Term paper topics, due February 8

ODV mini-projects, due March 13 (10% final grade)
Individuals or teams of two
Using any available datasets, put together a ~7-10 minute talk to present in class on March 13
Aim for a blend of interesting content (but not necessarily earth-shattering or novel) and effective, beautiful visualizations
If you’re hitting a technical wall using ODV, ask your more senior graduate students and postdocs for help, try harder, then email Mariko but do NOT abuse her kindness and willingness to help ;-)
Nutrients; Aerobic Carbon Production and Consumption

OCN 623 – Chemical Oceanography

Reading: Libes, Chapters 8 and 9
“Every (other) breath you take…” is a by-product of plankton primary production
Formation and respiration of organic matter

Dissolved Inorganic Nutrients $\Rightarrow$ POM
Primary Producers
Autotrophs

Mostly **photosynthesizers** (they use light energy) called phytoplankton
phyto = light
plankton = small drifting organisms

Some **chemotrophs** (don’t need light)
live in ‘unusual’ environments like
hydrothermal vents, anoxic environments

C, H, O, N, P, S + trace elements
Redfield-Richards Equation:

\[ \text{CO}_2 + \text{N} + \text{P} + \text{H}_2\text{O} \xrightleftharpoons{\text{PR}} \text{Organic matter} + \text{O}_2 \]

“inorganic nutrients”: N, P and Si

They are also called “biolimiting elements” -- Why?

1. Small reservoir size in oceans
2. Fast turnover time
3. Required for many kinds of biological activity
### Chemical Composition of Biological Particulate Material

**Hard Parts - Shells**

<table>
<thead>
<tr>
<th>Name</th>
<th>Mineral</th>
<th>Size (um)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coccoliths</td>
<td>CaCO₃ Calcite</td>
<td>5</td>
</tr>
<tr>
<td>Diatoms</td>
<td>SiO₂ Opal</td>
<td>10-15</td>
</tr>
<tr>
<td>Silicoflagellates</td>
<td>SiO₂ Opal</td>
<td>30</td>
</tr>
<tr>
<td>Foraminifera</td>
<td>CaCO₃ Calcite</td>
<td>~100</td>
</tr>
<tr>
<td>Radiolaria</td>
<td>SiO₂ Opal</td>
<td>~100</td>
</tr>
<tr>
<td>Pteropods</td>
<td>CaCO₃ Aragonite</td>
<td>~1000</td>
</tr>
<tr>
<td>Acantharia</td>
<td>SrSO₄ Celestite</td>
<td>~100</td>
</tr>
</tbody>
</table>
Soft Parts - protoplasm

Atomic Ratios of the Principal Elements Present in Plankton

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>N</th>
<th>P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zooplankton</td>
<td>103</td>
<td>16.5</td>
<td>1</td>
</tr>
<tr>
<td>Phytoplankton</td>
<td>108</td>
<td>15.5</td>
<td>1</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td>106</td>
<td>16</td>
<td>1</td>
</tr>
</tbody>
</table>

1934-1958-1963
from Redfield, Ketchum and Richards (1963)
The Sea Vol. 2
Also for particles caught by sediment traps.

Limiting nutrients, blooms, hypoxia

Residence time >> mixing time = stable 16:1
**The Redfield or "RKR" Equation (A Model)**

The mean elemental ratio of marine organic particles is given as:

\[
P : N : C = 1 : 16 : 106
\]

The average ocean photosynthesis (forward) and aerobic (O₂) respiration (reverse) is written as:

\[
106 \text{ CO}_2 + 16 \text{ HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} + \text{trace elements (e.g. Fe, Zn, Mn...)}
\]

\[
\text{light (h ν) ⤷}
\]

\[
(\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P}) + 138 \text{O}_2
\]

or

\[
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)
\]

Algal Protoplasim

The actual chemical species assimilated during this reaction are:

- HCO₃⁻
- NO₃⁻
- PO₄³⁻
- NO₂⁻
- NH₄⁺
1. This is an **organic oxidation-reduction reaction** - during photosynthesis C and N are reduced and water (O) is oxidized. During respiration the reverse occurs. There are no changes in the oxidation state of P.

