## 12.742 - Marine Chemistry

Fall 2004

Lecture 13 - Primary Production: Water Column Processes

Prof. Scott Doney

- Somewhat different organization from years past start with surface productivity and work our way down the water column
- Try to fold methods in as we go
- Electronic notes still missing many of the figures also somewhat different order.

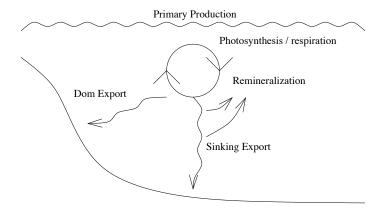


Figure 1.

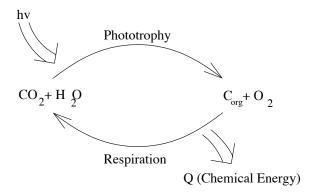


Figure 2.

- Formation and respiration of organic matter
- Formation and dissolution of  $CaCO_3$ ,  $SiO_3$
- Transport of dust, resuspended sediments, particles
- Scavenging onto particles
- Elemental stoichiometry
- Water column distributions
- Rates
- Categorize organisms by source of energy, inorganic electron donor and carbon source.
  - · Chemo litho autotrophy
  - · Chemo organo heterotrophy
  - · Photo litho autotrophy

- Light absorbed by pigments.
  - mainly chlorophyll a
  - also accessory pigments (which absorb different wavelengths) including forms of chlorophyll (b, c1, c2) carotenoids, bilioproteins

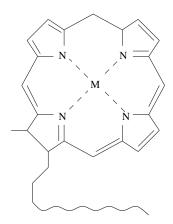
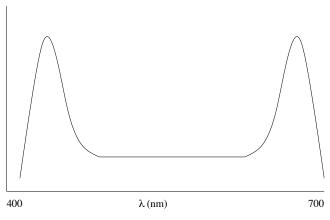


Figure 3.



Absorb in Blue and Red (leave Green)

Figure 4.

- Chlorophyll has conjugated double bonds non-localized  $\pi$  orbital electrons, can absorb solar radiation, bump up to higher electron state
- PAR photosynthetic available radiation (350 - 700 nm)
- Convert light energy into electron energy
- Light harvesting pigment-protein complexes involved in electron transfer, funneling excited electrons to reaction sites.

- Two types of reactions
  - Light reactions

Photosystems I and II - redox/electron exchange

ATP - adenosine triphosphate

Photosystem I - reduction of  $NADP \rightarrow NADPH_2$ 

Nicotinamide adenine dinucleotide phosphate (NADP)

Photosystem II - liberation of  $O_2$  from water

Interconnected photosystem II  $\rightarrow$  photosystem I (photosynthetic unit)

Light reactions (light into energy and reducing power),

$$2H_2O + 2NADP^+ \xrightarrow{8h\nu} O_2 + 2NADPH + 2H^+$$
 Delta G = +105.5kcal/mol

Coupled with phosphorylation reaction,

$$4ADP + 4P_i \rightarrow 4ATP$$

- Dark reactions

Calvin/Benson cycle - biochemistry ( $CO_2 \rightarrow \text{carbohydrate}$ )

$$2H^+ + CO_2 + 2NADPH \rightarrow (CH_2O) + 2NADP^+$$

which requires 3ATP:

$$3ATP \rightarrow 3ADP + 3P$$

where  $(CH_2O)$  is a generic carbohydrate. The net reaction is:

$$CO_2 + 2H_2O \xrightarrow{8h\nu} (CH_2O) + H_2O + O_2$$

- Respiration by phytoplankton (light and dark)
  - Use stored organic matter to regenerate energy

$$CO_2 + H_2O \leftrightharpoons CH_2O + O_2$$

- Forward reaction Gross Primary Production (GPP)
- Reverse reaction respiration (autotroph)
- Net Primary Production (NPP) = GPP autotroph respiration
- Typically respiration small:  $\leq 0.1$  GPP, but can be higher in tropical oligotrophic  $\sim 0.4$  GPP
- What limits/controls primary production?
  - autotroph biomass (grazing, excretion, mortality)
  - light
  - nutrients
  - temperature (growth rates versus photosynthesis)
- So where is most of the biomass (phytoplankton)?
  - Photosynthetic Quotient  $\left[-\frac{O_2}{CO_2}\right]$

$$CO_2 + H_2O \leftrightharpoons CH_2O + O_2 \qquad PQ \sim 1$$

requires  $\sim 532$  kJ.

