Vernal Blooming of Phytoplankton.

By

H. U. Sverdrup,
Norsk Polarinstitutt, Oslo.

J. Cons. int. Explor. Mer (1953) 18 (3): 287-295.



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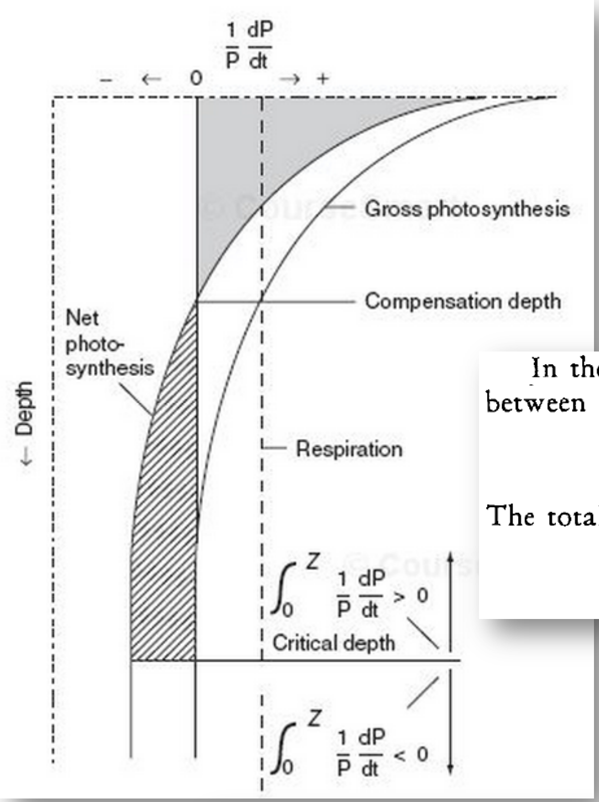
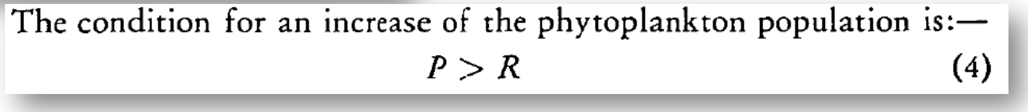


In the time, T, the total production by photosynthesis between the surface and the depth $z = -D$ is:—

$$P = m \int_0^T \int_{-D}^0 I_e e^{kz} \, dt dz = \frac{m}{k} (1 - e^{-kD}) \int_0^T I_e dt$$

The total destruction is:—

$$R = n \int_0^T \int_{-D}^0 = nTD$$



The condition for an increase of the phytoplankton population is:—

$$P > R \tag{4}$$

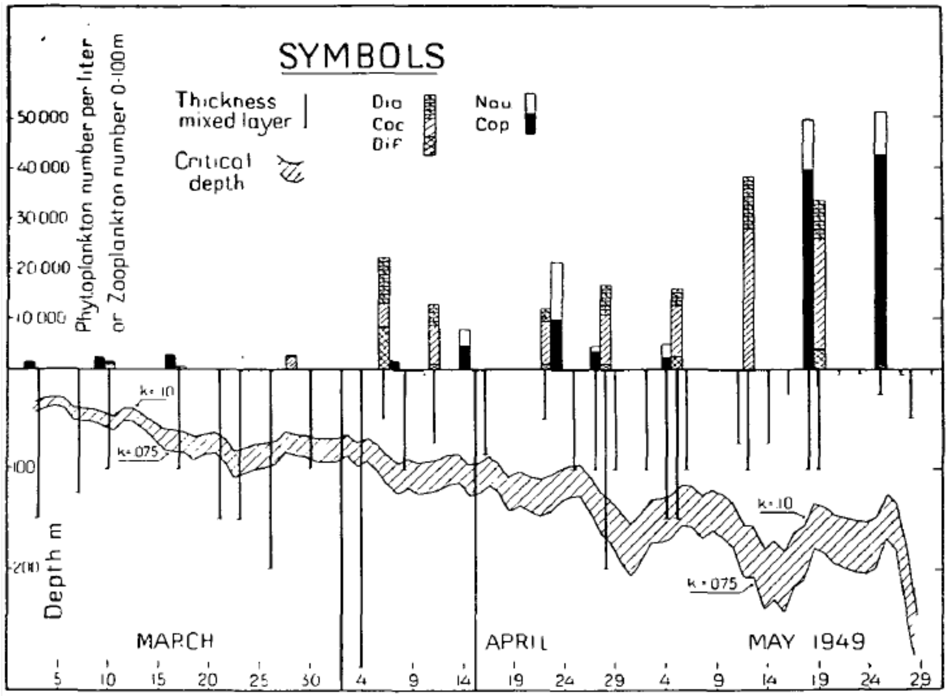
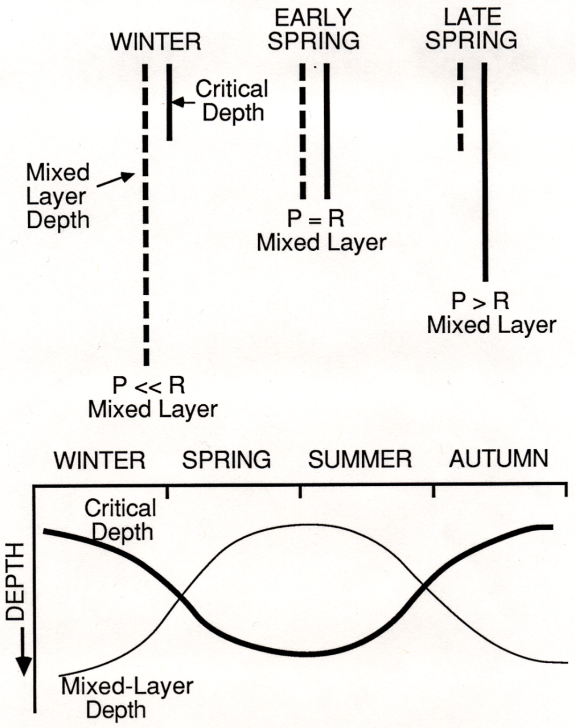


Figure 2. Results of observations at Weather Ship "M" (66°N., 2°E. Gr.). The symbols are explained in the graph, where the following abbreviations have been used:—Dia, *Diatomaceae;* Coc, *Coccolithophoridae;* Dif, *Dinoflagellatae;* Nau, Nauplii; and Cop, Copepods.

Sverdrup’s critical depth hypothesis (1953)



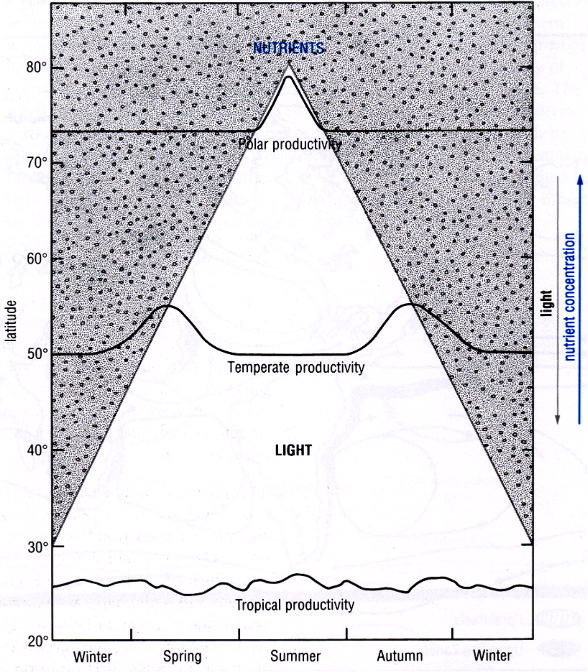
Criticisms of the practical applications of Critical Depth Theory

The concept is captivating, though it glosses over important details:

1. specificity to the "*spring bloom"* period
    a. no nutrient limitation
    b. prioritizes light (over temperature or nutrients)
2. horizontal/vertical advection!
3. oversimplification of the effect of grazers

But I think it is valuable to understand. It does give some sense of the interacting processes that need to be considered when attempting to estimate primary productivity in the ocean.

When considering the full seasonal cycle, nutrient limitation is important in conceptual models



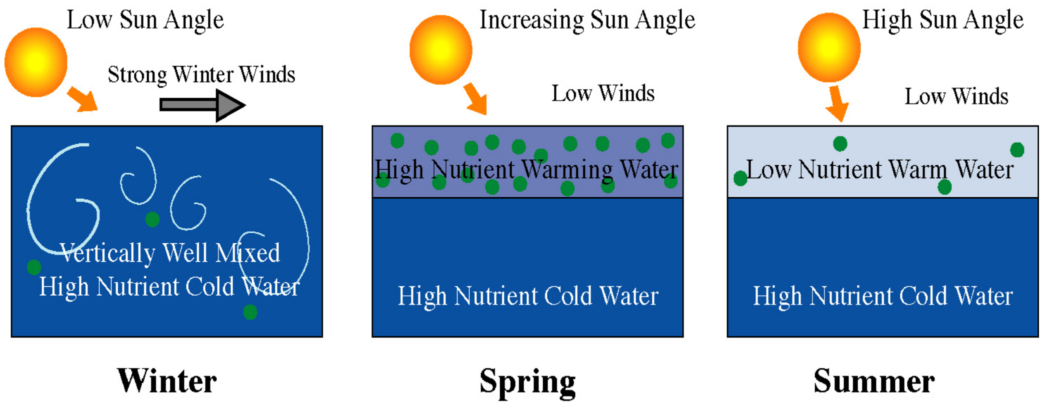
Timing:

Temperate - spring-bloom; coincident light, stratification & nutrients

Polar - abundant nutrients, delayed bloom, ice melt

Tropics - year-round light & stratification, variability due to nutrient infusions

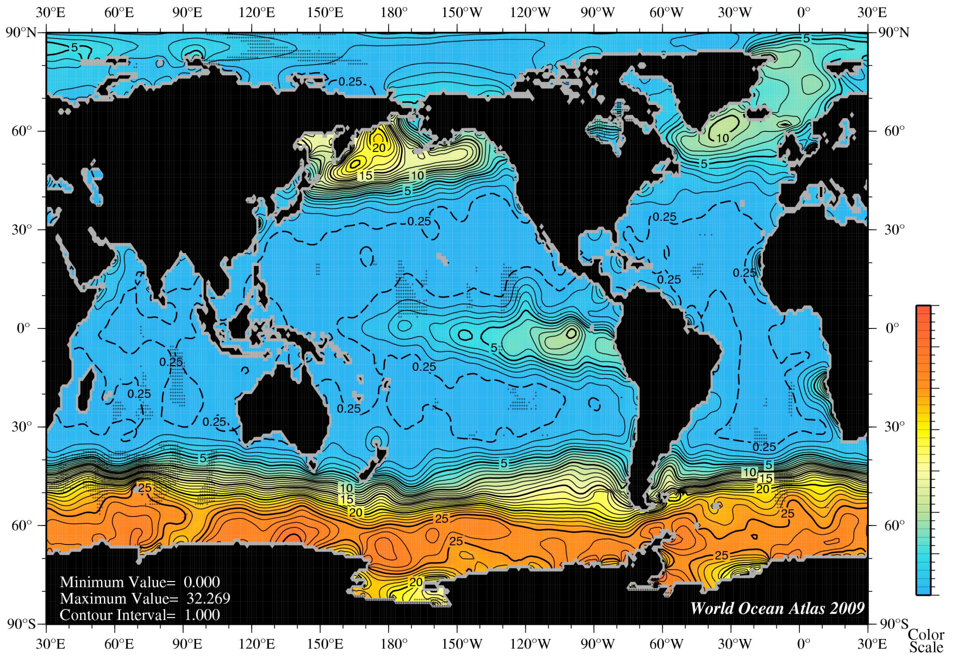
When considering the full seasonal cycle, nutrient limitation is important in conceptual models



Q: What removes nutrients from the euphotic zone in the first place?

Surface NO_3^-

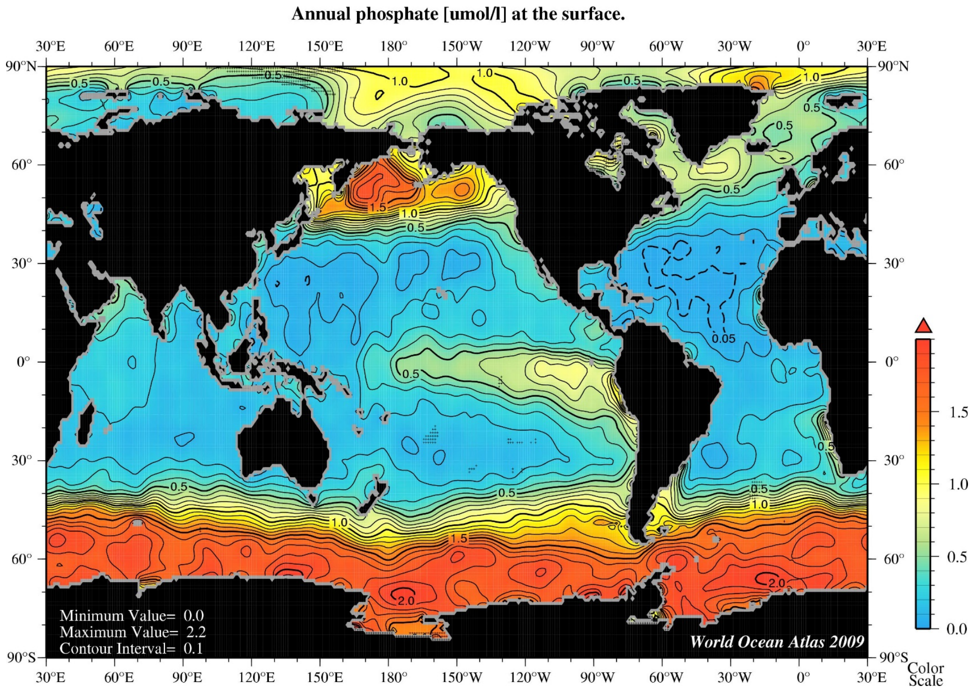
Annual nitrate [umol/l] at the surface.



Minimum Value= 0.000
Maximum Value= 32.269
Contour Interval= 1.000

World Ocean Atlas 2009

Surface PO_4^{3-}



Annual phosphate [umol/l] at the surface.

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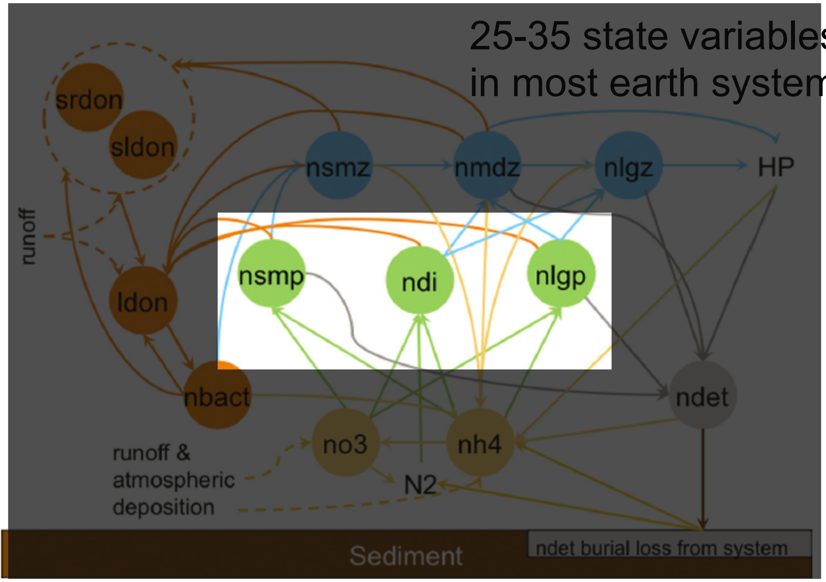
    Stock et al., 2014 (*Progress in Oceanography*)

Who are the major players?

Plankton food webs in biogeochemical models are simplified to the processes that have a key influence on the dynamics of interest.

The simpler the better, as long as caveats are understood.



Stock et al. 2014, COBALT

25-35 state variables are included in most earth system models.

- zooplankton
- phytoplankton
- dissolved organic matter
- detritus
- heterotrophic bacteria

Who are the major *phytoplankton* players?

To represent the most basic diversity of phytoplankton, many biogeochemical models include different phytoplankton groups to simulate differences in nutrient uptake/demand kinetics, sinking rates, nitrogen fixation, and loss to zooplankton (i.e. grazing) or viruses:

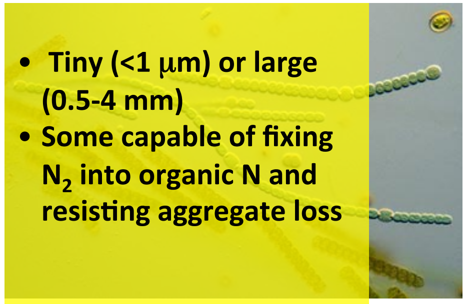
- Tiny phytoplankton that have low nutrient requirements per cell, but relatively slow nutrient uptake kinetics.
- Large phytoplankton that have high nutrient uptake rates, but also high demand.
- Phytoplankton that require Si, are ballasted, and sink to depth rather quickly.
- Phytoplankton that are capable of converting N_2 to organic-N.

The four major *phytoplankton* players

Diatoms

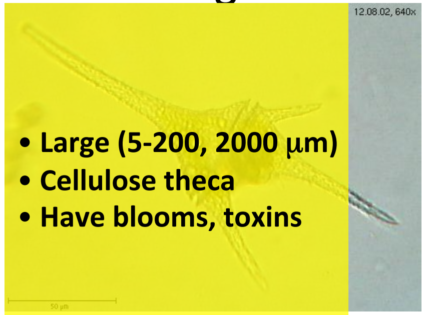
- Large (2-200, 2000 μm)
- Have silica frustules
- Potential to sink fast

Cyanobacteria



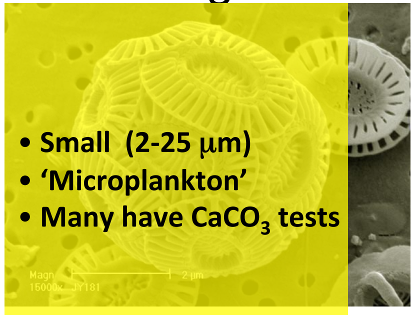
- Tiny (<1 μm) or large (0.5-4 mm)
- Some capable of fixing N_2 into organic N and resisting aggregate loss

Dinoflagellates



- Large (5-200, 2000 μm)
- Cellulose theca
- Have blooms, toxins

Microflagellates



- Small (2-25 μm)
- 'Microplankton'
- Many have $CaCO_3$ tests

The Prokaryotic phytoplankton: Cyanobacteria

Cyanobacteria—

Main players in the pelagic environment are:

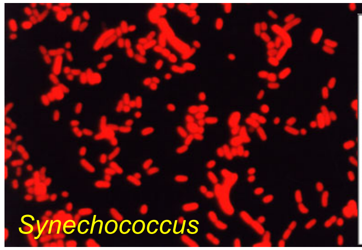
Synechococcus *Prochlorococcus*	**Picophytoplankton**
Trichodesmium	**"Net" plankton**

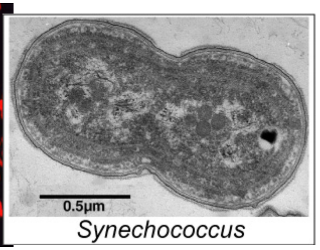
***Prochlorococcus* is the most abundant autotroph on earth** *(> 100,000 cells* ml^{-1}*).*

Numerous (about 2.8 to 3.0 *octillion* individuals, globally).

(that's 1×10^{27}*)*

Cyanobacteria: *Synechococcus* & *Prochlorococcus*

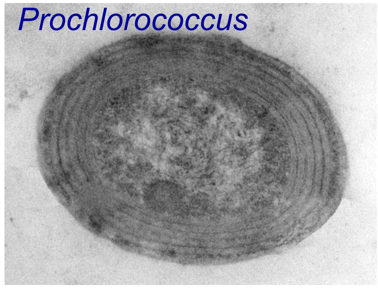




Synechococcus

Counted with epifluorescence microscopy or flow cytometry.