   We assume C has an oxidation state of 0 which is the value of C in formaldehyde (CH$_2$O), that N has an oxidation state of -III and that H and P do not change oxidation states.

2. Photosynthesis is **endothermic**. This means is requires energy from an outside source. In this case the energy source is the sun. Essentially plants convert the photo energy from the sun into high energy C - C bonds. This conversion happens in the plants’ photosystems.

   Respiration is **exothermic**. This means it could occur spontaneously and release energy. In actuality it is always mediated by bacteria which use the reactions to obtain their energy for life.
The greater the difference in potential (E) between the oxidizing and reducing agents, the greater the free energy yield for the reaction. This sets up a sequence of favorable oxidants for organic matter oxidation. Organic matter oxidation by O₂ is greatest in terms of free energy yield.

**Why is organic matter such a good electron donor?**
## Environmentally Important Organic Matter Oxidation Reactions

<table>
<thead>
<tr>
<th>Reducing Half-reaction</th>
<th>$E_h$ (V)</th>
<th>$\Delta G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction of $O_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$</td>
<td>+0.812</td>
<td>-29.9</td>
</tr>
<tr>
<td>Reduction of $NO_3^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$2NO_3^- + 6H^+ + 6e^- \rightarrow N_2 + 3H_2O$</td>
<td>+0.747</td>
<td>-28.4</td>
</tr>
<tr>
<td>Reduction of Mn (IV)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$</td>
<td>+0.526</td>
<td>-23.3</td>
</tr>
<tr>
<td>Reduction of Fe (III)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$</td>
<td>-0.047</td>
<td>-10.1</td>
</tr>
<tr>
<td>Reduction of $SO_4^{2-}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$</td>
<td>-0.221</td>
<td>-5.9</td>
</tr>
<tr>
<td>Reduction of $CO_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$</td>
<td>-0.244</td>
<td>-5.6</td>
</tr>
</tbody>
</table>
3. **Stoichiometry breakdown of oxygen production**

\[
\begin{align*}
\text{CO}_2 & + \text{H}_2\text{O} \rightarrow (\text{CH}_2\text{O}) + \text{O}_2 \\
\text{H}^+ & + \text{NO}_3^- + \text{H}_2\text{O} \rightarrow (\text{NH}_3) + 2\text{O}_2
\end{align*}
\]

\[
\begin{align*}
\text{C} : \text{O}_2 & \rightarrow 1 : 1 \\
\text{N} : \text{O}_2 & \rightarrow 1 : 2
\end{align*}
\]

4. **Total oxygen production**: \(106 \text{ C} + 16 \text{ N} \times 2 = 138 \text{ O}_2\)

5. If **ammonia** is available it is preferentially taken up by phytoplankton.

If \(\text{NH}_3\) is used as the N source then less \(\text{O}_2\) is produced during photosynthesis

\[
\begin{align*}
106 \text{ CO}_2 & + 16 \text{ NH}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} + \text{ trace elements} \\
\text{light (hv)} & \downarrow \\
(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) & + 106 \text{ O}_2
\end{align*}
\]

The relationship between \(\text{O}_2\) and \(\text{NO}_3/\text{NH}_4\) is 2:1 (as shown in point #3)

\[
16 \text{ HNO}_3 + 16 \text{ H}_2\text{O} = 16 \text{ NH}_3 + 32 \text{ O}_2
\]
Inorganic Nutrients

1. Physical Speciation (operational definitions!)

A. Dissolved -- pass thru a specified filter

B. Particulate -- retained by a specified filter

C. Colloidal -- pass thru conventional filters, but are not ‘dissolved’…think ‘aqueous phase nanoparticles’
2. Chemical Speciation

