Term paper topics, due February 9

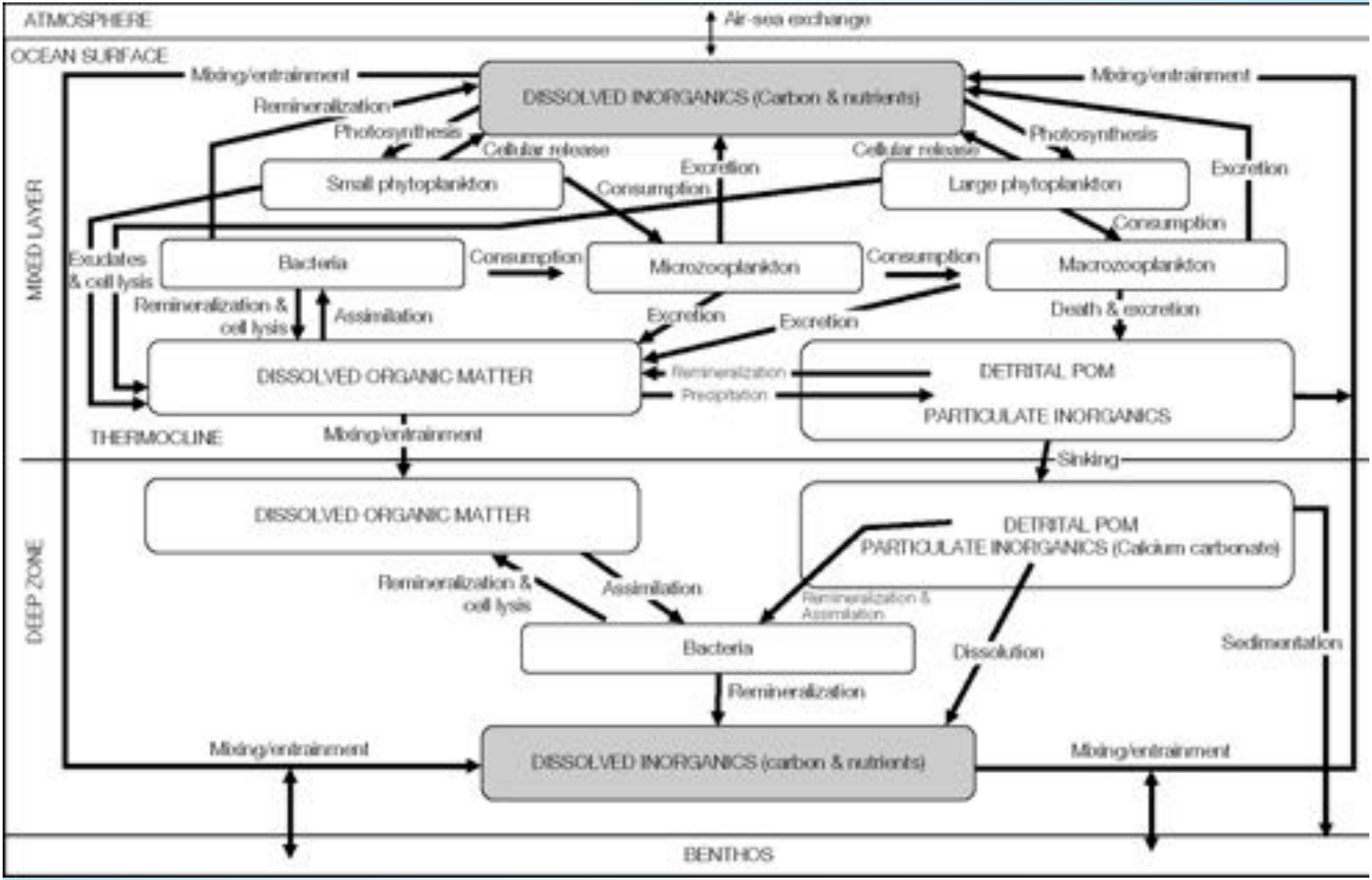
ODV mini-projects, due March 14 (10% final grade)
Individuals or teams of two
Using any available datasets, put together a ~7-10 minute talk to present in class on March 14
Aim for a blend of interesting content (but not necessarily earth-shattering or novel) and effective, beautiful visualizations
If 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