Fluoresce orange when excited with green light; contain phycoerythrin & phycocyanin.



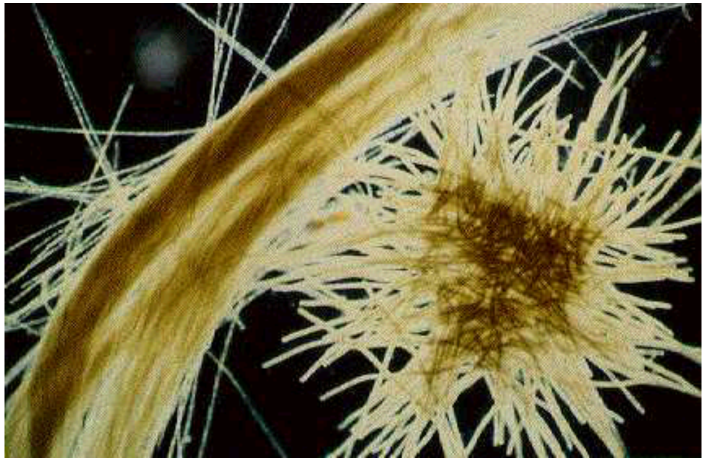
Contain divinyl chl *a* and chl *b*
Discovered in 1988 (Chisholm *et al*.).
Counted by flow cytometry.

Both Prochlorococcus and Synechoccus are autotrophs.

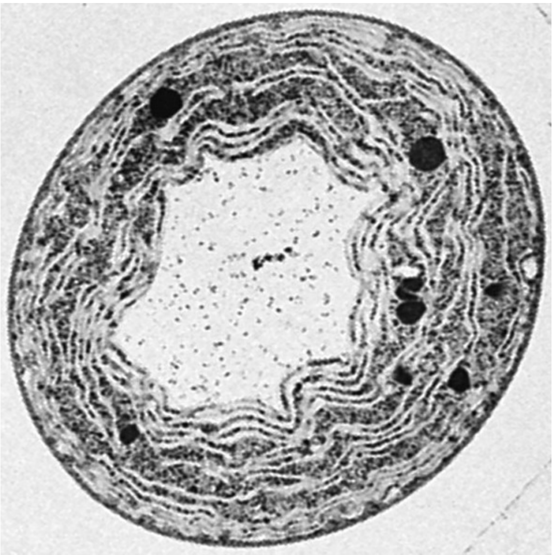
Cyanobacteria: Trichodesmium

- Macroscopic (~ size of an eyelash)
- Easily seen from ship or space.
- Two morphologies: puff and tuft.

Trichodesmium bloom



One filament = trichome = is composed of many cells in a row



Trichos are DIAZOTROPHS!

Found in N-poor regions

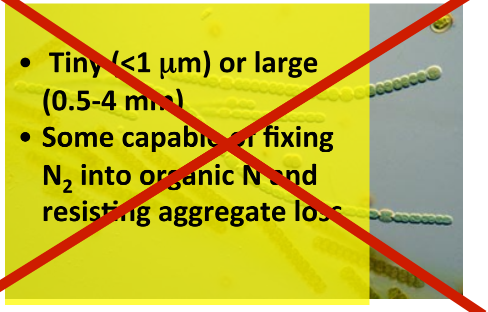
- They can “fix” atmospheric N
- N_2 is converted to NH_4^+, used to fuel growth

The four major “phytoplankton” players

Diatoms

- Large (2-200, 2000 µm)
- Have silica frustules
- Potential to sink fast

~~Cyanobacteria~~



- ~~Tiny (<1 µm) or large (0.5-4 mm)~~
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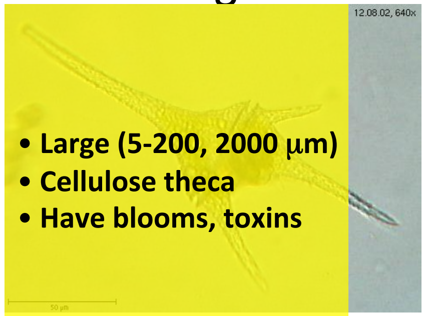
Dinoflagellates



- Large (5-200, 2000 µm)
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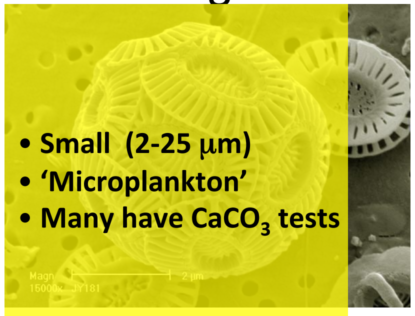
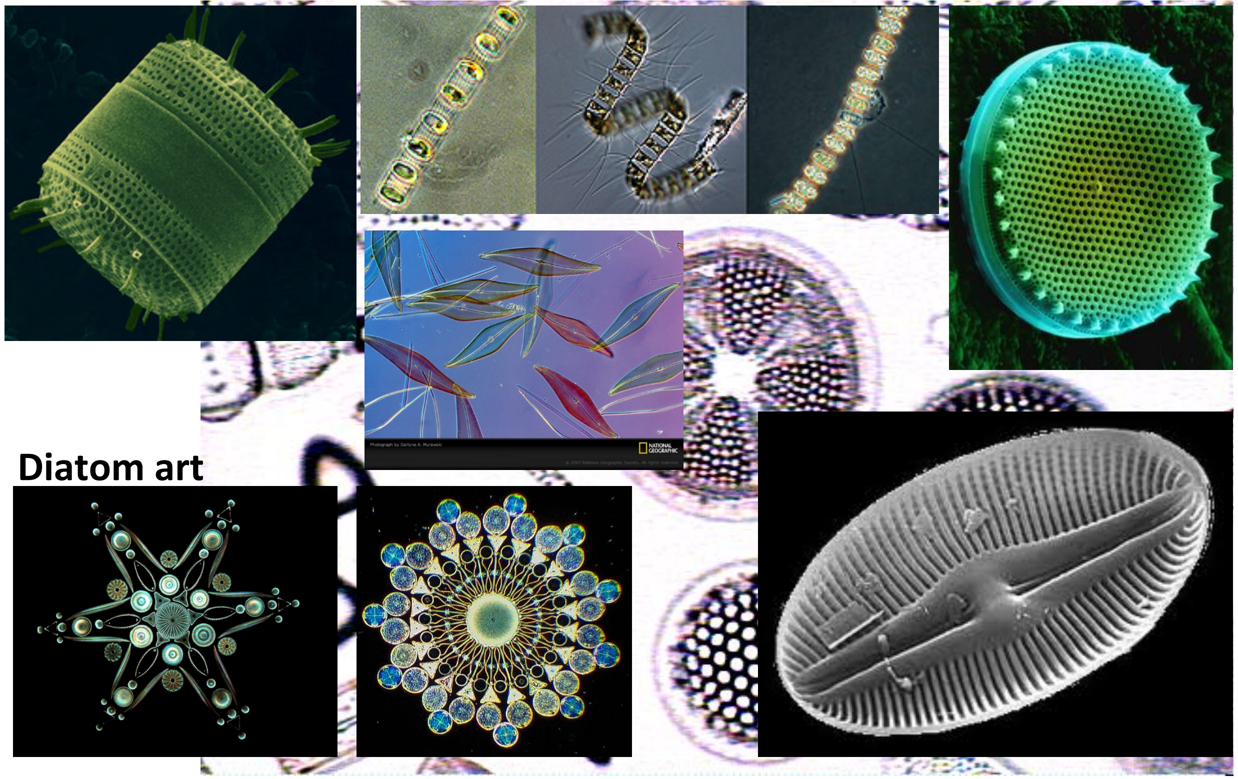
- Have blooms, toxins

Microflagellates



- Small (2-25 µm)
- ‘Microplankton’
- Many have $CaCO_3$ tests

Diatoms (Bacillariophytes)



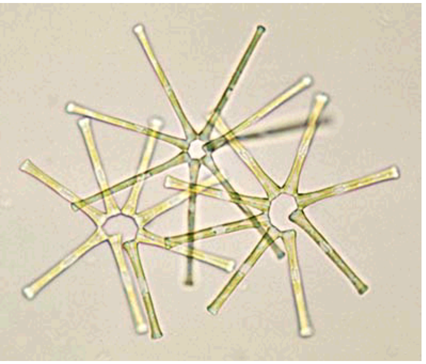
Diatom art

Diatoms (Bacillariophytes)

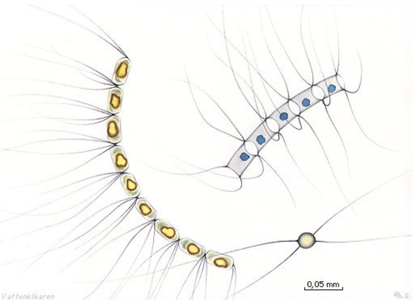
Range in size from 2 μm to 2000 μm.

Have an opal $Si(OH)_4$ frustule; tend to sink, need re-suspension by currents.

Often dominate the phytoplankton community in coastal oceans.

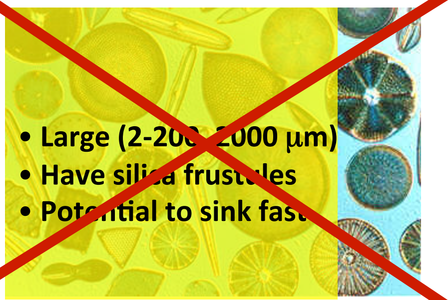


Pennate and centric forms; classified based on frustule morphology.



The four major “phytoplankton” players

Diatoms



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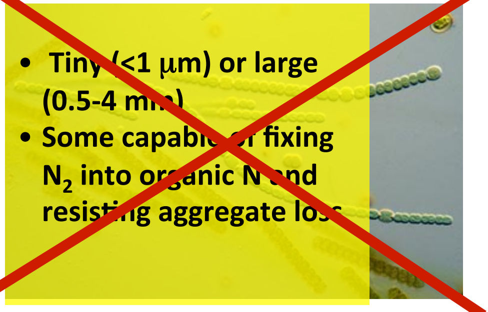
- ~~Potential to sink fast~~

Cyanobacteria



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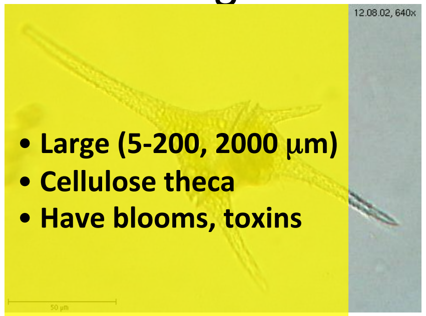
Dinoflagellates



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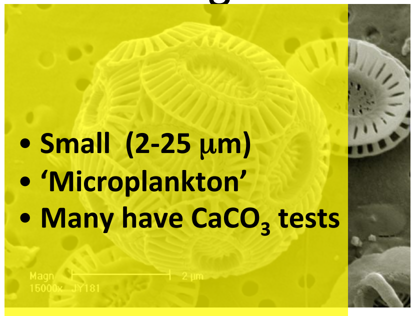
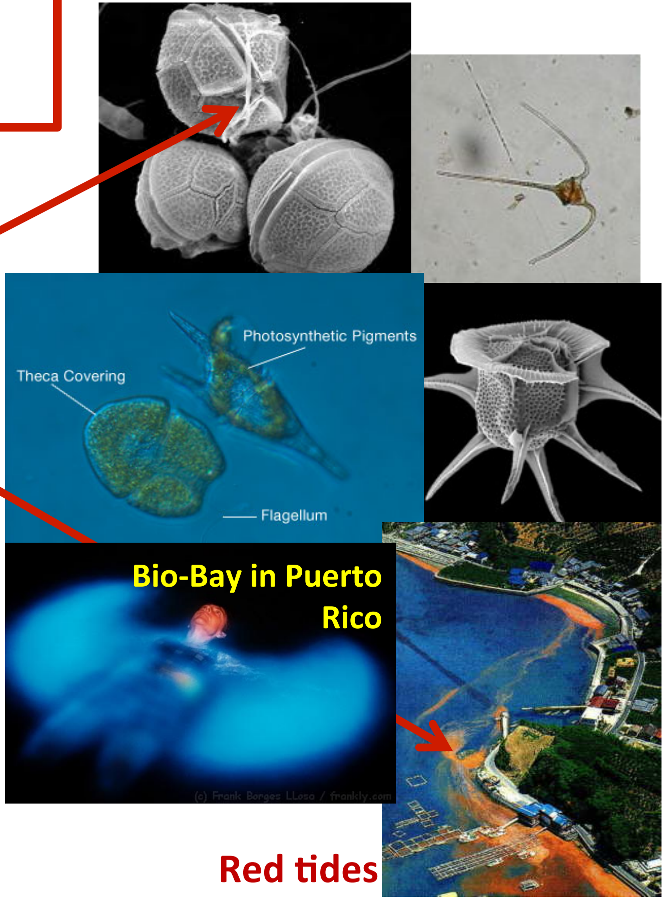


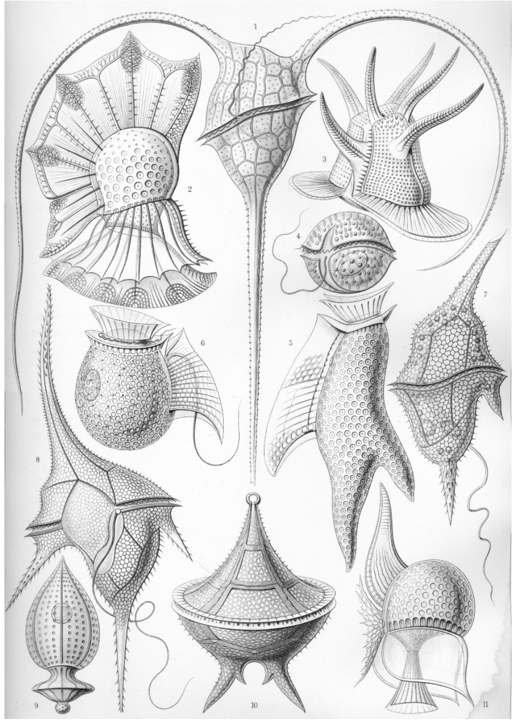
- Small (2-25 μm)
- ‘Microplankton’
- Many have $CaCO_3$ tests

Dinoflagellates

- Single-celled
- Cellulose ‘theca’
- Have two *flagella* for movement
- Some have bioluminescence
- Some species are the zooxanthellae in corals



Dinoflagellates



Cause Harmful Algal Blooms (HABs) (‘red tides’)

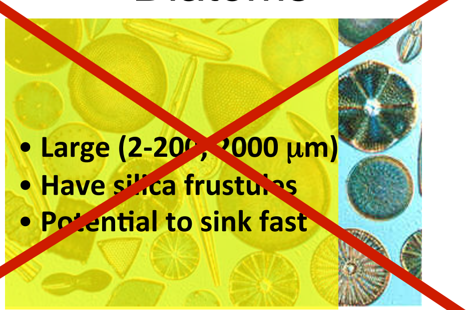
High concentrations cause production of neurotoxins

Accumulate in shellfish

Most are capable of phagocytosis (there are autotrophic, heterotrophic and mixotrophic species.)

The four major “phytoplankton” players

Diatoms



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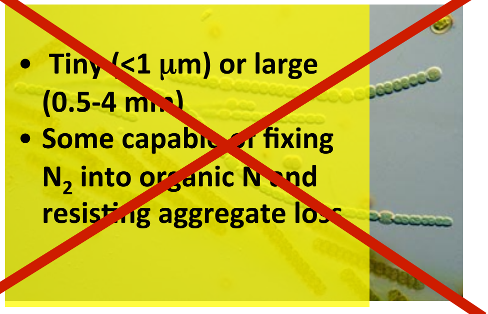

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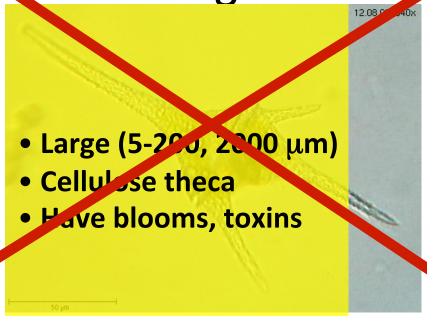
Dinoflagellates



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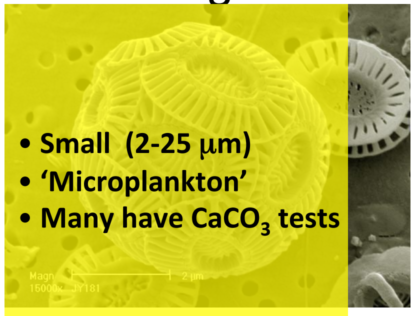


- Small (2-25 µm)
- ‘Microplankton’
- Many have $CaCO_3$ tests

Coccolithophores (a dominant type of microflagellate)

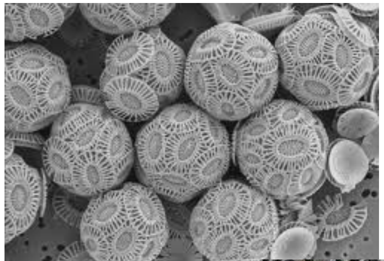
Carbonate test ($CaCO_3$)

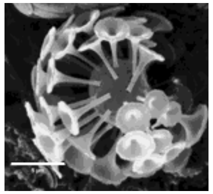
Order of magnitude smaller than diatoms – nanoplankton

Important carbonate sediment formation

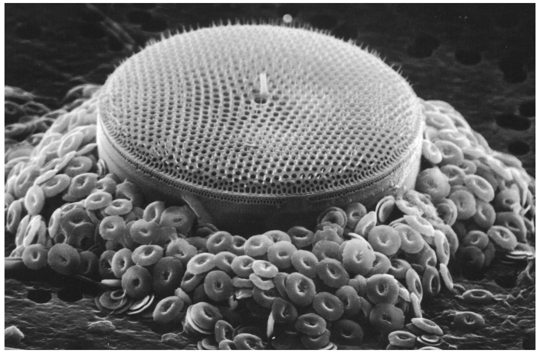
Some are *mixotrophic*

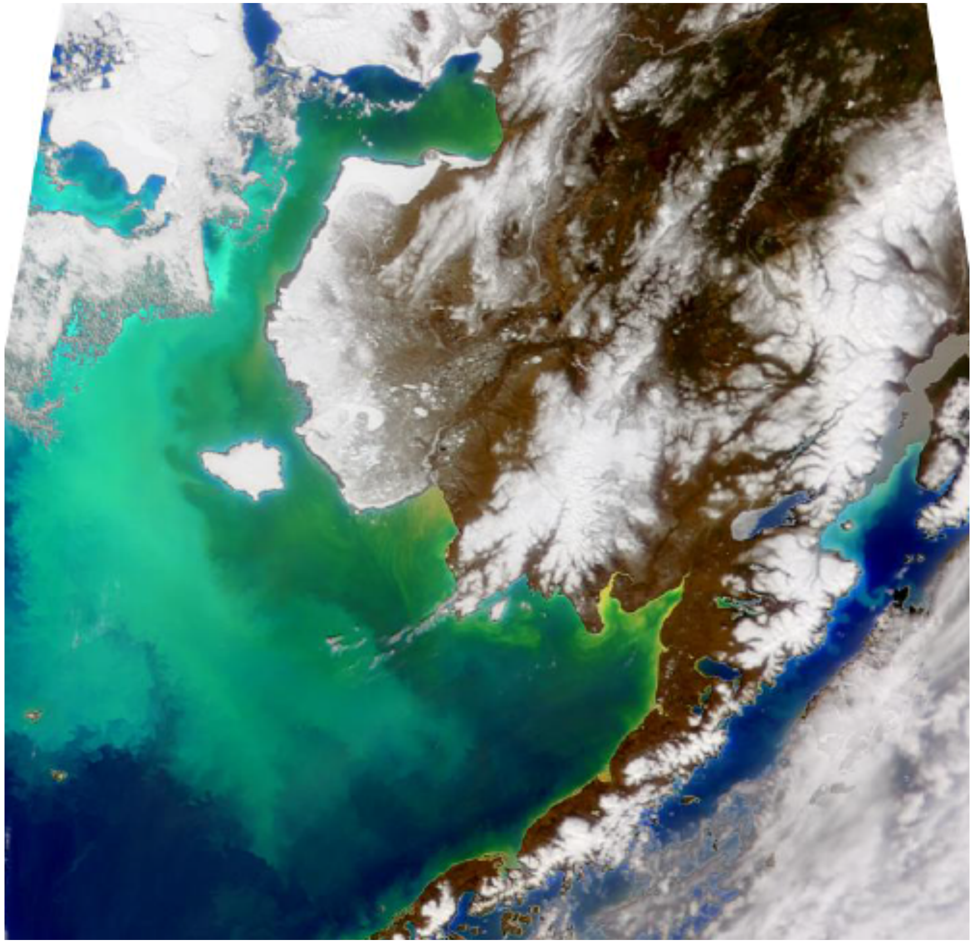
Form noticeable blooms





Images by courtesy of M.Geisen





Dimensions of variability (with interest on carbon export)

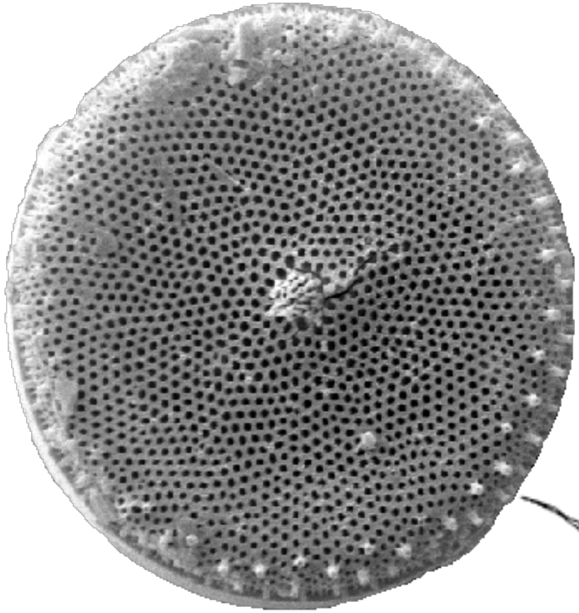
Given these properties, we can see a few dimensions of variability among phytoplankton.