But PQ for algae is > 1 because of production of proteins and lipids (carbohydrates, DNA)

Eg: fatty acid  $CH_3 - (CH_2)_{10} - COOH$ 

$$C_{12}H_{24}O_2 + 17O_2 \leftrightharpoons 12CO_2 + 12H_2O \qquad PQ \sim \frac{17}{12} \approx 1.42$$

Alfred Redfield in the 1930s-1950s examined the elemental composition of marine phytoplankton (now call "Redfield ratios")

Anderson proposed

$$C_{106}H_{175}O_{42}N_{16}P + 150O_2 \leftrightharpoons 106CO_2 + 16HNO_3 + H_3PO_4 + 78H_2O_3$$

- Main primary producers:
  - by phylogeny (genomics, metabolics, and cellular form) phylogenitvely rich/diverse taxonomy  $2 \cdot 10^4$  species (?) cyanobacteria (prokaryote), eukaryotes (green and red algae), red (diatom, dinoflagellates)
  - by size (important later for grazing, export, etc) haptophytes (coccolithophorids), chrysophytes (Note: pico 0.2 20  $\mu$ m, nano 2.0 20  $\mu$ m, micro 20 2000  $\mu$ m, micro > 2000  $\mu$ m
  - guild/geochemical function group nitrogen fixers, calcifiers, silicon shells, etc

Spatial distribution based on field surveys and satellite remote sensing

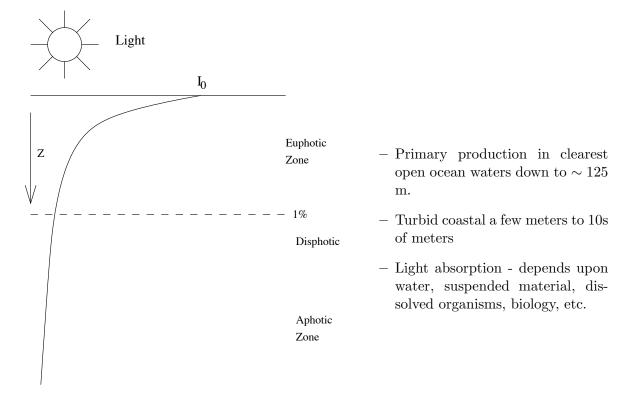


Figure 5.

Lights falls off with depth  $I(\lambda, z) = I_0(\lambda)e^{-k(\lambda)z}$  (For PAR, exponential is only an approximation)

 $k = k_w + k_c Chl + other absorbers$ , PAR  $\sim 0.5$  total irradiance

Change spectral character of light (strip out all of the red, for example)

## Photosynthesis - irradiance curves

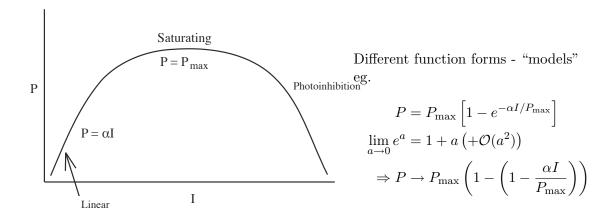


Figure 6.

Light and mixing

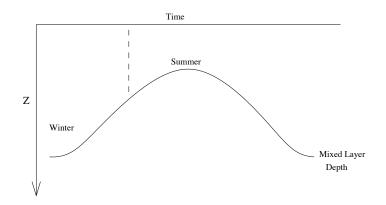


Figure 7.

Trigger spring bloom when have enough "average" light (when mixing depth shoals to the critical depth  $Z_{\rm CR}$ )

$$\frac{1}{kZ_{\rm CR}} \left( 1 - e^{-kZ_{\rm CR}} \right) = \frac{R_0}{P_0} = \frac{I_c}{I_0}$$

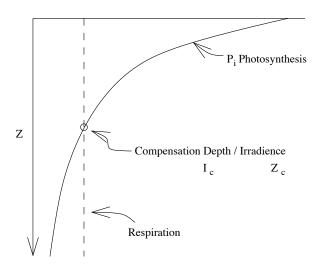


Figure 8.

at the compensation irradiance,  $I_c$ ,  $P_c = R_c$  (autotroph production equals community respiration)

$$I_c = I_0 e^{-kZ_c}$$
  $P = \alpha I, P_0 = \alpha I_0$ 

At critical depth, total integrated respiration = integrated production Harold Sverdrup first identified critical depth  $Z_{\rm CR}$  defined as depth where depth integrated respiration = depth integrated production.

$$R_0 Z_{\rm CR} = \int_0^{Z_{\rm CR}} dz \, \alpha I_0 e^{-kz}$$

## ullet Nutrient limitation N

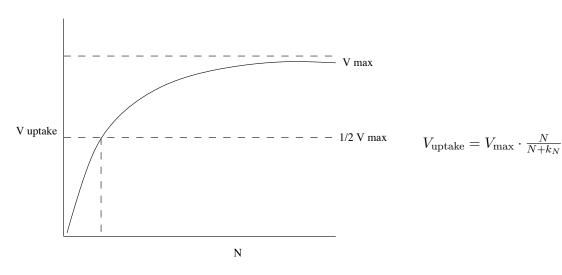


Figure 9.