Libes Figure 8.1

Formation and respiration of organic matter

Dissolved Inorganic Nutrients ⇒ POM

Primary Producers

Autotrophs

Mostly **photosynthesizers** (they use light energy) called phytoplankton

phyto = light

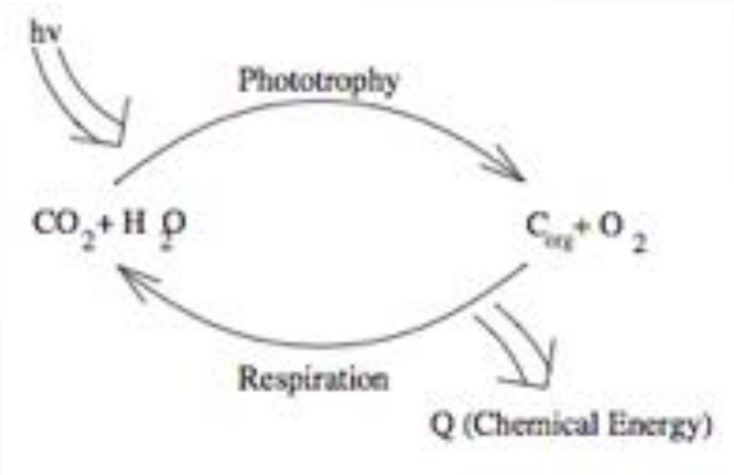
plankton = small drifting organisms

Some **chemotrophs** (don't need light)

live in 'unusual' environments like

hydrothermal vents, anoxic environments

C, H, O, N, P, S + trace elements



Production and destruction biogeochemistry

Redfield-Richards Equation:

$$CO_2 + N + P + H_20 \underset{R}{\overset{P}{\rightleftharpoons}} \text{Organic matter} + O_2$$

"*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

Name	Mineral	Size (um)
Coccoliths	$CaCO_3$ Calcite	5
Diatoms	SiO_2 Opal	10-15
Silicoflagellates	SiO_2 Opal	30
Foraminifera	$CaCO_3$ Calcite and Aragonite	~100
Radiolaria	SiO_2 Opal	~100
Pteropods	$CaCO_3$ Aragonite	~1000
Acantharia	$SrSO_4$ Celestite	~100

Soft Parts - protoplasm

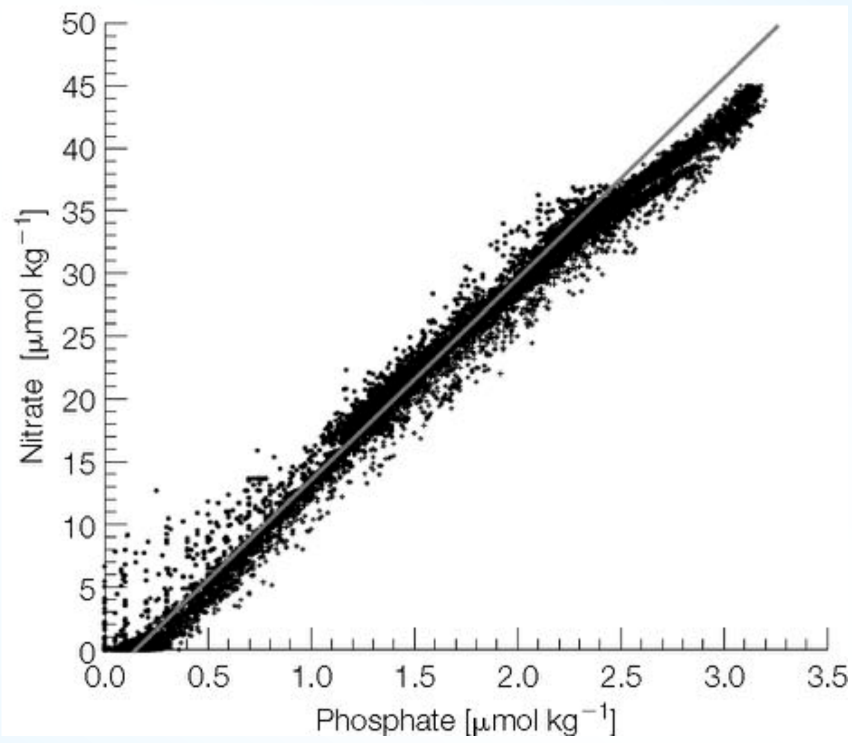
Atomic Ratios of the Principal Elements Present in Plankton