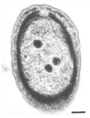
Size
Enzymatic ability to fix nitrogen (N_2) into organic nitrogen
Mineral ballasting (do they have a Si frustule or calcareous test or not)

Perhaps the most pervasive of these characteristics is *size*.

Nutrient uptake ability
Nutrient demand
Sinking
Susceptibility to predation

Nutrient uptake kinetics are dependent on cell surface area, while nutrient utilization is modeled as a function of volume





Who takes up nutrients faster?

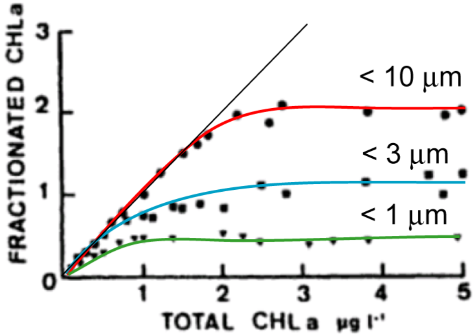
Who satisfies their nutrient requirement faster?

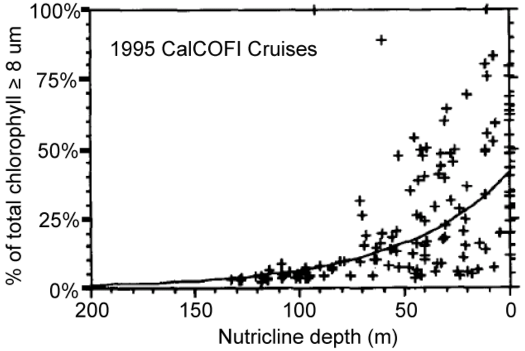
Who sinks out of the euphotic zone faster?

Such allometric scaling is pervasive in ecosystem models

Generally, when nutrient concentrations are low, phytoplankton biomass is low and is composed of small individuals.

Allometric scaling is used to parameterize nutrient scavenging, ingestion and respiration rates, and predator-prey interactions.





R. Goericke, M. Mullin, CalCOFI

Outline

1. Mass balance in marine biogeochemistry

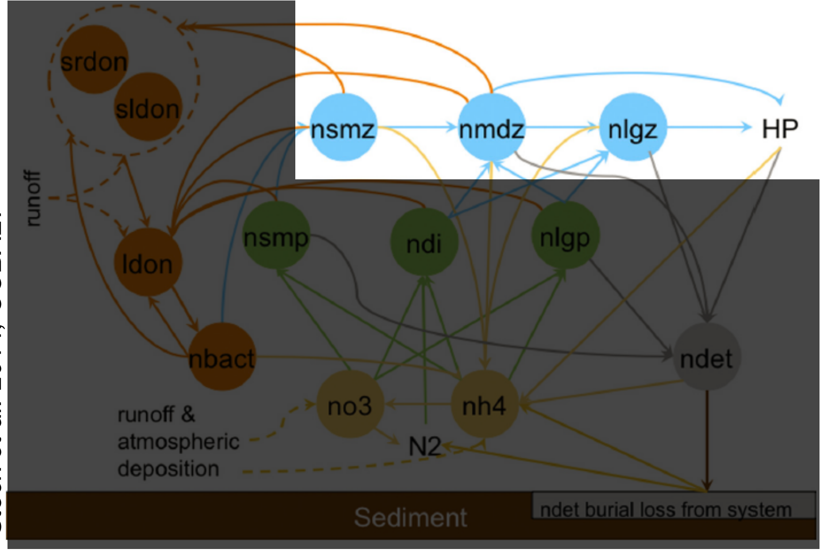
2. What types of organisms are we concerned with?

3. An example of a global marine biogeochemical model – COBALT.
   Stock et al., 2014 (*Progress in Oceanography*)

Who are the major players?

Process resolution of global biogeochemical models decreases with trophic level.

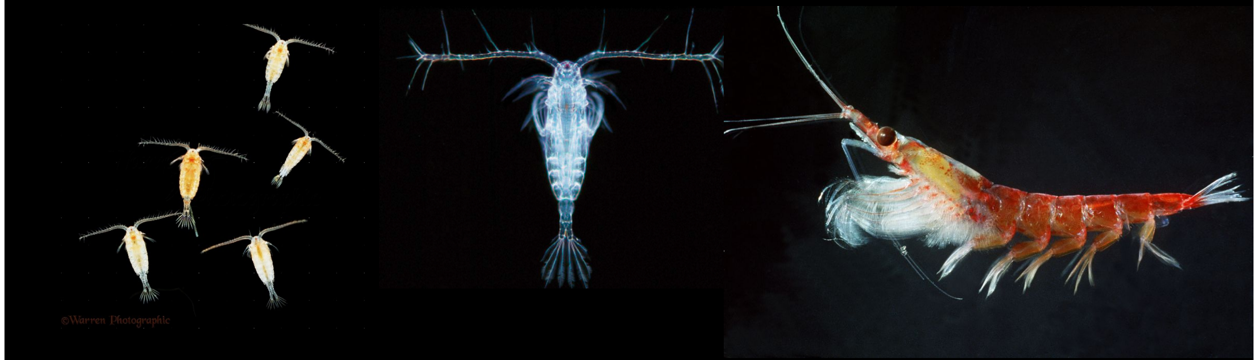
Processes-level distinctions among zooplankton groups are minor in comparison to the phytoplankton and largely allometric.



Stock et al. 2014, COBALT

- zooplankton
- phytoplankton
- dissolved organic matter
- detritus
- heterotrophic bacteria

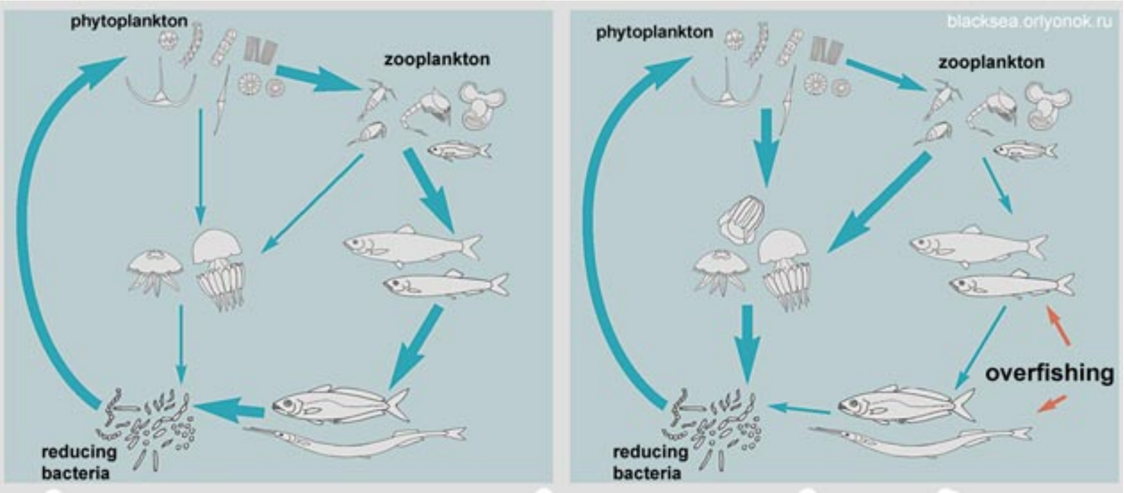
Models are parameterized for crustaceaus zooplankton (more so because of limited data on other groups than anything else)



At regional scales, focus on influential groups of interest is possible. For example, gelatinous zooplankton have played a dominate role in the ecology of the Black and Caspian Seas in recent decades.

Mnemiopsis (early 1980s introduction to Black Sea; 1999 to Caspian)

Consideration of the role of gelatinous zooplankton at the global scale is one of the next steps to be explored



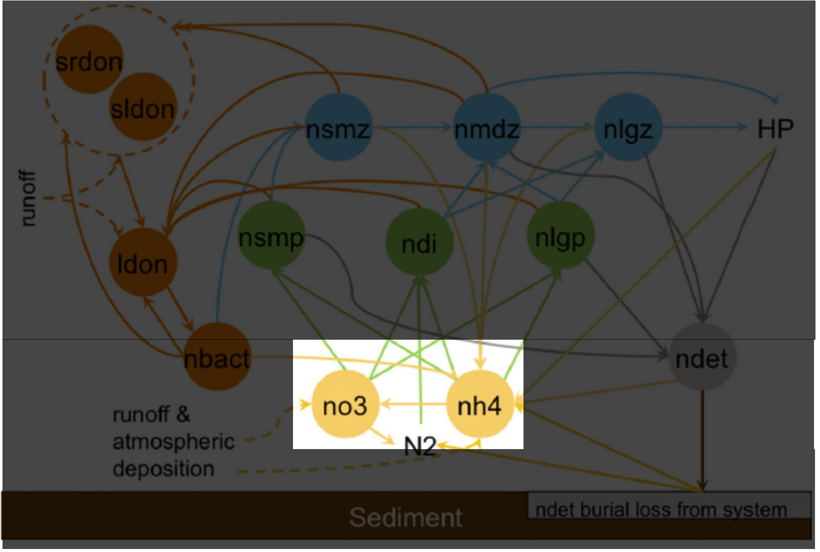
Changes in the Black Sea pelagic food web due to overfishing and *Mnemiopsis* introduction.

Sorokin, 2002

Representation of nutrient cycling is limited to major nutrient species

Nutrients (typically N) act as the currency in models for biomass of plankton and higher tropic levels.

N:Chl values are dynamically dependent on light levels and nutrient availability.



Stock et al. 2014, COBALT

- zooplankton
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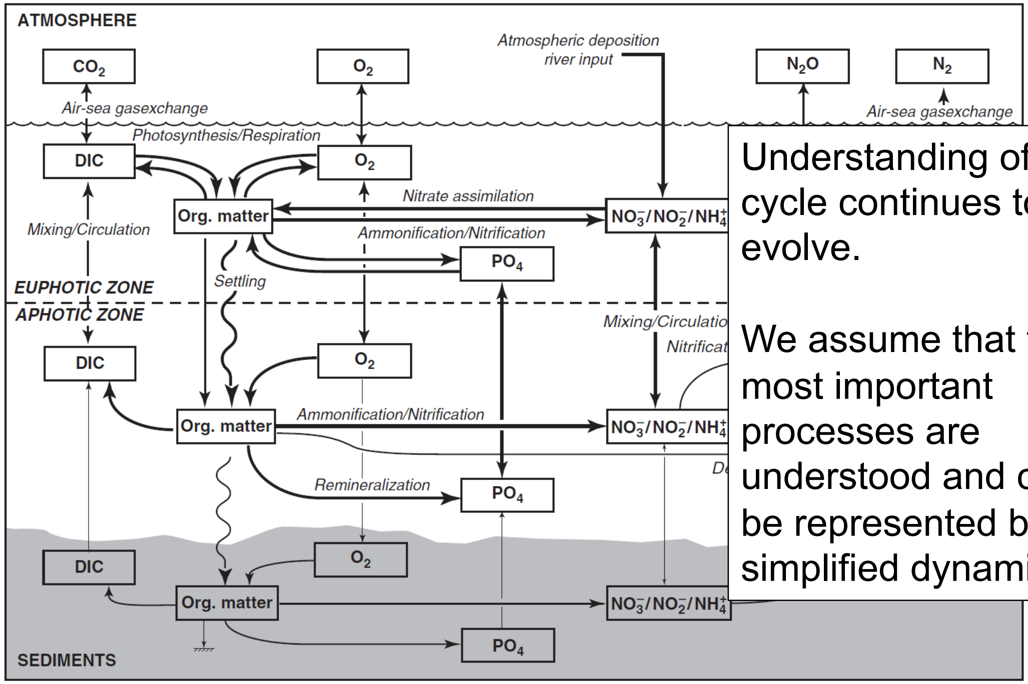
The nitrogen cycle is one of the more important, but also more complex of the nutrient cycles.



Understanding of the cycle continues to evolve.

We assume that the most important processes are understood and can be represented by simplified dynamics.

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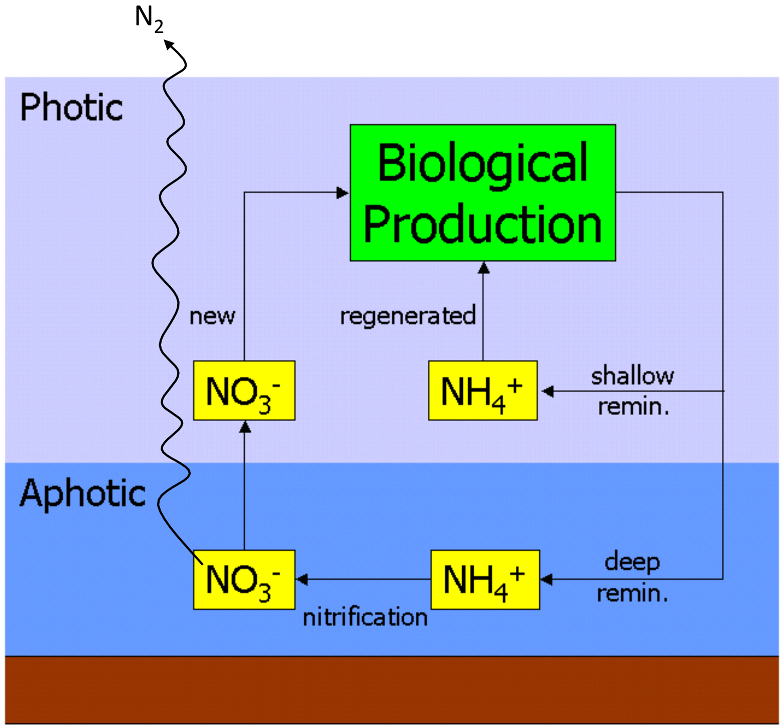


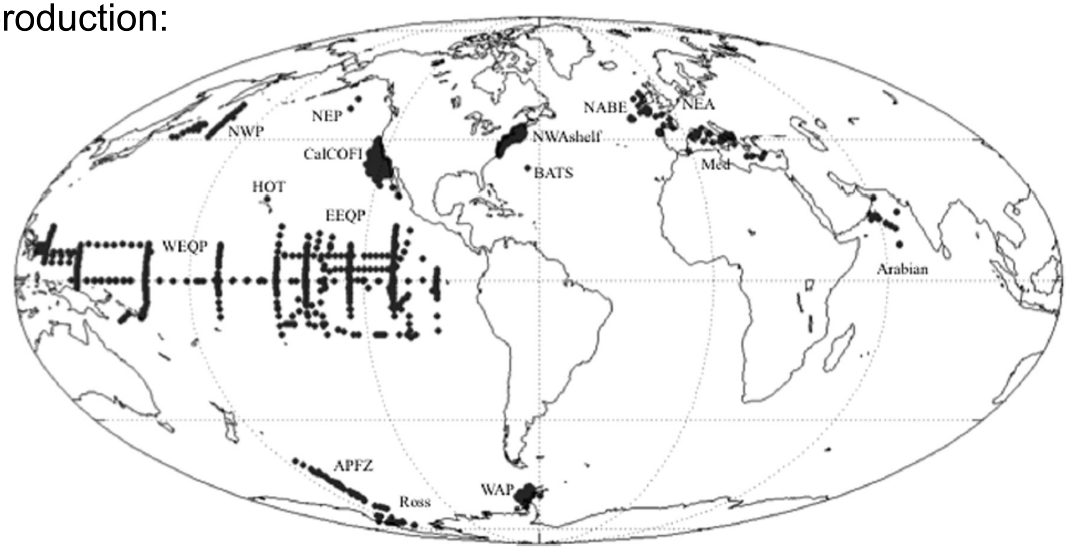
Understanding of the cycle continues to evolve.

We assume that the most important processes are understood and can be represented by simplified dynamics.

How do such models perform on the global scale?

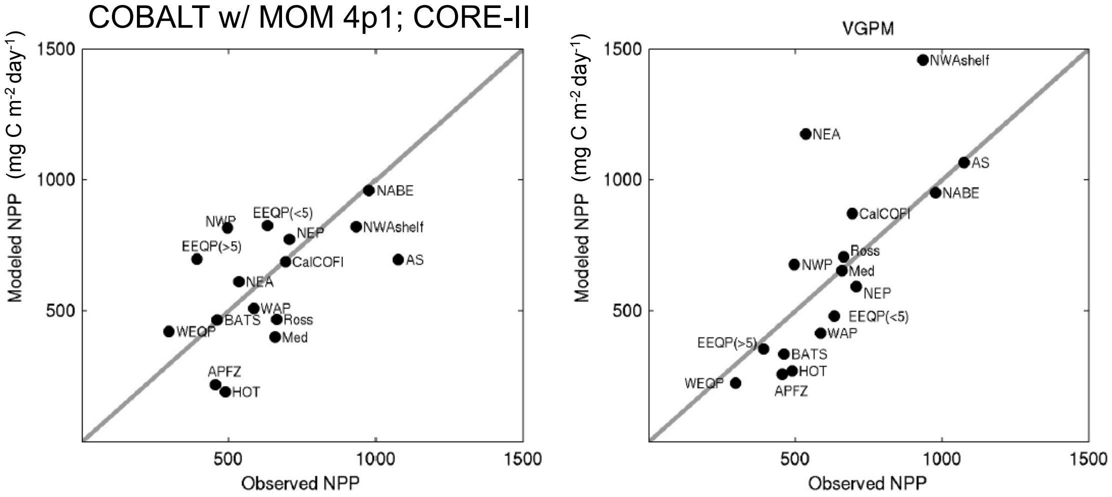
Who knows? In comparison to physical oceanography, biogeochemical data are extremely rare.