# • Complications

- Many different possible limiting nutrients N, P, Si (diatoms), also, trace elements  $Fe, Co, Zn, \ldots$
- Multiple forms of nutrients  $\underbrace{NH_4^+}_{\text{most easily}}$ ,  $\underbrace{NO_3^-}_{\text{in ocean}}$
- Dissolved organic matter as source of nutrients
- Nutrient inhibition (eg.  $NH_4^+$  on nitrate)
- Multiplicative i.e. Liebig's law of minimum; nutrient-light co-inhibition

# • Temperature limitation T

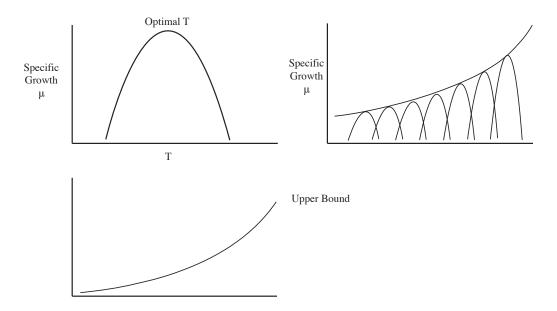


Figure 10.

Eppley curve [1972] for maximum autotroph specific growth rates  $\mu$  (1/day)  $\mu(T)=\frac{0.6}{d}1.066^{T({\rm deg.~}C)}$ 

alternative temperature curves defined with form similar to Arrehnius relationship

## • Time-Space variations

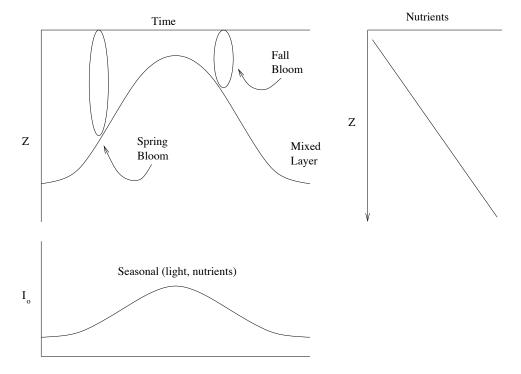


Figure 11.

during spring, have increased light (solar, mixed layer depth) and higher nutrients (from deep winter mixing)

Balance of light versus nutrient limitation depends upon location

## • Variations with depth

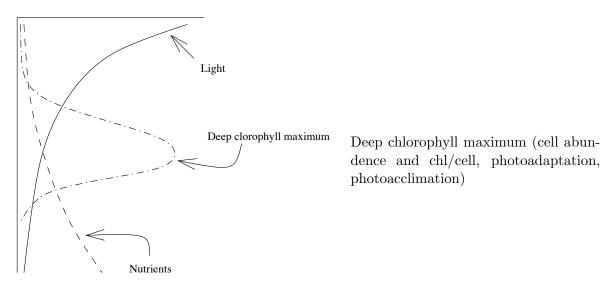


Figure 12.

# Globally

- Spatial maps of chlorophyll (proxy for biomass)
- Primary determinant is nutrient supply
- Regions of upwelling (equatorial divergence, coastal upwelling, subpolar gyres)
- Regions of deep seasonal mixing (eg. North Atlantic spring bloom)

Stratified regions have relatively low biomass (subtropical gyres)

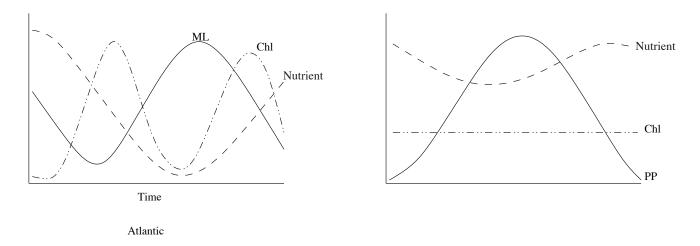


Figure 13.