A. Phosphorus

i. *Dissolved Inorganic Phosphorus (DIP)*

   a. pH-dependent speciation of *Orthophosphate*:

   \[
   \begin{align*}
   &H_3PO_4 \\
   &H_2PO_4^- \\
   &HPO_4^{2-} \quad \text{(most important at sw pH)} \\
   &PO_4^{3-}
   \end{align*}
   \]

   b. *Polyphosphate* – linked phosphate polymers

*Dissolved Organic Phosphorus (DOP)* – e.g., Phospholipids, ATP, ADP
THE GLOBAL PHOSPHORUS CYCLE

TERRESTRIAL

MARINE

Characteristic deep-sea dissolved phosphate profiles for three ocean basins

Ruttenberg, 2002
Seasonal P variations from Fe speciation
B. Nitrogen

Redox-dependent speciation of dissolved forms:

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxid State</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_3^-$ ((\textit{nitrate}))</td>
<td>+V</td>
</tr>
<tr>
<td>NO$_2^-$ ((\textit{nitrite}))</td>
<td>+III</td>
</tr>
<tr>
<td>N$_2$O ((\textit{nitrous oxide}))</td>
<td>+I</td>
</tr>
<tr>
<td>N$_2$ ((\textit{dinitrogen}))</td>
<td>0</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>-III</td>
</tr>
<tr>
<td>Organic-N</td>
<td>-III</td>
</tr>
</tbody>
</table>

**Dissolved Inorganic Nitrogen (DIN)**

**Dissolved Organic Nitrogen (DON)**

---

\(\text{NH}_4^+\) \((\text{ammonium ion})\)

\(\text{NH}_3\) \((\text{ammonia})\)
**Main Ocean Source of N**

**Nitrogen Fixation**
Enzyme catalyzed reduction of $\text{N}_2$

\[
\text{N}_2 + 8\text{H}^+ + 8\text{e}^- + 16\text{ ATP} \rightarrow 2\text{NH}_3 + \text{H}_2 + 16\text{ ADP} + 16\text{P}_i
\]

Mediated by a two protein (Fe and Fe-Mo) complex called nitrogenase

Inactivated when exposed to $\text{O}_2$

---

**Main Ocean Sink of N**

Fixed Nitrogen ($\text{NO}_3^-$, $\text{NO}_2^-$, $\text{NH}_4^+$) is converted to $\text{N}_2$ in low oxygen zones of the ocean

**Two Pathways**

**Denitrification** ($<$2 to 10 mM $\text{O}_2$):

\[
2\text{NO}_3^- + \text{organic matter} \rightarrow \text{N}_2
\]

**Anammox** ($<$2 mM $\text{O}_2$)

\[
\text{NH}_4^+ + \text{NO}_2^- \rightarrow \text{N}_2 + \text{H}_2\text{O}
\]

How do photosynthesizers avoid inactivating nitrogenase?
Aquatic microbial N cycling

A) nitrogen fixation
B) NOx assimilation
C) ammonification
D) NH4+ assimilation
E) NH4+ oxidation
F) NO2- oxidation
G) NO3- ammonification
H) Denitrification
I) anammox

a, burial
b, downward diffusion
c, upward diffusion
d, NH4+ adsorption
e, NH4+ desorption
Nutrient Regeneration and AOU

The Redfield-Richards equation:

106 CO₂ + 16 HNO₃ + 1 H₃PO₄ + 122 H₂O \rightarrow [(CH₂O)₁₀₆(NH₃)₁₆(H₃PO₄)] + 138 O₂

The forward reaction is Photosynthesis
The reverse reaction is Respiration

The elemental changes during respiration:

\[ \begin{align*}
\Delta C &= +106 \\
\Delta N &= +16 \\
\Delta P &= +1 \\
\Delta O₂ &= -138
\end{align*} \]

\( \Delta P = \text{Oxidative Phosphate} = P_{\text{oxid}} = P \text{ released during respiration} \)

\( \Delta O₂ = \text{Apparent Oxygen Utilization (AOU)} \)

Dissolved oxygen concentration is a tracer for respiration

Detrital POM + lateral water mass movement + aerobic respiration = O₂ consumption