Consider stations measuring the annual cycle of primary production:



Stock et al. 2014

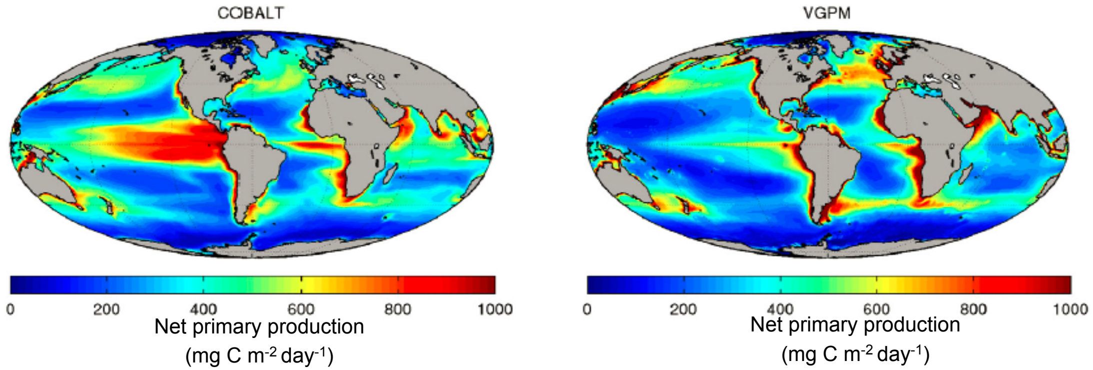
But estimates of primary production are similar to the estimates and to satellite-based algorithms

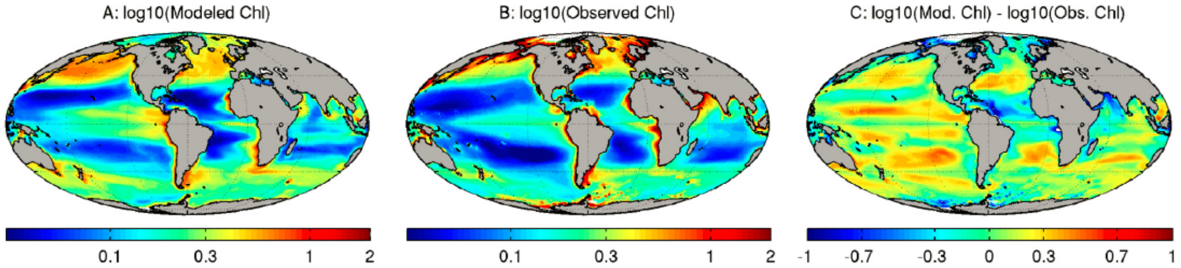


Biases are the attributable to the physical and biogeochemical portions of the model

Stock et al. 2014

But estimates of primary production are similar to the estimates and to satellite-based algorithms





Stock et al. 2014

Conclusions and outlook

Biogeochemical models offer insight to the relationships between physical processes and issues of public impact and interest.

These models are computationally expensive and typically limited to the simplest suitable representation for a given question. Model components will be highly dependent on the region and question of interest. Higher-trophic-levels and human activities are typically included off-line.

Limited observations of biogeochemical properties (particularly Fe, primary production, and zooplankton) are serious obstacles to model assessment.

Understanding of key processes continues to evolve; as a result, model development is in its infancy.

Thanks for your attention.

Ryan Rykaczewski
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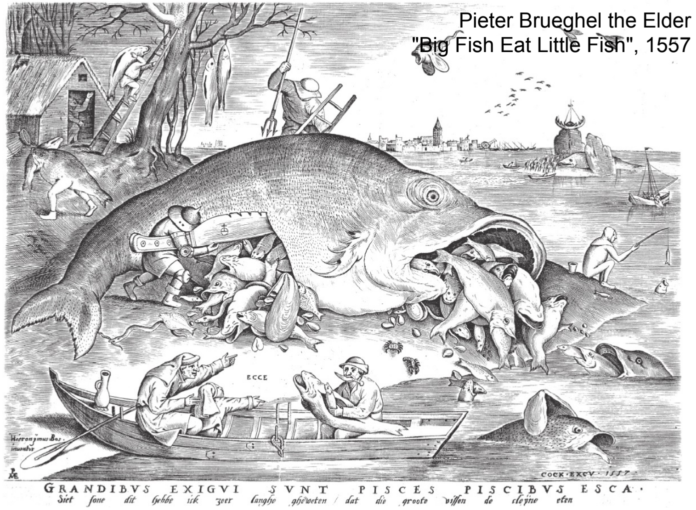
SOUTH CAROLINA



Pieter Brueghel the Elder
"Big Fish Eat Little Fish", 1557

What does this mean for distributions of nutrients and gases?

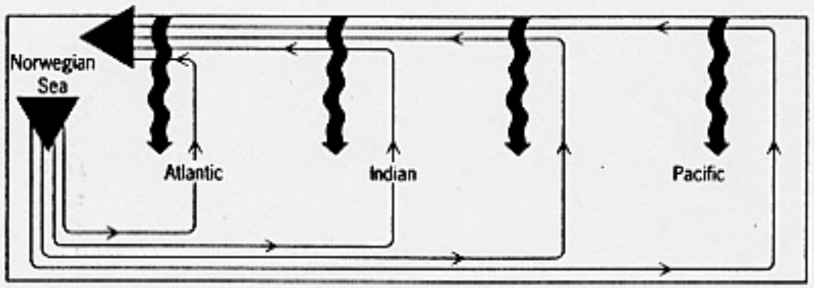
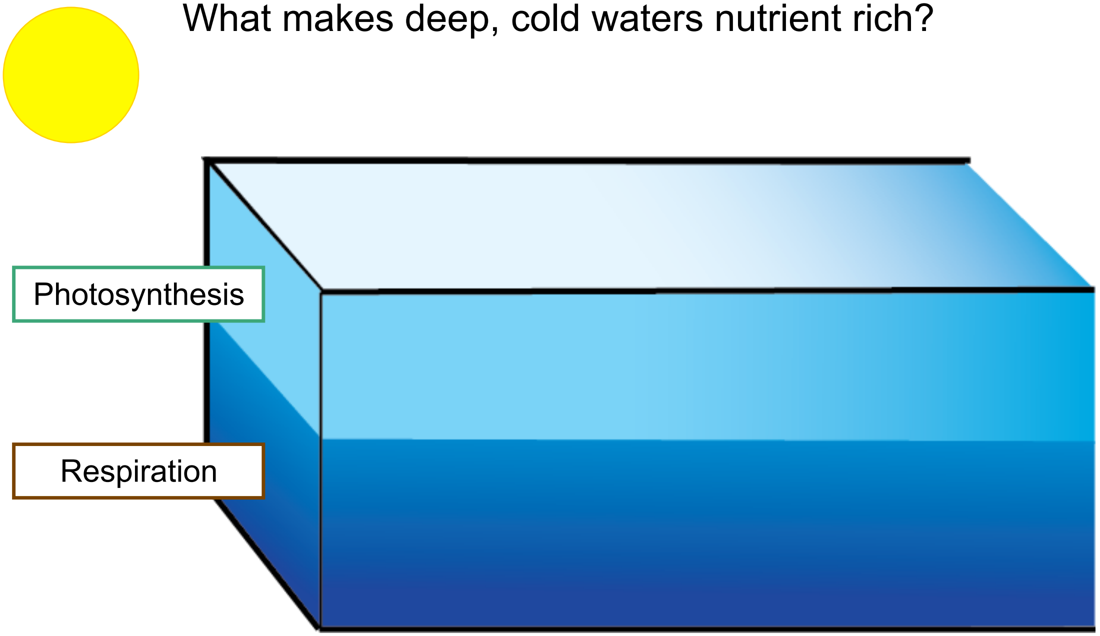


FIGURE 10.5. Idealized vertical section running from the North Atlantic to the North Pacific showing the major advective flow pattern (solid lines) and the rain of biogenic particles (wavy lines). *Source:* From *Chemical Oceanography*, W. S. Broecker, copyright © 1974 by Harcourt, Brace and Jovanovich,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

Review of photosynthesis and respiration

What makes deep, cold waters nutrient rich?

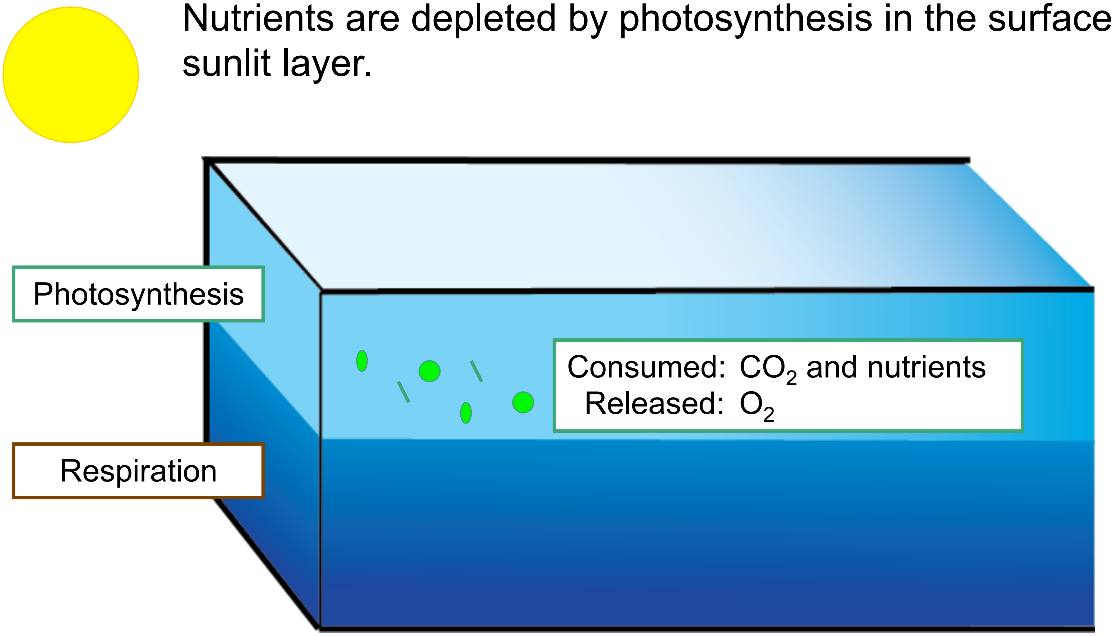


Photosynthesis

Respiration

Review of photosynthesis and respiration

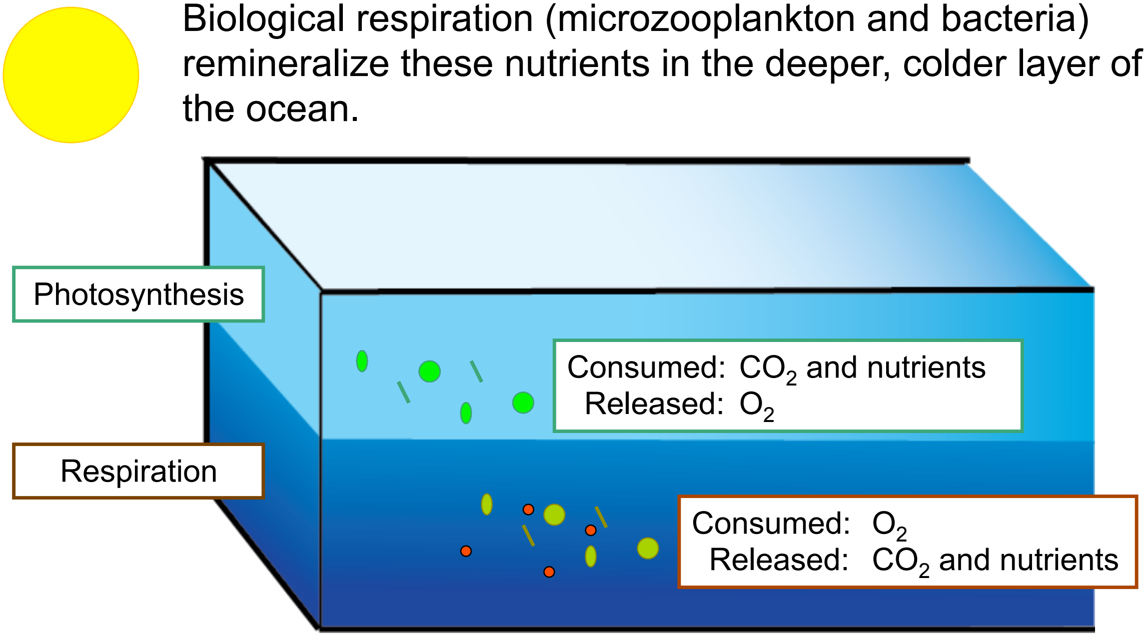
Nutrients are depleted by photosynthesis in the surface, sunlit layer.



Consumed: CO_2 and nutrients
Released: O_2

Review of photosynthesis and respiration

Biological respiration (microzooplankton and bacteria) remineralize these nutrients in the deeper, colder layer of the ocean.



Photosynthesis

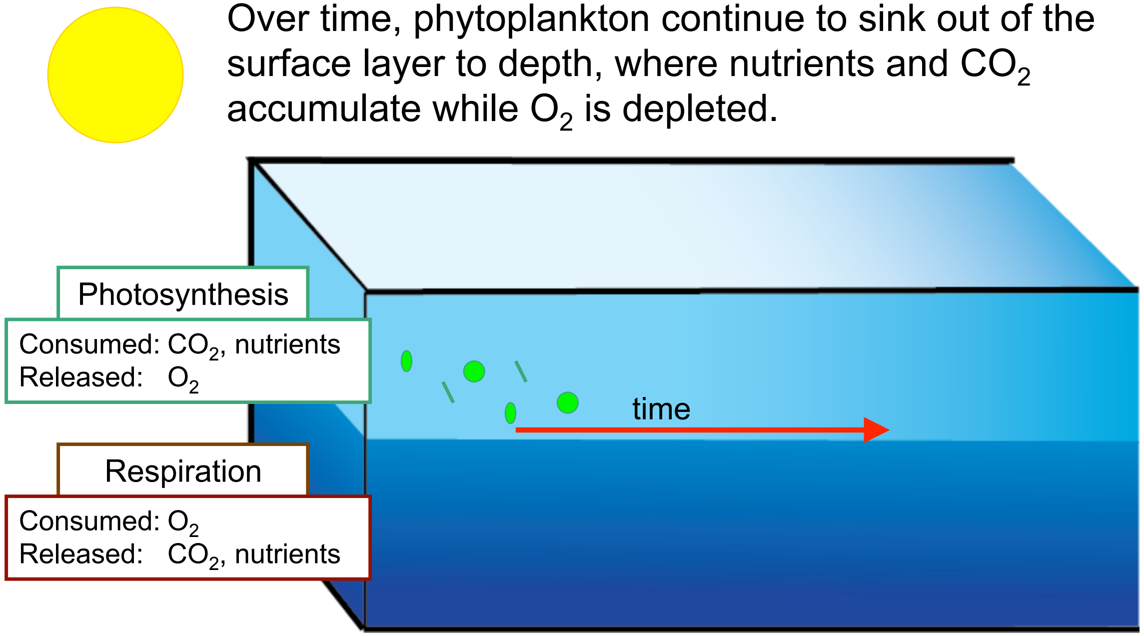
Consumed: CO_2 and nutrients
Released: O_2

Respiration

Consumed: O_2
Released: CO_2 and nutrients

Review of photosynthesis and respiration

Over time, phytoplankton continue to sink out of the surface layer to depth, where nutrients and CO_2 accumulate while O_2 is depleted.



Photosynthesis

Consumed: CO_2, nutrients
Released: O_2

Respiration

Consumed: O_2
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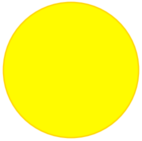
Review of photosynthesis and respiration



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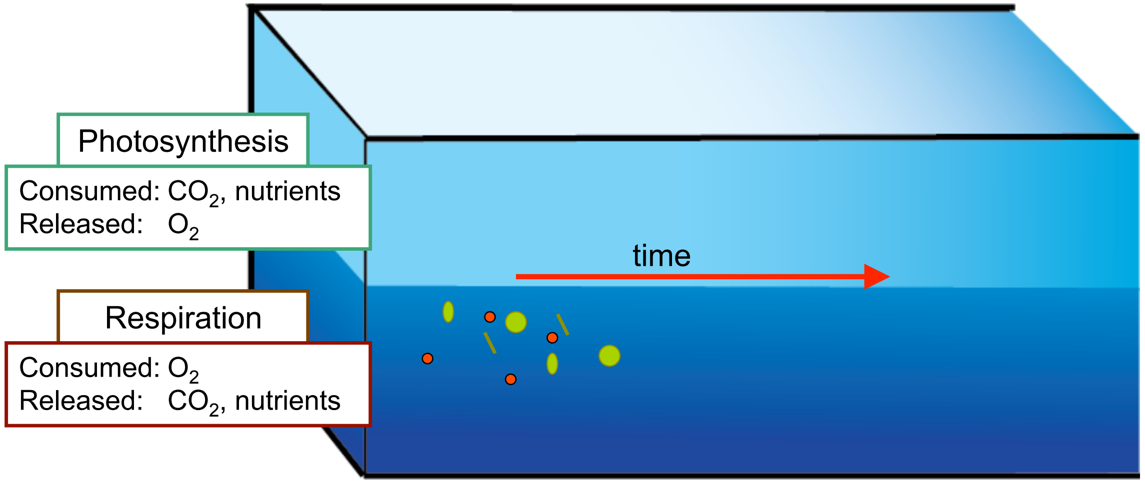

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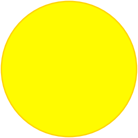

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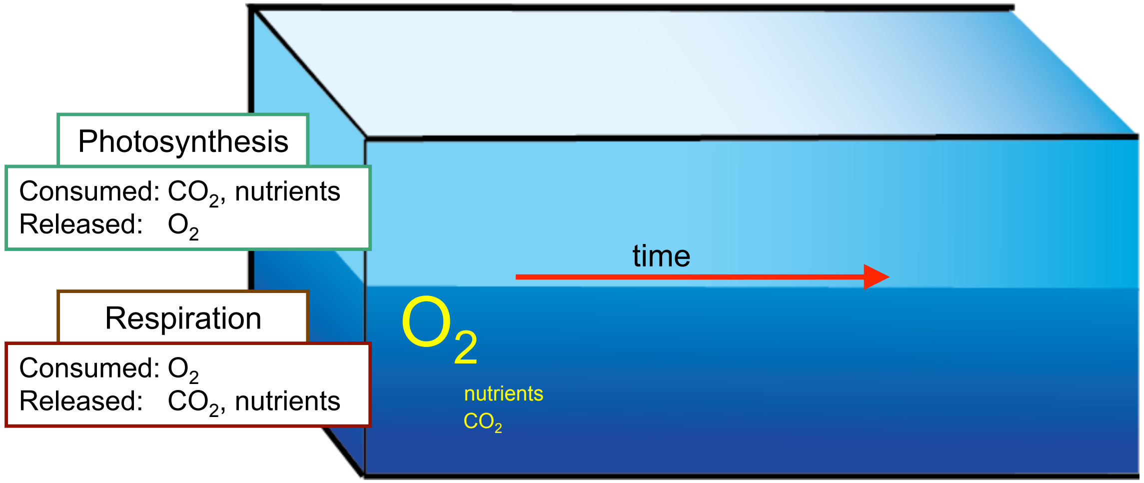

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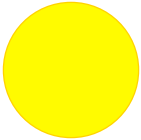

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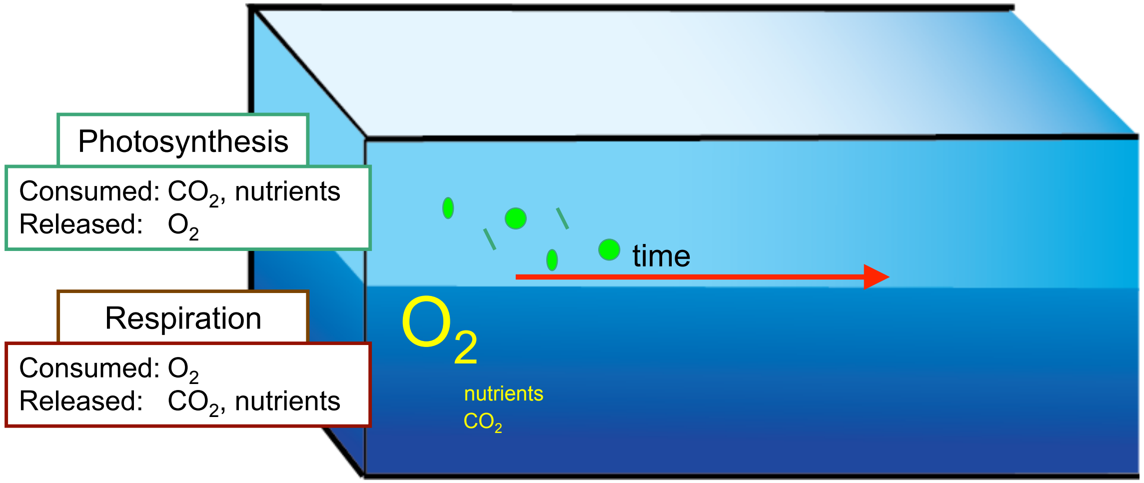