	C	N	P
Zooplankton	103	16.5	1
Phytoplankton	108	15.5	1
Average	106	16	1

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 (O_2) respiration (reverse) is written as:

$$\mathbf{106\ CO_2 + 16\ HNO_3 + H_3PO_4 + 122\ H_2O + \text{trace elements } (\textit{e.g. Fe, Zn, Mn}\ldots)}$$

light (h ν) ⇓

$$\mathbf{(C_{106}H_{263}O_{110}N_{16}P) + 138\ O_2}$$

or

$$\mathbf{(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)}$$

Algal Protoplasm

The actual chemical species assimilated during this reaction are:

HCO_3^-	NO_3^-	PO_4^{3-}
	NO_2^-	
	NH_4^+	

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_2O), 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.

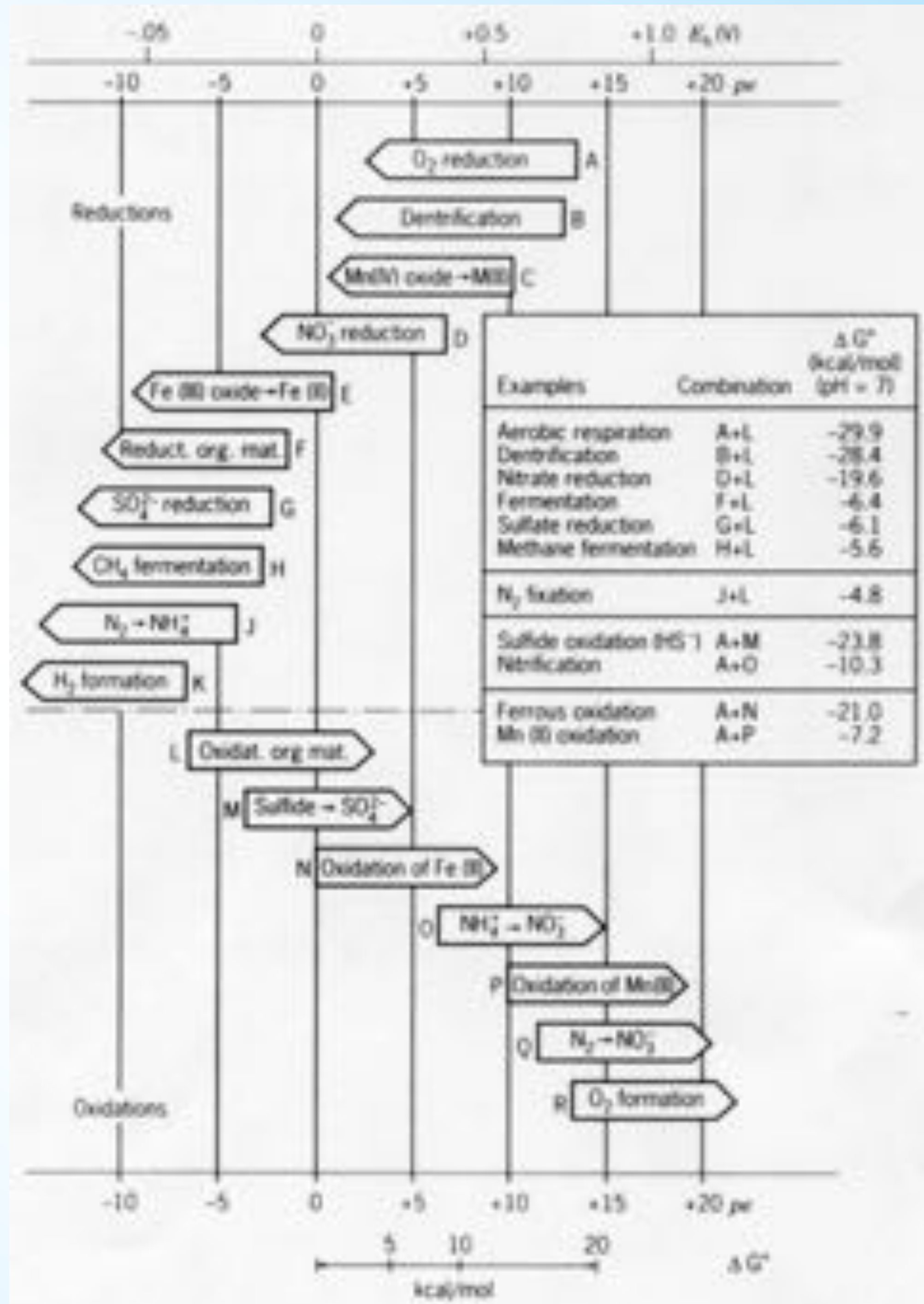
   Respiration is **exothermic**. This means it could occur spontaneously and release energy. In actuality it is always mediated by bacteria which use the reactions to obtain their energy for life.