AOU = Normal Atmospheric Equilibrium Conc – \([O₂]_{\text{in situ}}\)
For biogeochemically regenerated elements in seawater, the Redfield-Richards Equation indicates:

\[ [\text{Measured}] = [\text{Preformed}] + [\text{Oxidative}] \]

\[ [\text{Oxidative}] \equiv \text{Change in conc due to organic matter oxidation} \]
\[ \text{106 CO}_2 + 16 \text{ HNO}_3 + 1 \text{ H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} \rightleftharpoons \left[(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)\right] + 138 \text{ O}_2 \]

The elemental changes during respiration:

\[
\begin{align*}
\Delta \text{C} & \quad +106 \\
\Delta \text{N} & \quad +16 \\
\Delta \text{P} & \quad +1 \\
\Delta \text{O} & \quad -276 \\
\Delta \text{O}_2^- & \quad -138
\end{align*}
\]

\[\text{[Measured]} = \text{[Preformed]} + \text{[Oxidative]}\]
APPLICATION:

Calculate organic matter oxidation rate in a given water mass using AOU:

1. Measure: T, S, [O$_2$$_{meas}$]

2. Calculate [O$_2$$_{preformed}$] from T and S data

3. Calculate: AOU = [O$_2$$_{preformed}$] - [O$_2$$_{meas}$] (mol/L)

4. Calculate organic carbon oxidized in the water mass since its formation ($\Delta$C):

   $\Delta$C / AOU = 106 / 138 = 0.77  \hspace{1em} (Solve for $\Delta$C)

5. Calculate average rate of organic matter oxidation:

   Rate = $\Delta$C / time since "formation" of the water mass

   [E.g., obtain age of the water mass from $\Delta^{14}$C, $^3$He/$^3$H data, or Freon-ratio data]

\[
106 \text{CO}_2 + 16 \text{HNO}_3 + 1 \text{H}_3\text{PO}_4 + 122 \text{H}_2\text{O} \rightarrow [(\text{CH}_2\text{O})_{16} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] + 138 \text{O}_2
\]

The elemental changes during respiration:

\[
\begin{array}{ccccc}
\Delta \text{C} & \Delta \text{N} & \Delta \text{P} & \Delta \text{O} & \Delta \text{O}_2^- \\
+106 & +16 & +1 & -276 & -138
\end{array}
\]
Note:

If you know \([P_{\text{preformed}}]\) and \([P_{\text{measured}}]\), a similar method can be used, even if you don’t know the AOU:

\[
[P_{\text{oxid}}] = [P_{\text{measured}}] - [P_{\text{preformed}}]
\]

\[
\frac{\Delta C}{[P_{\text{oxid}}]} = 106 / 1
\]

This can also be done with N.

Use appropriate local Redfield (C:P) ratio

\[
106 \text{ CO}_2 + 16 \text{ HNO}_3 + 1 \text{ H}_3\text{PO}_4 + 122 \text{ H}_2\text{O} \leftrightarrow [(\text{CH}_2\text{O})_{106} (\text{NH}_3)_{16} (\text{H}_3\text{PO}_4)] + 138 \text{ O}_2
\]

The elemental changes during respiration:

\[
\begin{array}{cccccc}
\Delta C & \Delta N & \Delta P & \Delta O & \Delta O_2^- \\
+106 & +16 & +1 & -276 & -138
\end{array}
\]
**Denitrification** (nitrate reduction):

\[2\text{NO}_3^- + \text{CH}_2\text{O} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O}\]
Fig. A2-30. Annual mean apparent oxygen utilization (ml/l) at 4000 m. depth.