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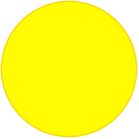

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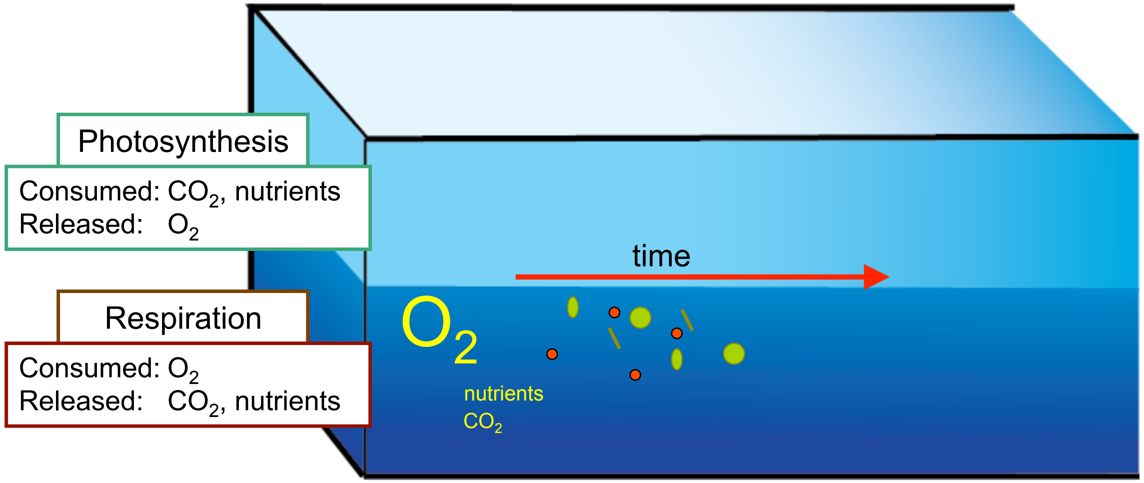

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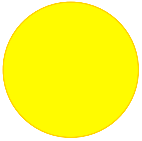

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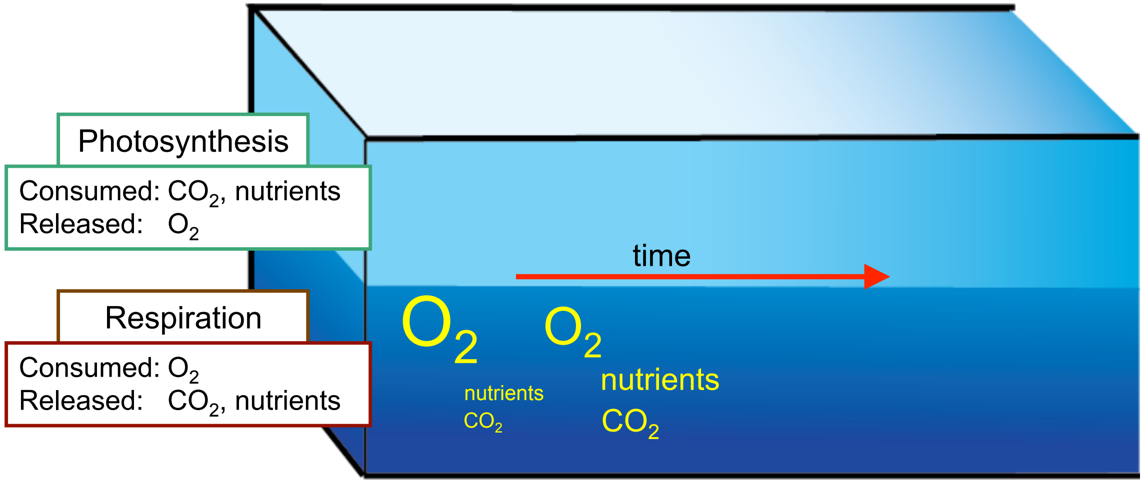


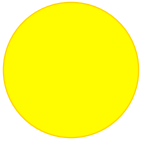
Photosynthesis

Consumed: CO_2, nutrients
Released: O_2

Respiration

Consumed: O_2
Released: CO_2, nutrients

Review of photosynthesis and respiration



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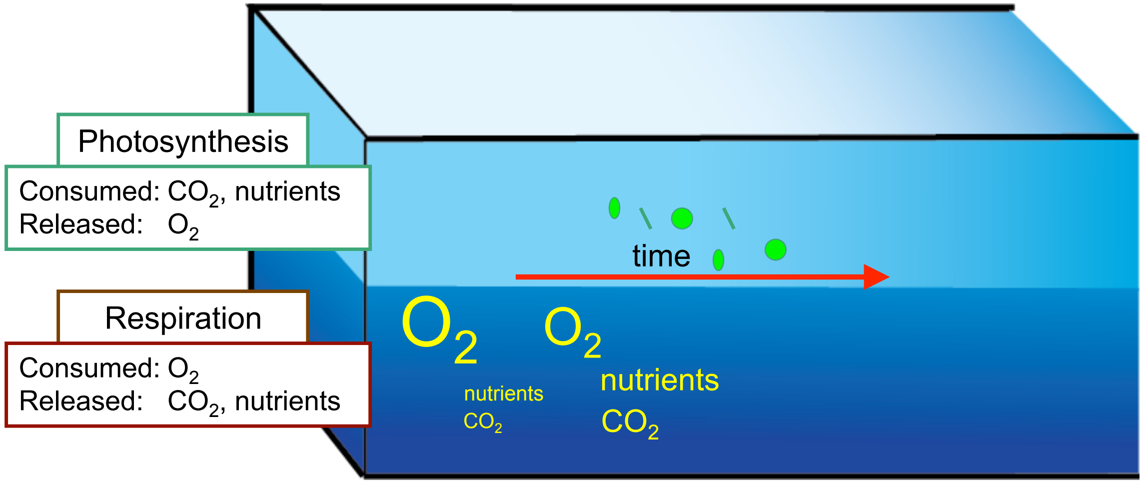

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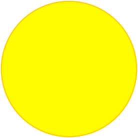

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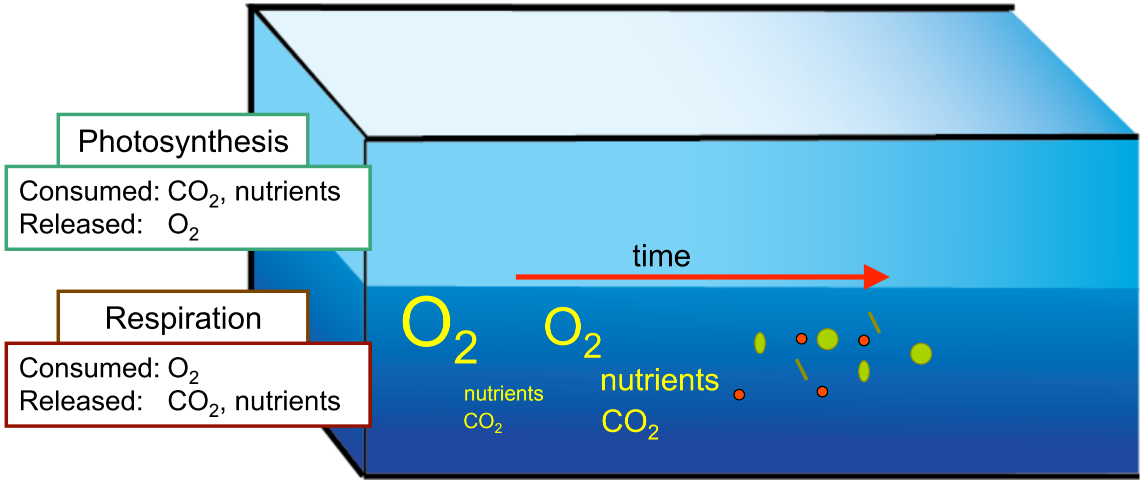

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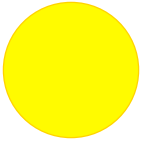

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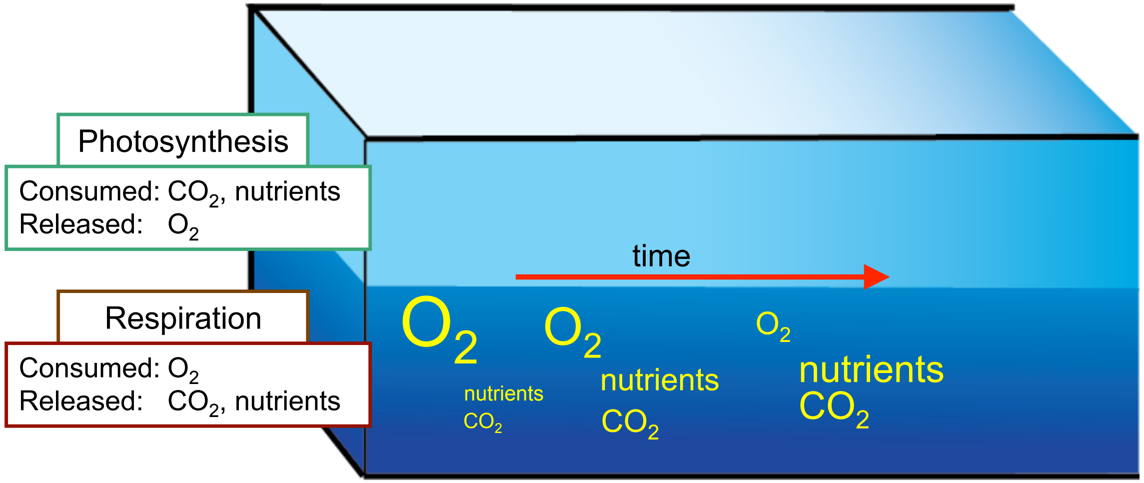

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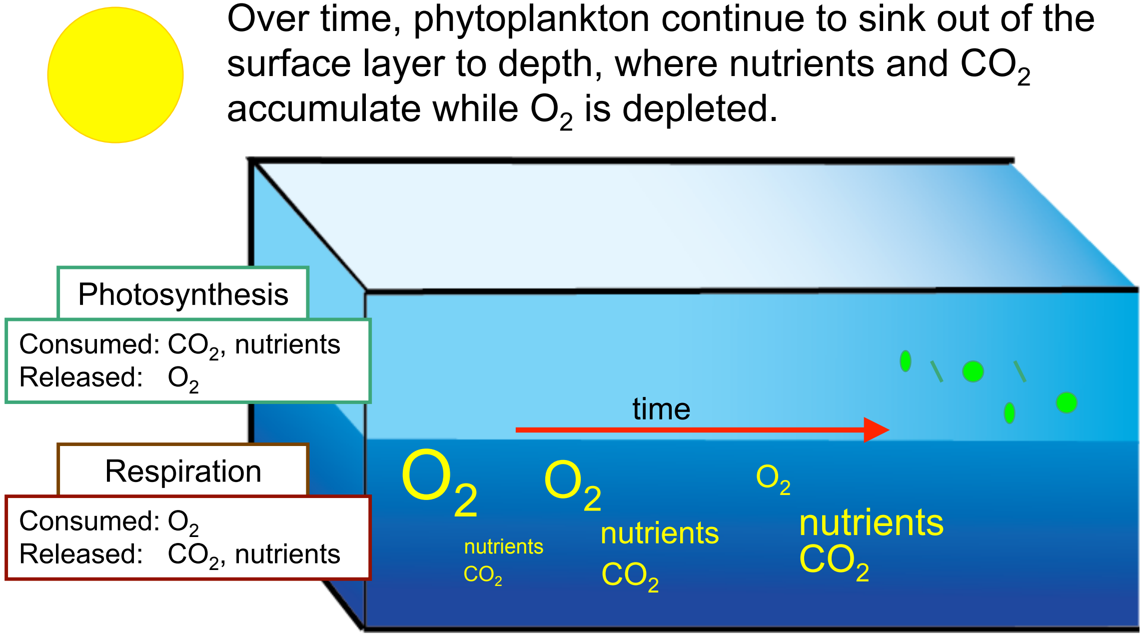

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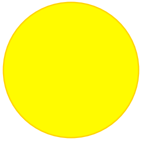

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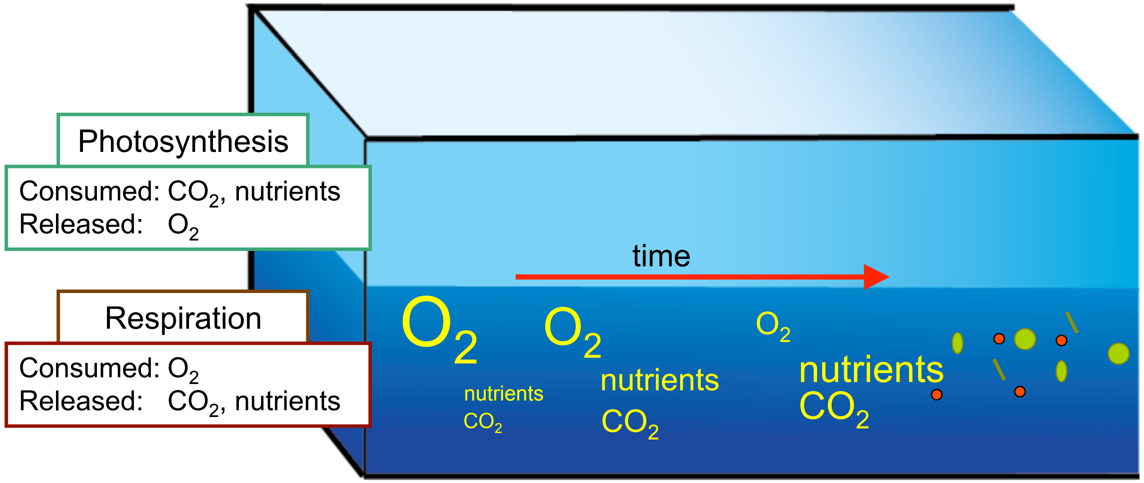

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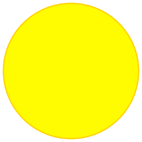

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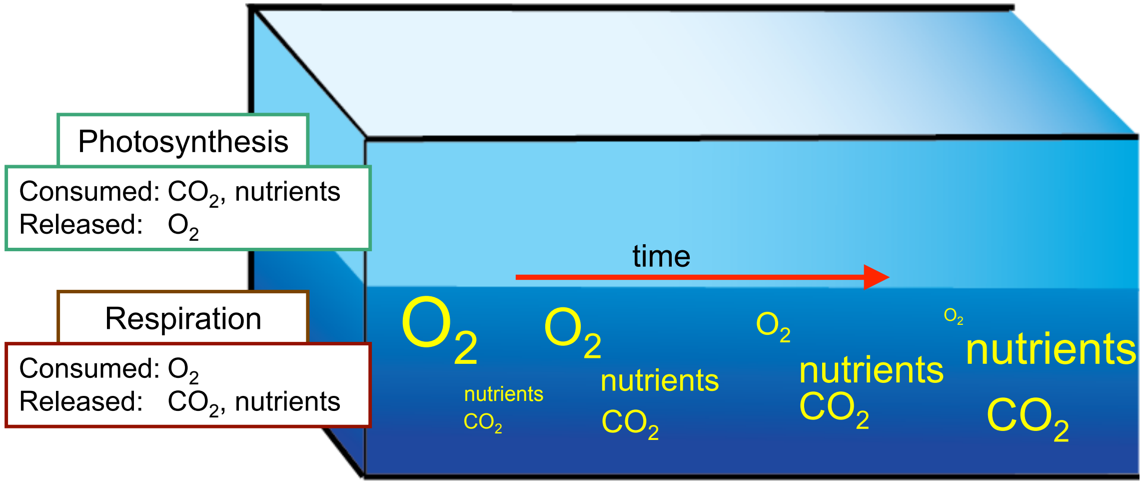

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Respiration

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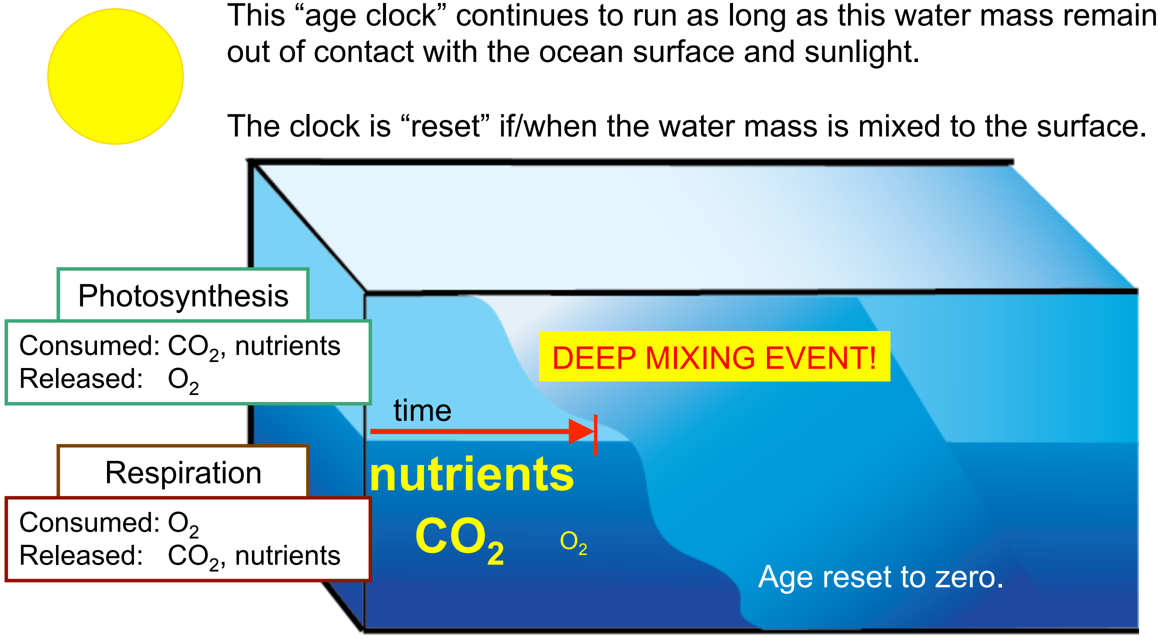
Released: CO_2, nutrients

“Old” means high nutrients, low O_2, low pH

This “age clock” continues to run as long as this water mass remains out of contact with the ocean surface and sunlight.

The clock is “reset” if/when the water mass is mixed to the surface.



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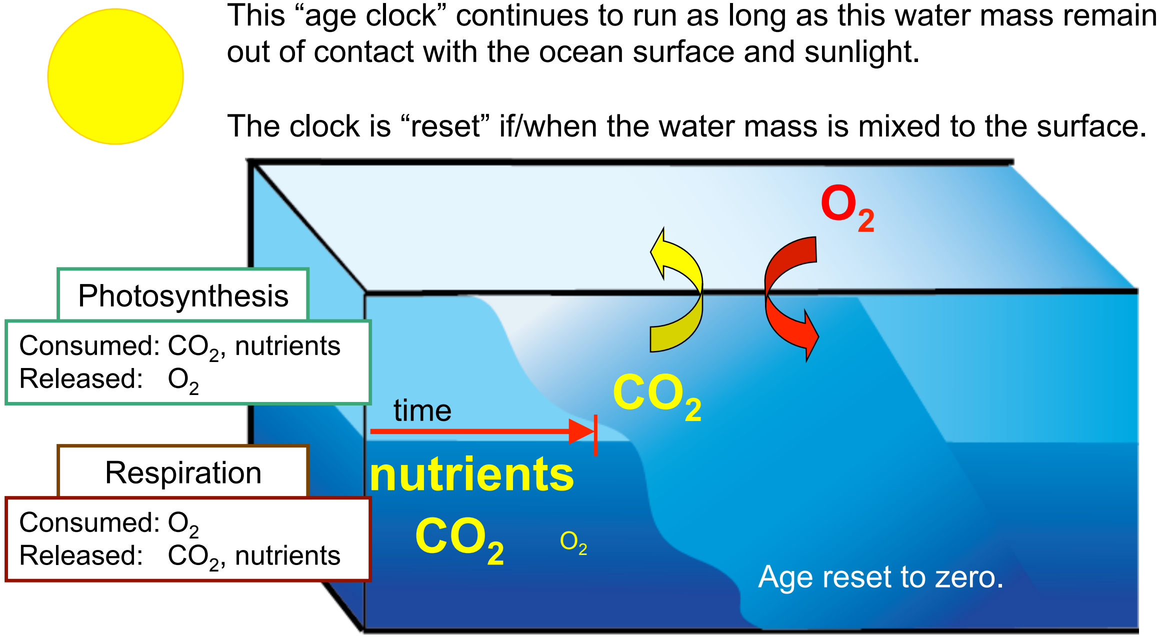

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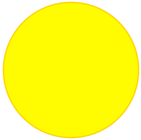

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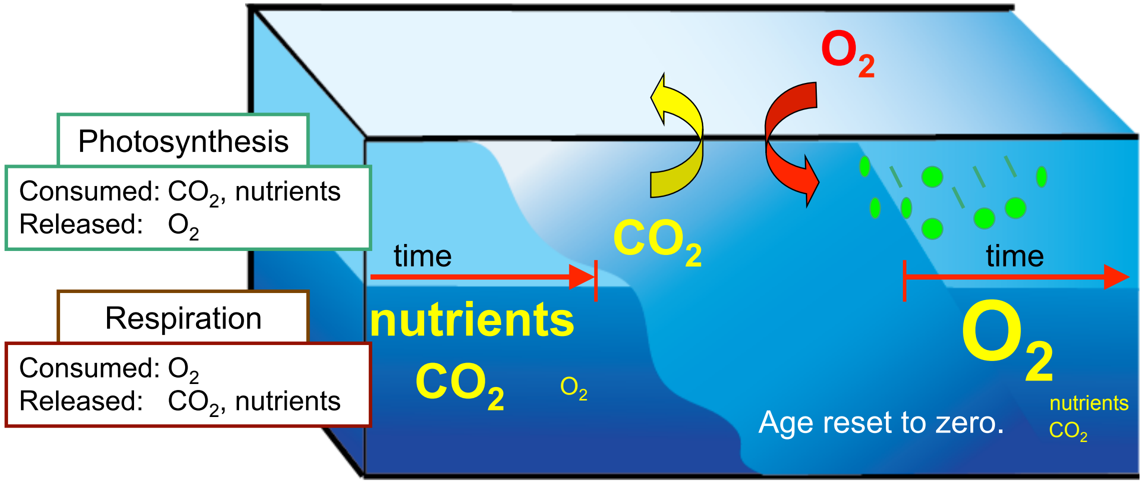

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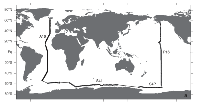
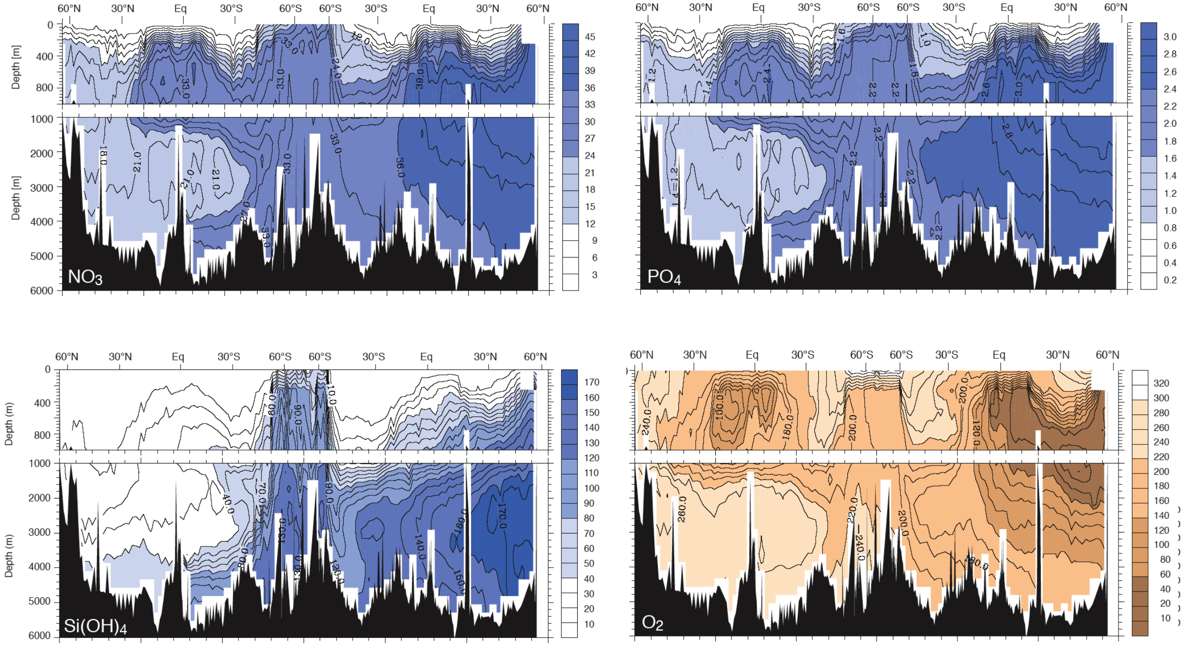
Respiration

Consumed: O_2
Released: CO_2, nutrients

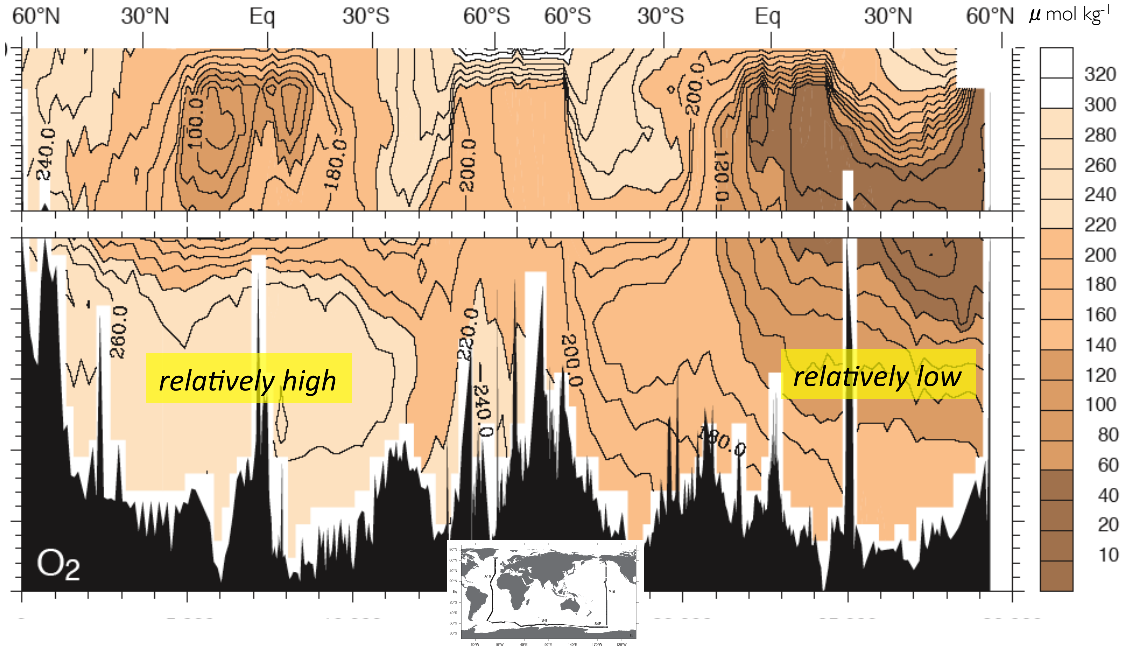
Nutrient “conveyor belt” sections





Sarmiento & Gruber (2006)

Dissolved oxygen section

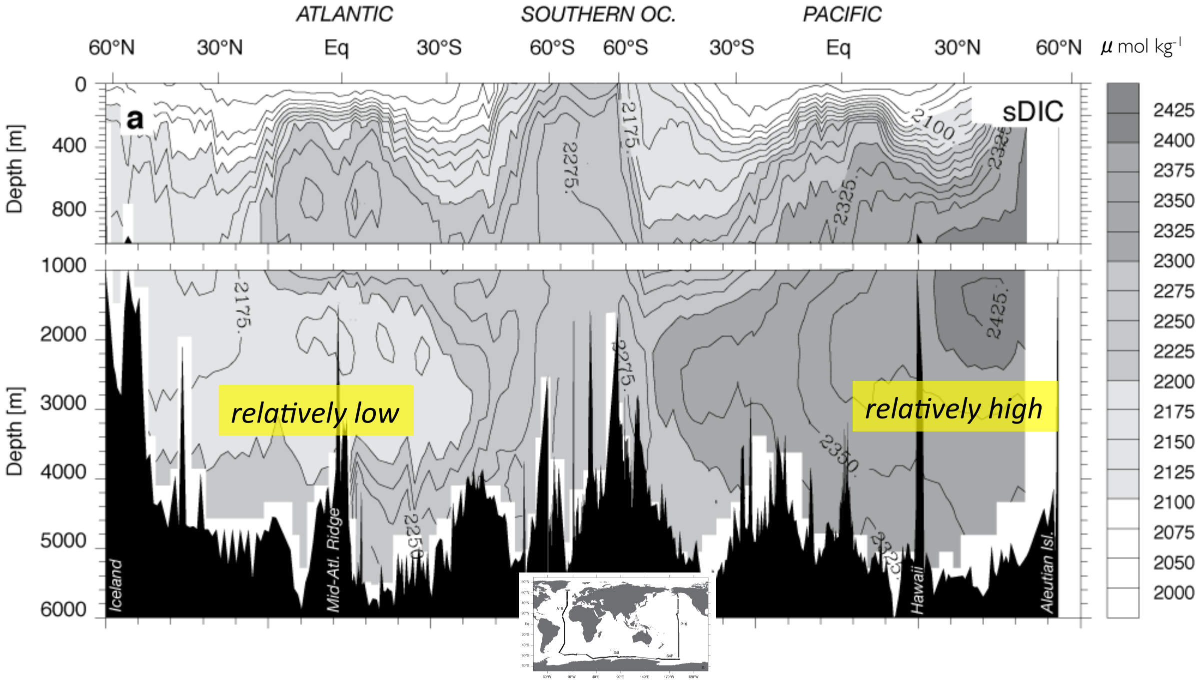


relatively high

relatively low

Dissolved inorganic carbon (DIC) section

Carbon chemistry in the ocean is complicated, but you can get a sense of the large-scale processes that may be involved by looking at DIC.



relatively low

relatively high

Nitrogen gets most of the attention, at least classically

- Fundamental constituent of proteins, nucleic acids, enzymes, cofactors
- “Limits” phytoplankton growth in much of the ocean (rate of demand often exceeds rate of supply).
- Phytoplankton grow mainly on nitrate and ammonium (“prefer” ammonium energetically, but most have the capacity to take up nitrate as well)
- Some bacteria are capable of “fixing” N_2 gas from atmosphere or ocean (abundant)

diazotrophs!

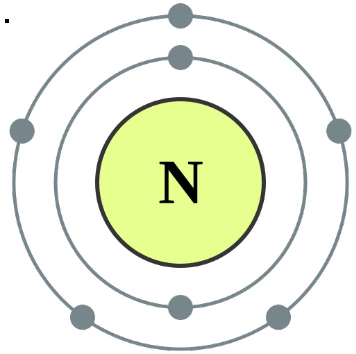
The nitrogen cycle

- ammonification
- ammonium oxidation
- assimilation
- denitrification
- nitrate reduction
- nitrite oxidation
- nitrification
- nitrite [illegible]ction
- nitrogen fixation

It all gets a little complicated

Why are there so many names?

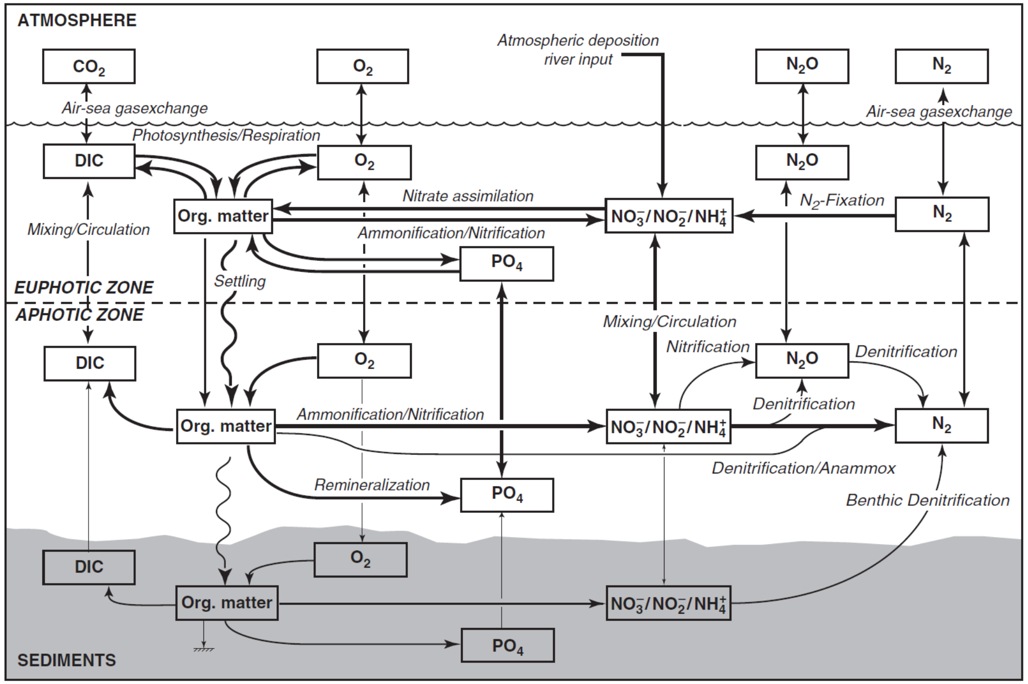
Because nitrogen can donate and accept electrons, and so can exist as a number of different ‘species’.



Remember: OIL RIG

oxidation is loss (of electrons)
reduction is gain (of electrons)

The marine nitrogen cycle



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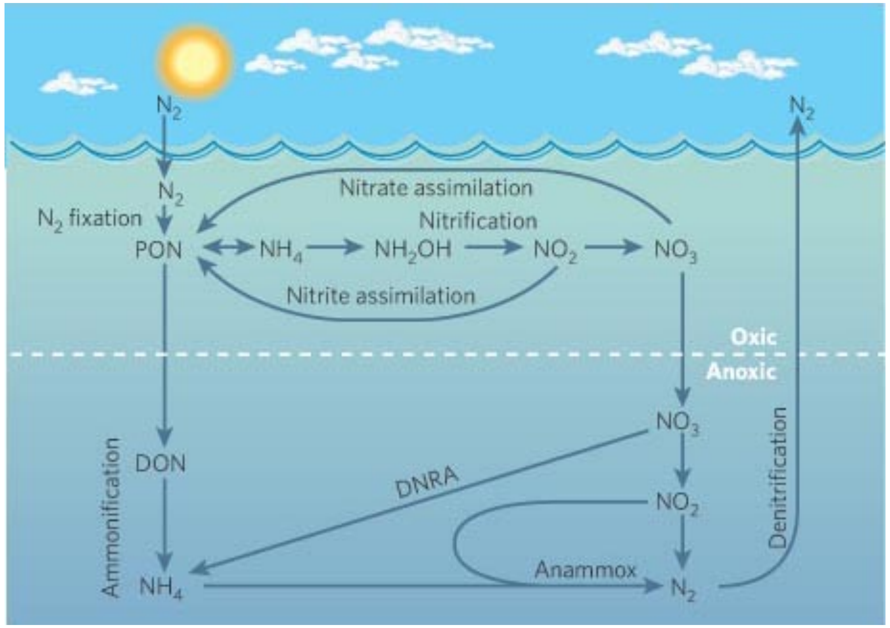
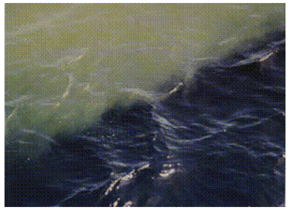
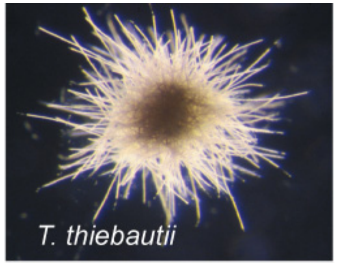
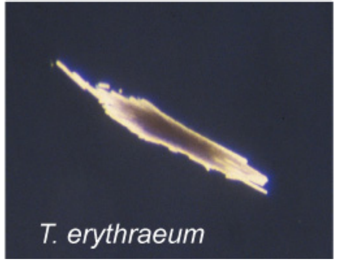


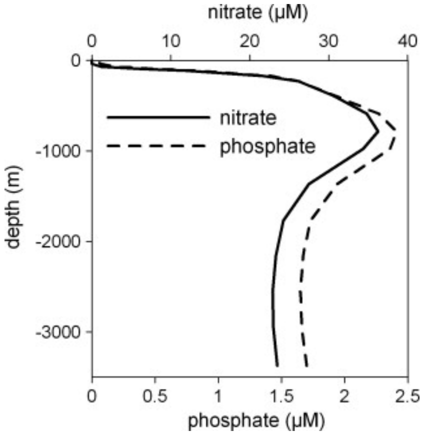
Nitrogen fixation



- Limited to bacteria and cyanobacteria
- Nitrogenase enzymes require molybdenum and Fe as cofactors (molybdoferredoxin and azoferredoxin)
- *Trichodesmium*, main fixer in open ocean also done by *Richelia* in *Rhizosolenia*
- Controversy about contributions to N cycling
- Important links to the C cycle