Minimum Value = 0.74
Maximum Value = 5.41
Contour Interval = 0.20

World Ocean Atlas 2001
Ocean Climate Laboratory/NODC

Libes Figure 8.2
Food Web Structure

Different N Sources

New Production - $\text{NO}_3^-$ as N source (from diffusion/upwelling from below and from the atmosphere via nitrogen fixation and nitrification)

Regenerated Production - $\text{NH}_4^+$ and urea as N source

New/Net/Export Flux

The f-ratio:
\[ f = \frac{\text{NO}_3 \text{ uptake}}{\text{NO}_3 + \text{NH}_4 \text{ uptake}} \]  
(defined by Dugdale and Goering, 1969)

If we write $P = \text{gross production}$ and $R = \text{respiration}$ then we can also approximate $f$ as:

\[ f = \frac{P - R}{P} \]  
also called the ratio of net to gross production
Main processes controlling vertical distribution of nutrients:

- High consumption of inorganic nutrients; high production of organic nutrients
- Slow release of inorganic nutrients due to decomposition of falling particles; slow utilization of organic nutrients
Mid-Ocean Nutrient Profiles - Nitrogen

Denitrification (nitrate reduction):

\[ 2\text{NO}_3^- + \text{CH}_2\text{O} + 8\text{H}^+ + 6\text{e}^- \rightarrow \text{N}_2 + \text{CO}_2 + 5\text{H}_2\text{O} \]
Nutrient Vertical Profiles

**FIGURE 10.1.** Vertical distribution of (a) nitrate, (b) phosphate, and (c) dissolved silicon in the Atlantic, Pacific, and Indian oceans. Note that 1 μg-atom/L is equivalent to 1 μM. Thus 1 μg-atom NO₃-N/L is equivalent to 1μmol of dissolved nitrogen (in the form of NO₃⁻) per liter of seawater.
Oxygen – Nutrient Diagrams

Redfield-Richards Equation in Action – NW Pacific

Actually, NO$_3^-$ + NO$_2^-$. For simplicity, ignore NH$_4^+$

Redfield: AOU/ΔP = 138/1 = 138

AOU/ΔN = 138/16 = 9
Dissolved Oxygen at 4000 m

Fig. A2-30. Annual mean oxygen (ml/l) at 4000 m depth.

Minimum Value= 1.46  Maximum Value= 7.06  Contour Interval= 0.20

World Ocean Atlas 2001
Ocean Climate Laboratory/NODC
Dissolved Nitrate at 4000 m

Fig. A2-30. Annual mean nitrate (µM) at 4000 m depth.
Minimum Value = 4.32
Maximum Value = 41.40
Contour Interval: 2.00

World Ocean Atlas 2001
Ocean Climate Laboratory/NODC
Dissolved Phosphate at 4000 m
"Particle" Production/Consumption Summary

C : N : P ratio of sinking particulate matter will reflect:

1) The C : N : P ratio of the sources (plankton (with and without structural material), fecal pellets, eolian deposition, etc.)

2) Differential losses during sinking (biological activity, photo-decomposition, dissolution, etc.)

3) Differential inputs during sinking (adsorption, biosynthesis, etc.)

<table>
<thead>
<tr>
<th>Location</th>
<th>C : N : P</th>
<th>C : N</th>
</tr>
</thead>
<tbody>
<tr>
<td>North Pacific Gyre</td>
<td>152 : 18 : 1</td>
<td>8.4</td>
</tr>
<tr>
<td>Central North Pacific</td>
<td>410 : 29 : 1 (highest C:N due to lack of nutrients)</td>
<td>14</td>
</tr>
<tr>
<td>Equatorial Atlantic</td>
<td>163 : 21 : 1</td>
<td>7.8</td>
</tr>
<tr>
<td>West. North Atlantic (Jan - winter)</td>
<td>59 : 5 : 1</td>
<td>11.8</td>
</tr>
<tr>
<td>West. North Atlantic (April - spring bloom)</td>
<td>68 : 13 : 1 (lowest C:N due to nutrient availability)</td>
<td>5.2</td>
</tr>
</tbody>
</table>

Note: C : N varies by 3
C : P varies by 7

THUS, IF YOU PLAN TO USE THE "REDFIELD RATIO", YOU’LL NEED DATA FROM YOUR FIELD SITE!!