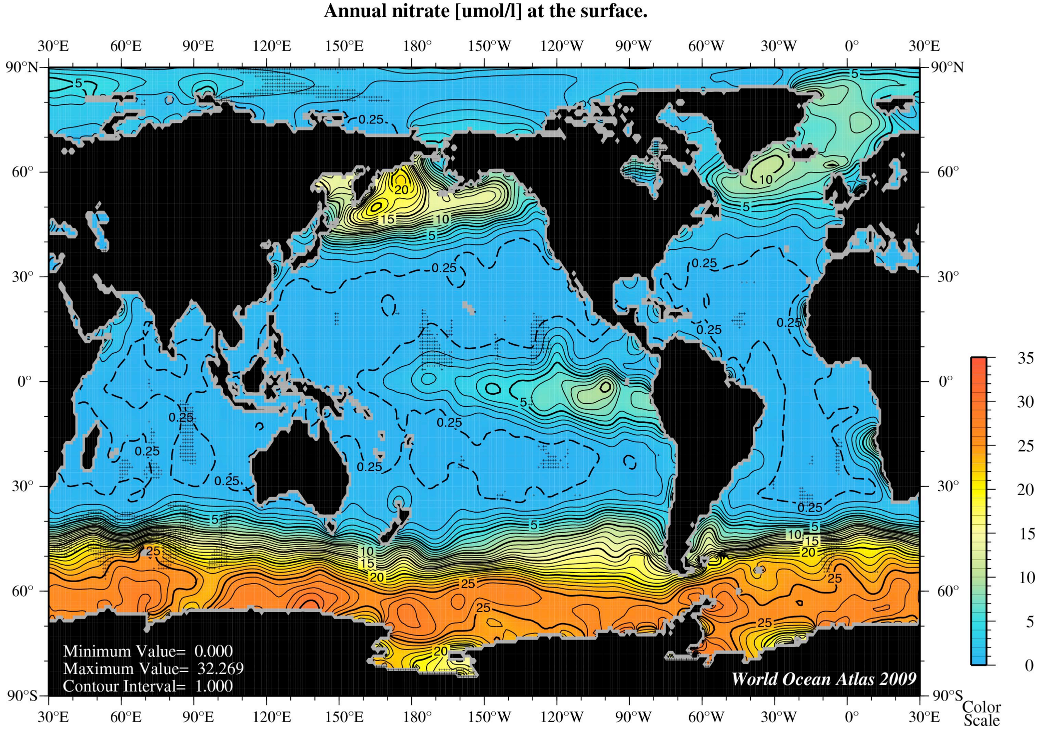




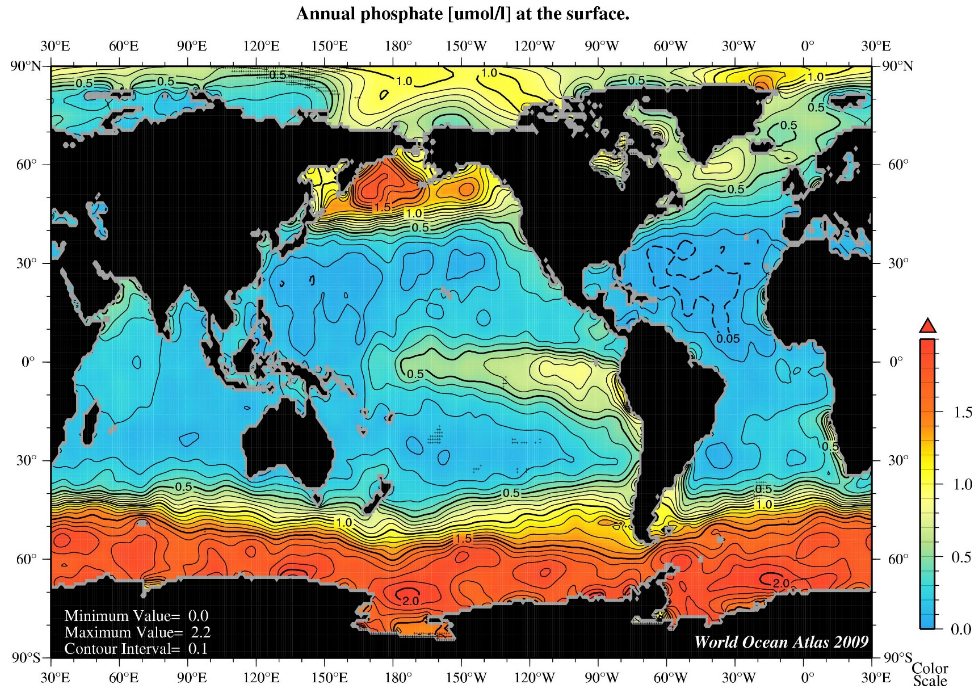


Patey et al., 2008

Surface NO_3^-


Annual nitrate [umol/l] at the surface.
30°E
60°E
90°E
120°E
150°E
180°
150°W
120°W
90°W
60°W
30°W
0°
90°N
60°
30°
0°
30°
60°
90°S
0.25
5
10
15
20
25
Minimum Value= 0.000
Maximum Value= 32.269
Contour Interval= 1.000
World Ocean Atlas 2009
Color Scale
35
30
25
20
15
10
5
0

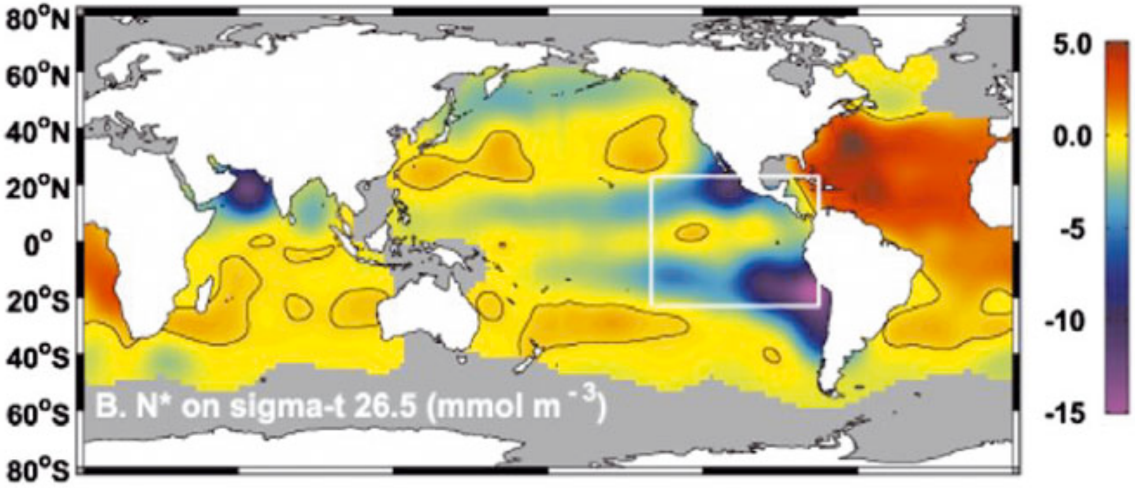
Surface PO_4^{3-}

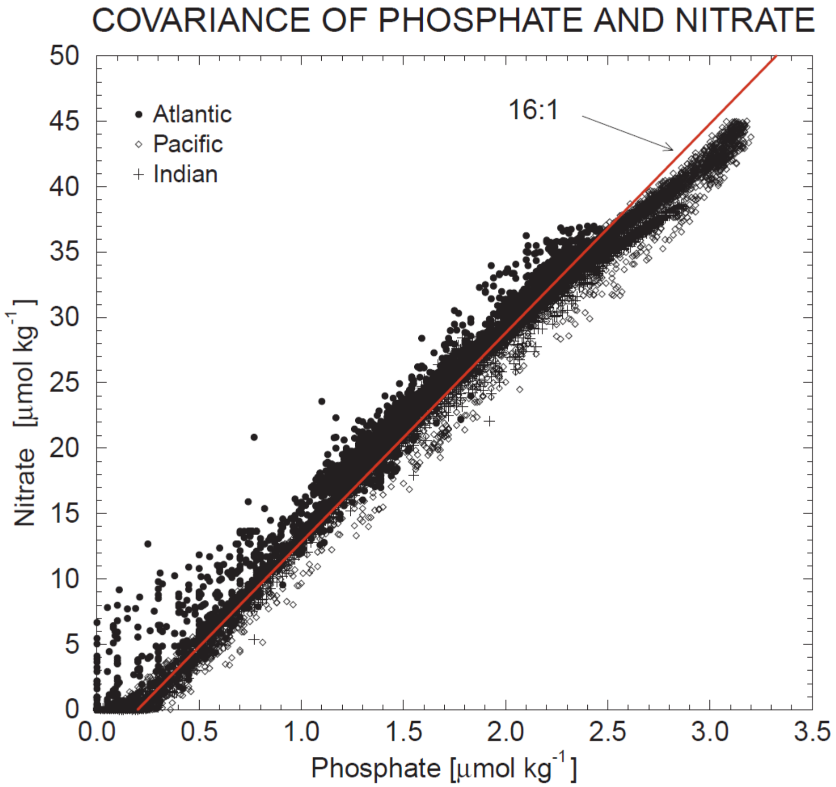


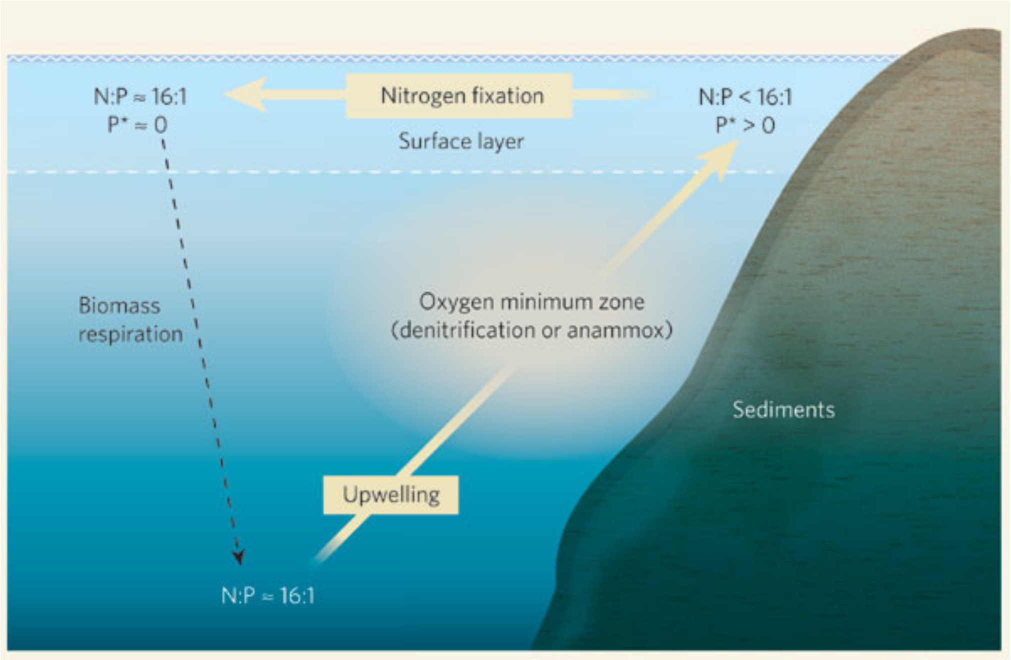
Denitrification

$NO_3^- \rightarrow NO_2^- \rightarrow NO + N_2O \rightarrow N_2$ (g)

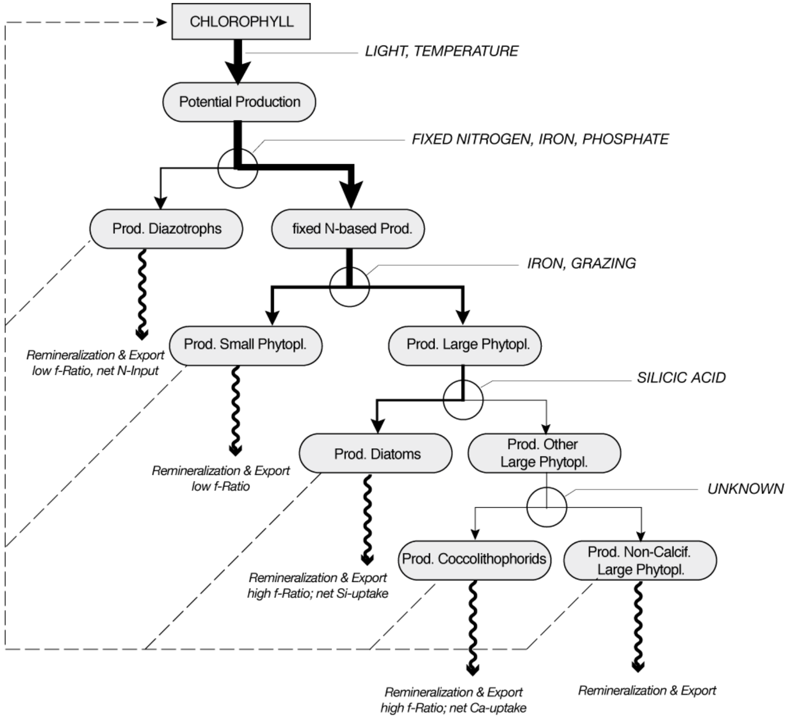
$N^* = [NO_3^-] - 16^*[PO_4^{3-}]$




COVARIANCE OF PHOSPHATE AND NITRATE
50
45
40
35
30
25
20
15
10
5
0
Nitrate [µmol kg^{-1}]
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Phosphate [µmol kg^{-1}]
● Atlantic
◇ Pacific
+ Indian
16:1



Capone and Knapp (2007) Nature, 445, 159


CHLOROPHYLL
LIGHT, TEMPERATURE
Potential Production
FIXED NITROGEN, IRON, PHOSPHATE
Prod. Diazotrophs
fixed N-based Prod.
IRON, GRAZING
Remineralization & Export
low f-Ratio, net N-Input
Prod. Small Phytopl.
Prod. Large Phytopl.
SILICIC ACID
Remineralization & Export
low f-Ratio
Prod. Diatoms
Prod. Other Large Phytopl.
UNKNOWN
Remineralization & Export
high f-Ratio; net Si-uptake
Prod. Coccolithophorids
Prod. Non-Calcif. Large Phytopl.
Remineralization & Export
high f-Ratio; net Ca-uptake
Remineralization & Export

Review of limiting processes

Light

Incoming radiation is a function of **season** and **latitude.**

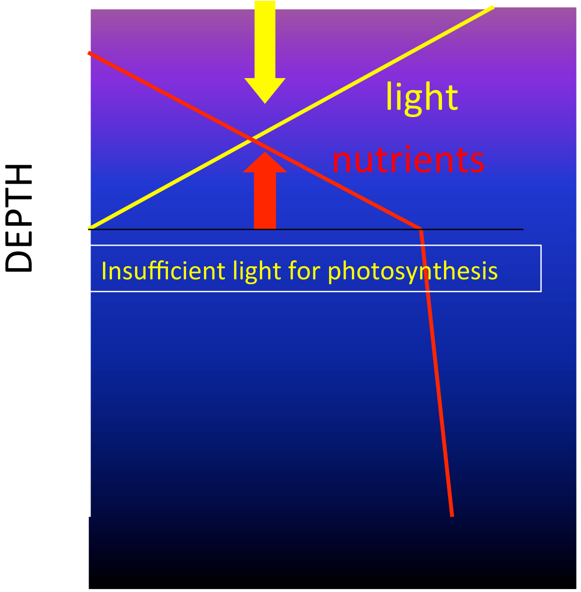
The light that phytoplankton receive is a function of **ocean mixed-layer-depth.**

Nutrients

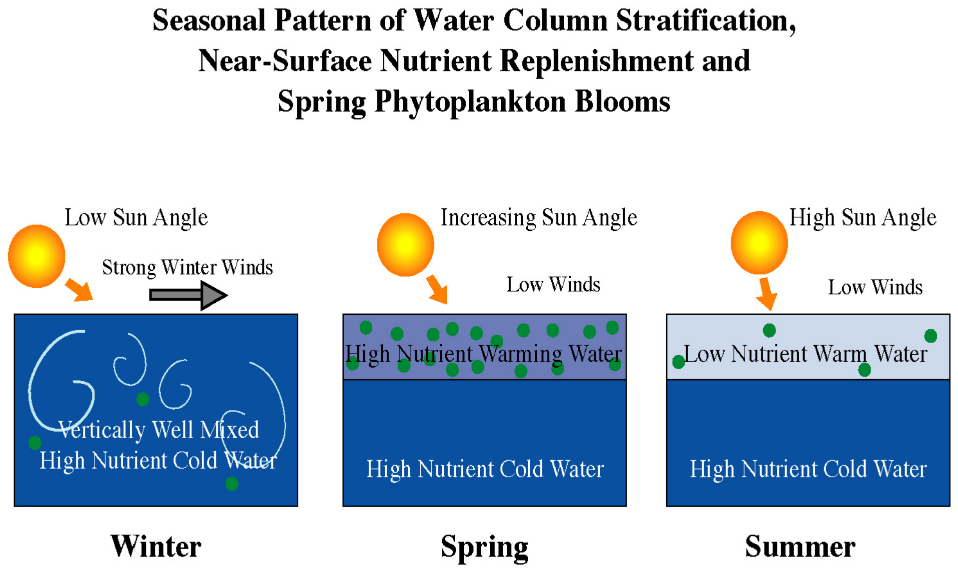
Depleted from the surface by phytoplankton.

Remineralized at depth.

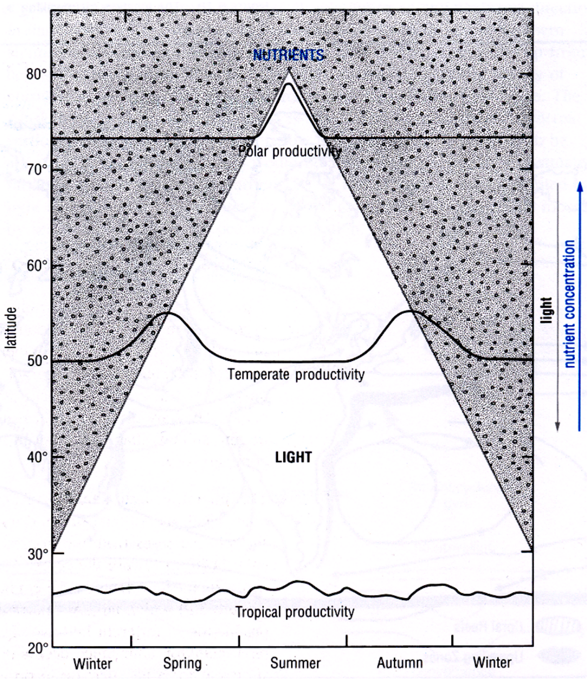
Returned to the surface by **mixing and/or upwelling.**



Review of seasonal cycle



Review of nutrient & light effects on pp



Latitudinal variability in relative abundance of light & nutrients

Timing:

Temperate - spring-bloom; coincident light, stratification & nutrients

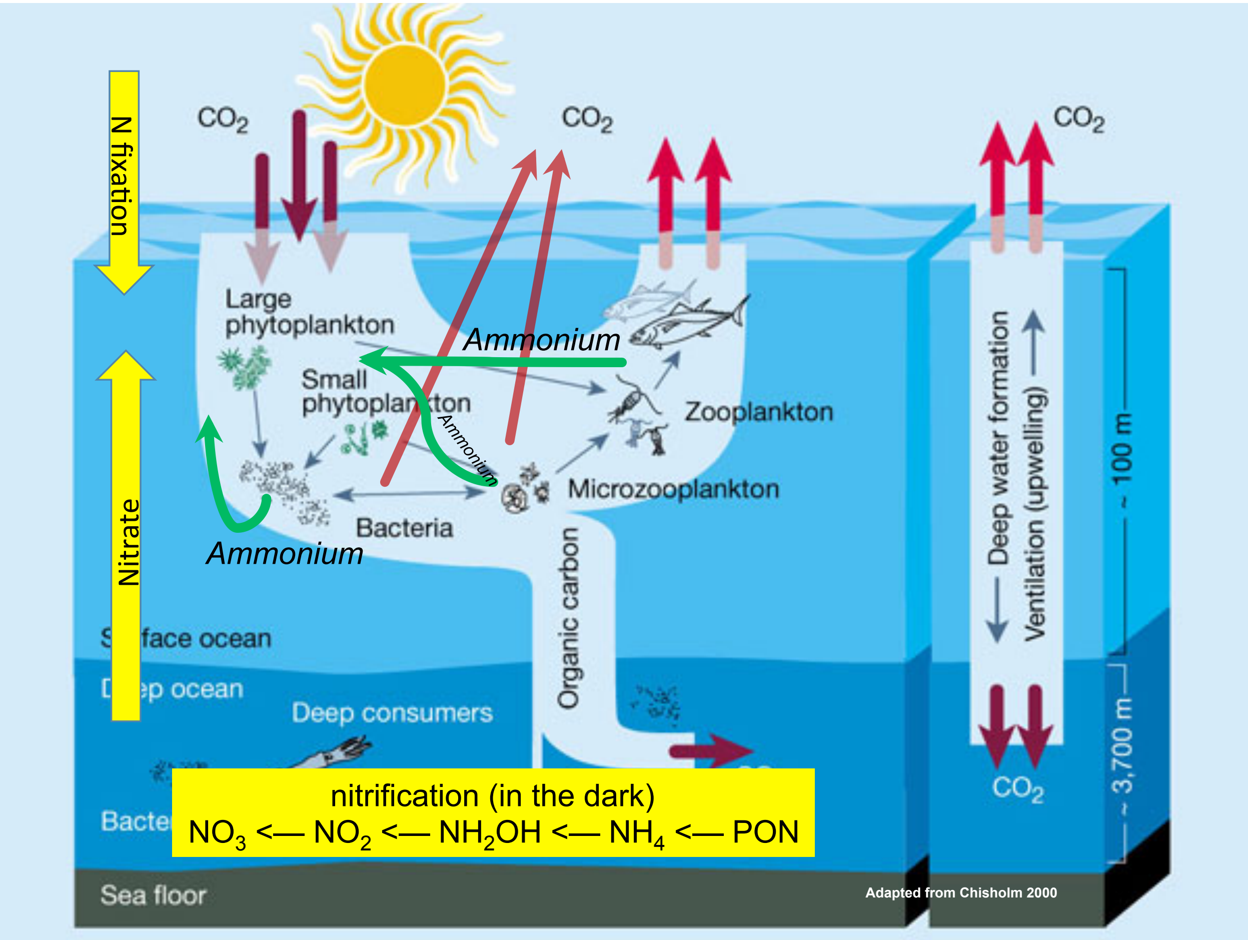
Polar - abundant nutrients, delayed bloom, ice melt

Tropics - year-round light & stratification, variability due to nutrient infusions

Q: Why don’t small phytoplankton just take over the whole ocean?

A1: Although the individuals do not sink very fast, these guys, in high densities, can “aggregate.” This reduces their effective surface-area-to-volume ratio, reducing some of that extra buoyancy they had due to drag, and allowing them to sink.

A2: They are eaten rapidly or infected by viruses!



nitrification (in the dark)

$NO_3 \longleftarrow NO_2 \longleftarrow NH_2OH \longleftarrow NH_4 \longleftarrow PON$

Adapted from Chisholm 2000

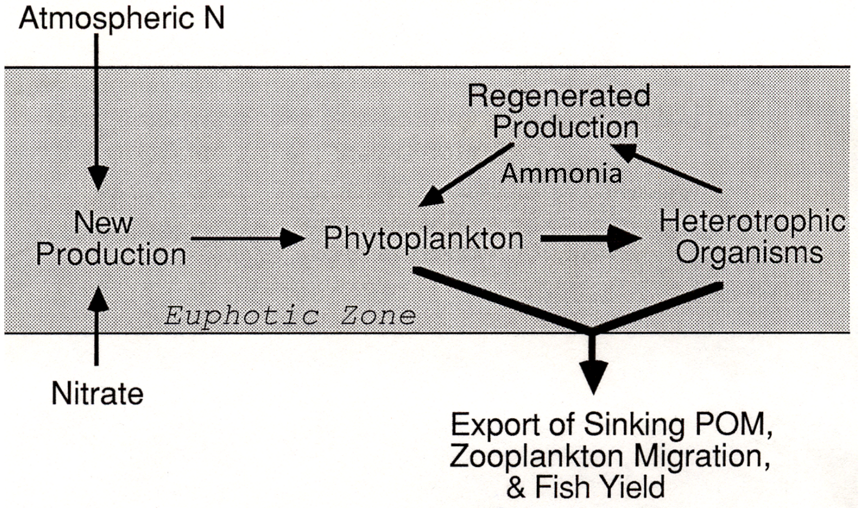
“New” production concept

Because production based on nitrate *(or N_2 for diazotrophs)* ***is using molecules newly arrived from outside the productive layer, it is term new production***.

Recycled production is the primary production that occurs as the result of nitrogen just being passed back and forth in the euphotic zone (microbial loop).

Dugdale & Goering, 1967

“New” production concept



“New” PP - associated with N entering the euphotic zone from external (allochtonous) sources — NO_3, N_2.

“Recycled” PP - associated with N recycled within the euphotic zone (autochtonous) — typically NH_4^+, urea.

“New” production concept

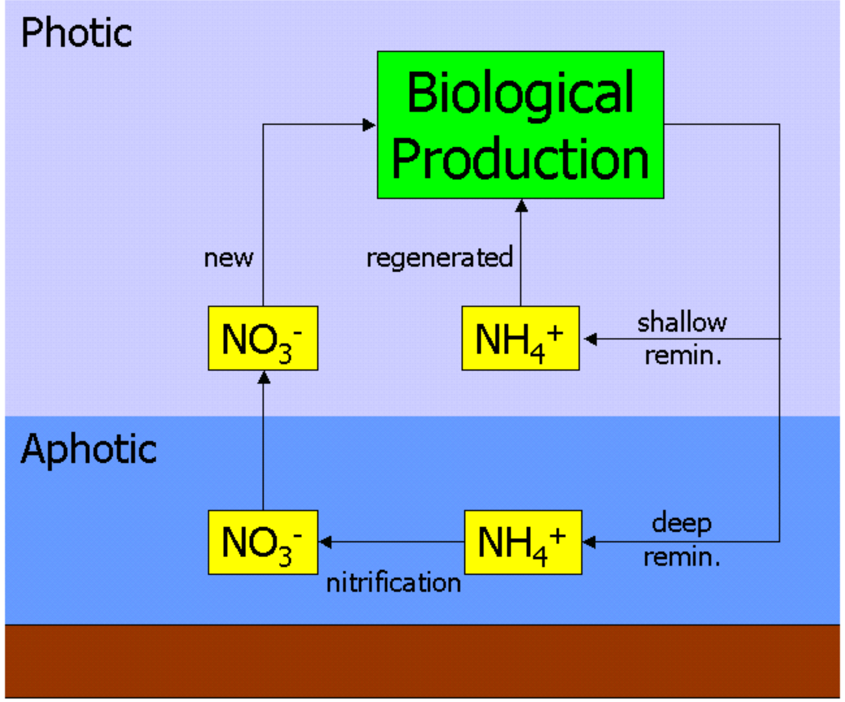
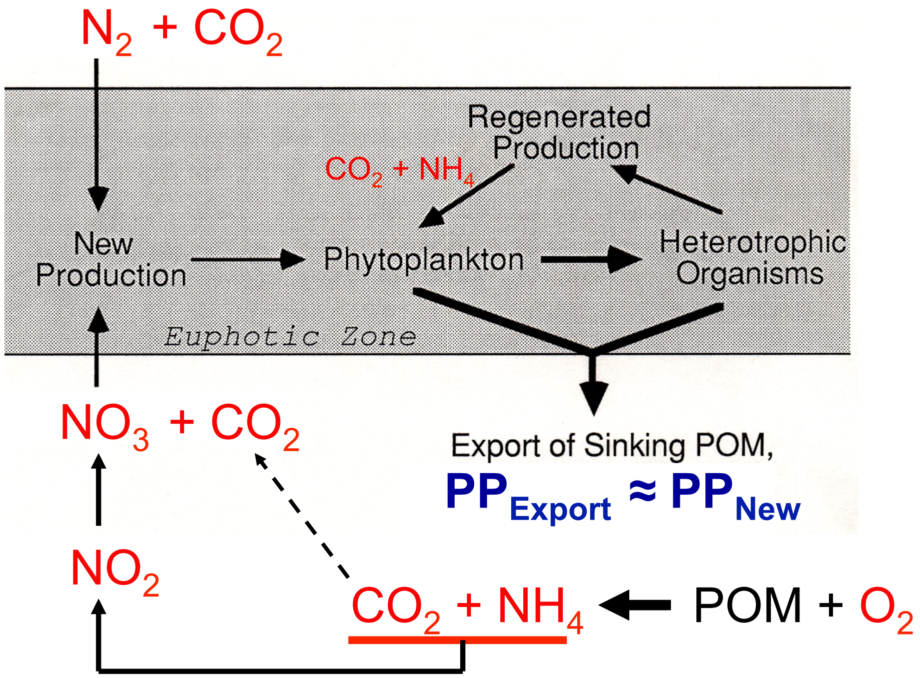


image from *Wikipedia*

Nitrogen-based perspective



$N_2 + CO_2$

Regenerated Production

$CO_2 + NH_4$

New Production

Phytoplankton

Heterotrophic Organisms

Euphotic Zone

$NO_3 + CO_2$

Export of Sinking POM,

$\mathbf{PP_{Export} \approx PP_{New}}$

NO_2

$CO_2 + NH_4$

POM + O_2

The f-ratio

f−*ratio* = *“new” Primary Production/total Primary Production*

Total PP = “New” + “Recycled” PP

The f-ratio is typically measured as a ratio of N uptake species

$$\text{f}{-}ratio \approx \text{“}new\text{”}\ N\ uptake\ /total\ N\ uptake \quad = NO_3^- uptake + N_2\ fixation/uptake\ of\ (NO_3^- + NH_4^+) + N_2\ fixation$$

The f-ratio

In practice, how is this measured?

$$f\text{-}ratio \approx {}^{15}NO_3^{-}\ uptake\ /\ {}^{14}CO_2\ uptake$$

Issues:
1. $DO^{15}N$ release by phytoplankton
2. low ambient NO_3^- (of only a few nM in oligotrophic gyres)

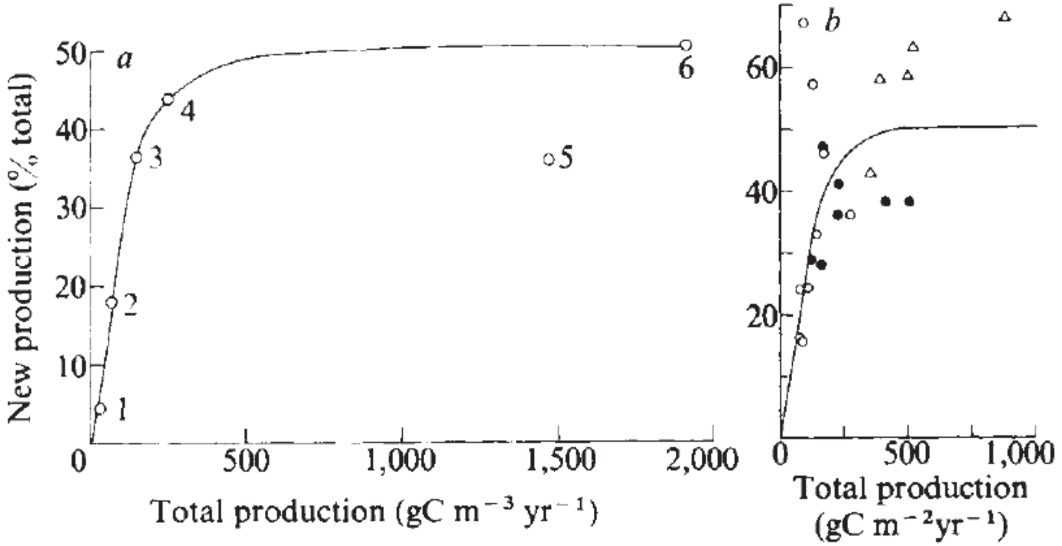


Fig. 2 *a*, New production as % of the total primary production versus total production for various ocean areas: (1) Central North pacific, (2) eastern Mediterranean Sea, (3) Southern California Bight, (4) eastern Tropical Pacific, (5) Costa Rica Dome, and (6) Peru upwelling. Total production was measured by the ^{14}C method. New : total production ratio measurements are based on the assimilation of ^{15}N-labelled nitrate and ammonium.

b, New : total production ratio versus total primary production at individual stations in the Southern California Bight. Nearshore stations in water depth

The e-ratio

Another important ratio is the “e-ratio.”

The e-ratio is the fraction of primary production that is exported from the euphotic zone.

$$\text{e}-ratio \approx export\ production/primary\ production$$

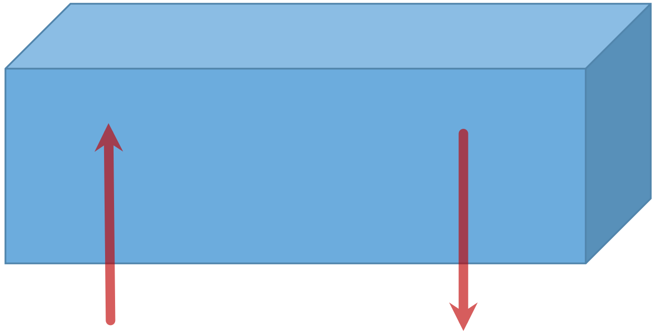
Measuring export

Photo: D. Luquet

The e-ratio, f-ratio, and the ef-ratio

Now, think about the euphotic zone as a box.

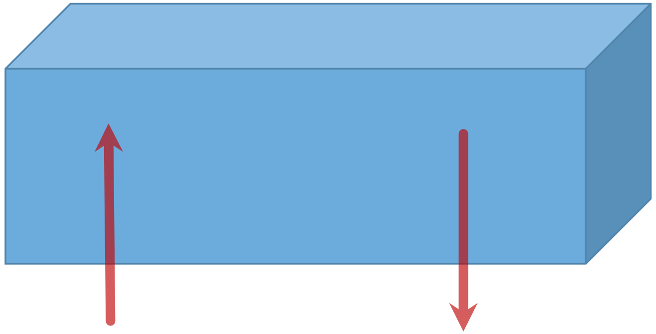
If, over the large scale and long term, the amount of total nitrate in the euphotic zone does not change (steady state), what goes in must come out.



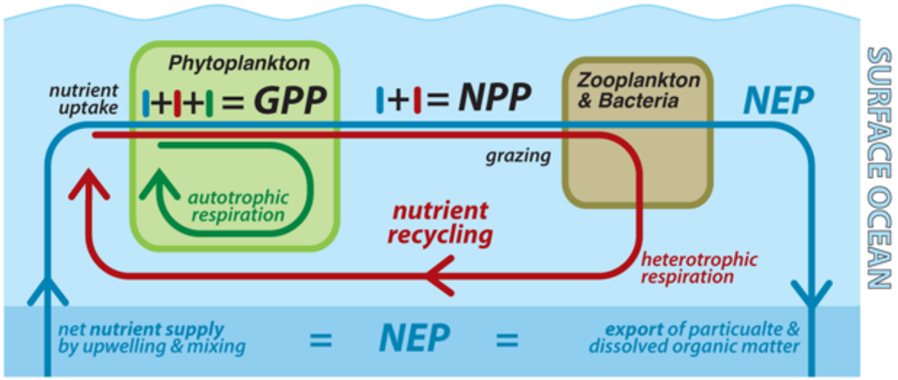
The e-ratio, f-ratio, and the ef-ratio

Over sufficiently large spatial and temporal scales, we often assume that the e-ratio and f-ratio are equal.

When this is assumed, the ambiguity is made obvious by using the term "ef-ratio" as opposed to "f-ratio".



http://www.nature.com/scitable/knowledge/library/the-biological-productivity-of-the-ocean-70631104

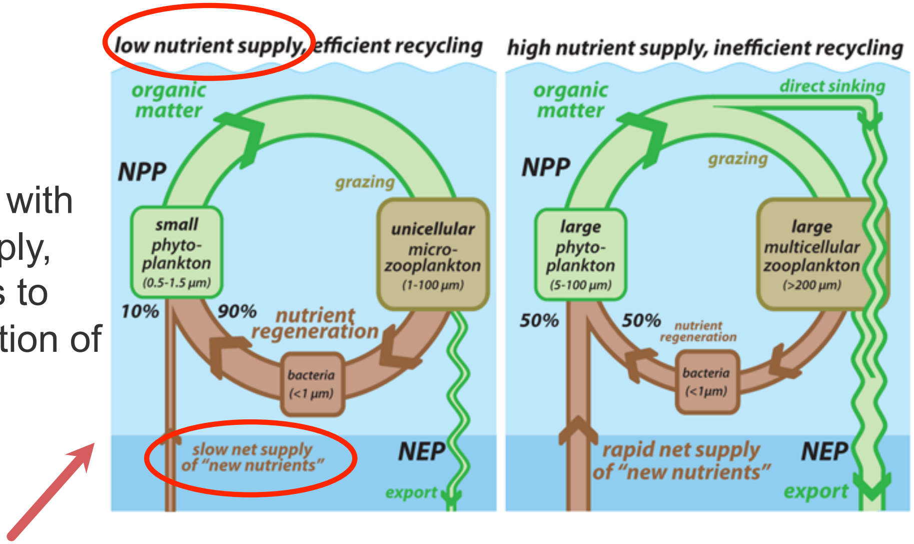


The blue cycle for “net ecosystem production” (NEP) (i.e. “new” or “export” production).

The red cycle for “recycled production” illustrates the fate of the majority of organic matter produced in the surface ocean, which is to be respired by heterotrophic organisms to meet their energy requirements, thereby releasing the nutrients back into the surface water where they can be taken up by phytoplankton once again.

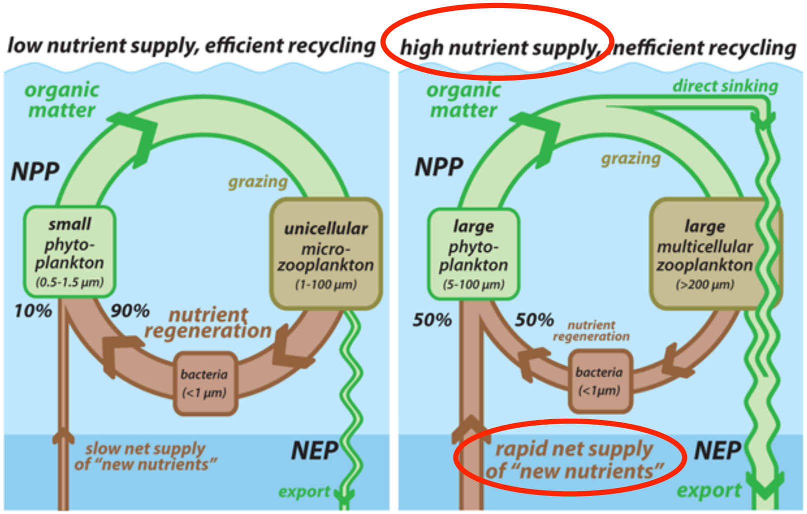
The green cycle represents the internal respiration of phytoplankton themselves, that is, their own use of the products of photosynthesis for purposes other than growth.

The fraction of NEP:NPP ratio appears to vary with the nutrient supply, because of links to the size distribution of the plankton.



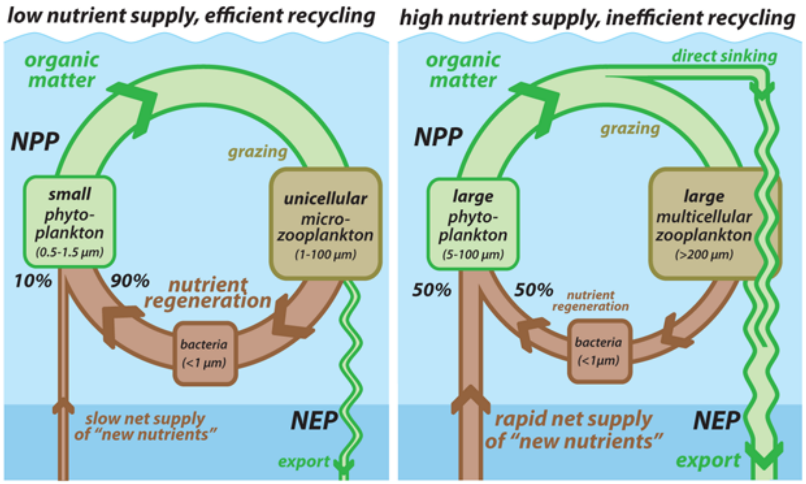
In the **nutrient-poor** tropical and subtropical ocean, the (**small**) cyanobacteria tend to be numerically dominant. The **microzooplankton graze** these small cells effectively, preventing phytoplankton from **sinking** directly.

Moreover, these single-celled microzooplankton **do not produce sinking fecal pellets**. Instead, any residual organic matter remains to be degraded by bacteria.



In nutrient-rich regions, large phytoplankton are more important, and these are often grazed directly by multicellular zooplankton.

But, these larger multicellular zooplankton cannot reproduce fast enough to keep up with phytoplankton growth, and the large phytoplankton can sometimes accumulate to high concentrations and produce abundant sinking material. In addition, the zooplankton export organic matter as fecal pellets.



Relationships between nutrient supply, phytoplankton size, zooplankton grazing, and sinking are key in understanding this view of biological cycling in the upper ocean.