The greater the difference in pe between the oxidizing & reducing agents, the greater the free energy yield for the reaction

Sets up a sequence of favorable oxidants for organic matter oxidation

Organic matter oxidation by O_2 is greatest free energy yield

Why is organic matter such a good electron donor?



Redox sidebar

Environmentally Important Organic Matter Oxidation Reactions

Reducing Half-reaction	E_h (V)	ΔG
Reduction of O_2		
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+0.812	-29.9
Reduction of NO_3^-		
$2NO_3^- + 6H^+ + 6e^- \rightarrow N_2 + 3H_2O$	+0.747	-28.4
Reduction of Mn (IV)		
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+0.526	-23.3
Reduction of Fe (III)		
$Fe(OH)_3 + 3H^+ + e^- \rightarrow Fe^{2+} + 3H_2O$	-0.047	-10.1
Reduction of SO_4^{2-}		
$SO_4^{2-} + 10H^+ + 8e^- \rightarrow H_2S + 4H_2O$	-0.221	-5.9
Reduction of CO_2		
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-0.244	-5.6

3. Stoichiometry breakdown of **oxygen production**

$CO_2 + H_2O \rightarrow (CH_2O) + O_2$ $\quad$ $C : O_2 \rightarrow 1 : 1$

$H^+ + NO_3^- + H_2O \rightarrow (NH_3) + 2O_2$ $\quad$ $N : O_2 \rightarrow 1 : 2$

4. **Total oxygen production**: 106 C + 16 N x 2 = 138 O_2

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

If NH_3 is used as the N source then less O_2 is produced during photosynthesis

$$106\ CO_2 + 16\ NH_3 + H_3PO_4 + 122\ H_2O + \text{trace elements}$$

$$\text{light } (h\nu) \quad \Downarrow$$

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

The relationship between O_2 and NO_3/NH_4 is 2:1 (as shown in point #3)

$$16\ HNO_3 + 16\ H_2O = 16\ NH_3 + 32\ O_2$$

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)*

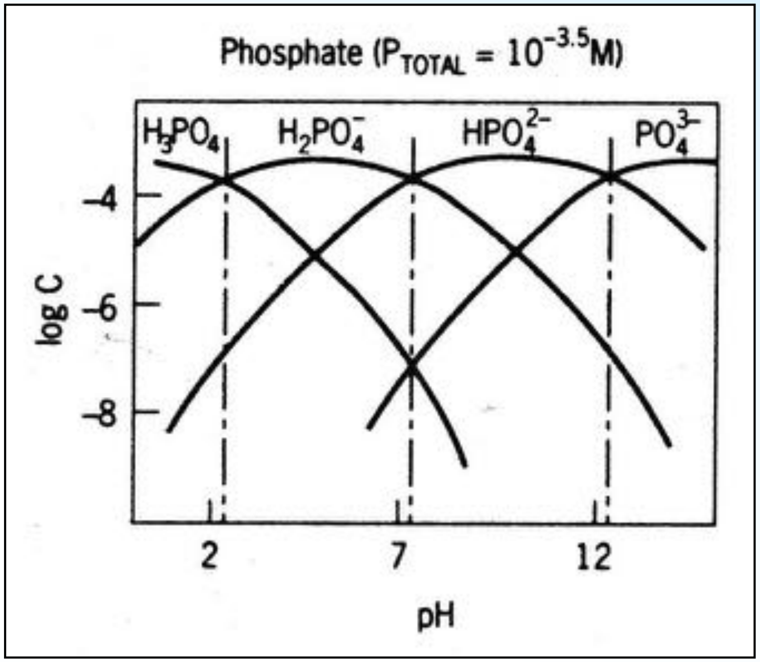
a. pH-dependent speciation of *Orthophosphate*:

H_3PO_4

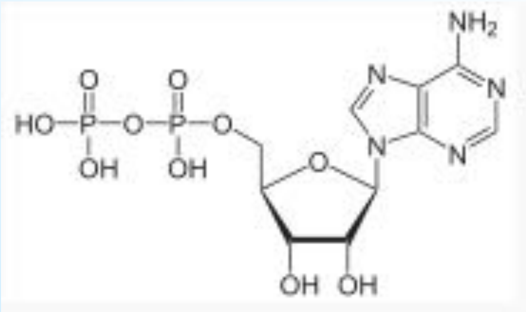
$H_2PO_4^-$

HPO_4^{2-} (most important at sw pH)

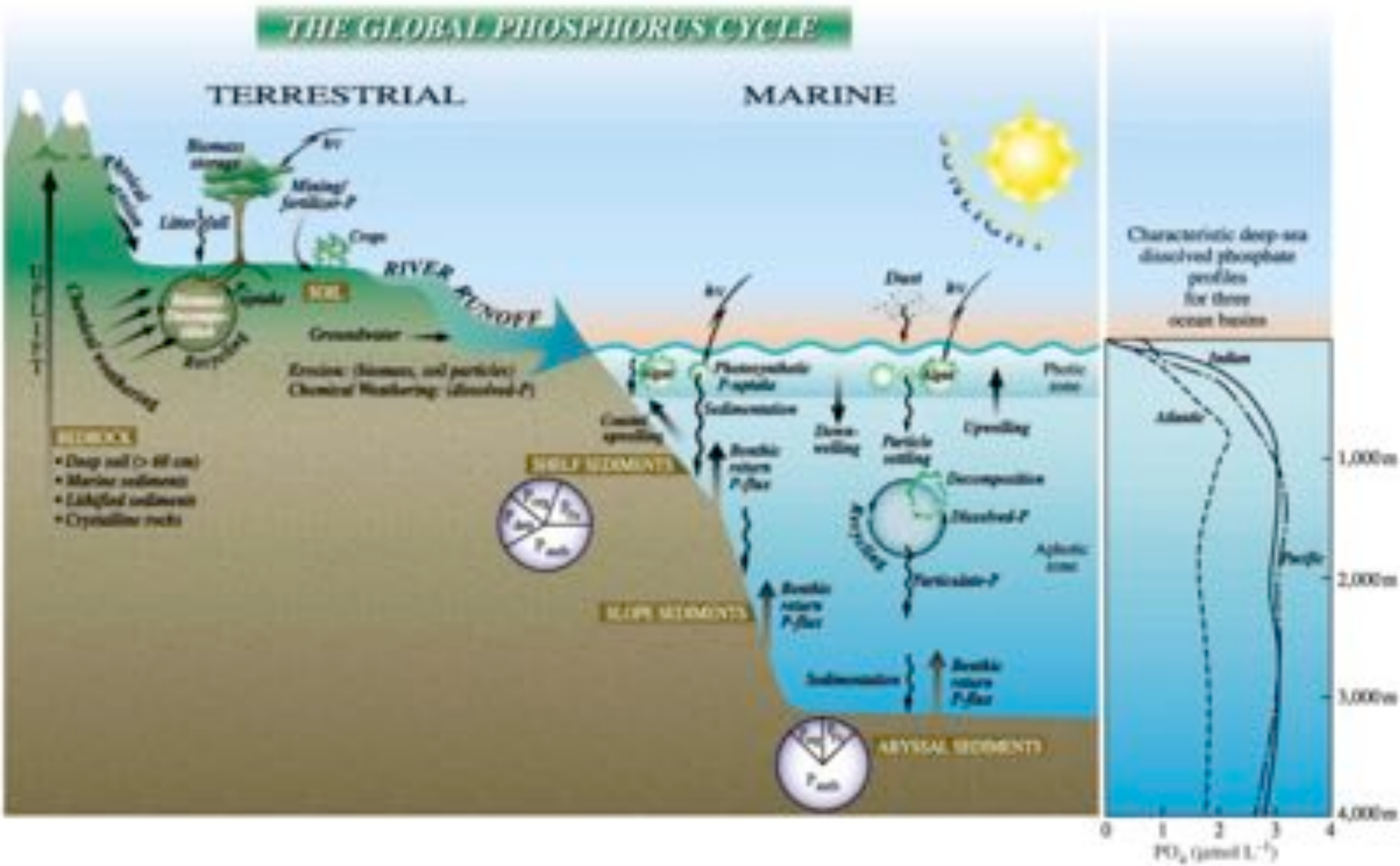
PO_4^{3-}



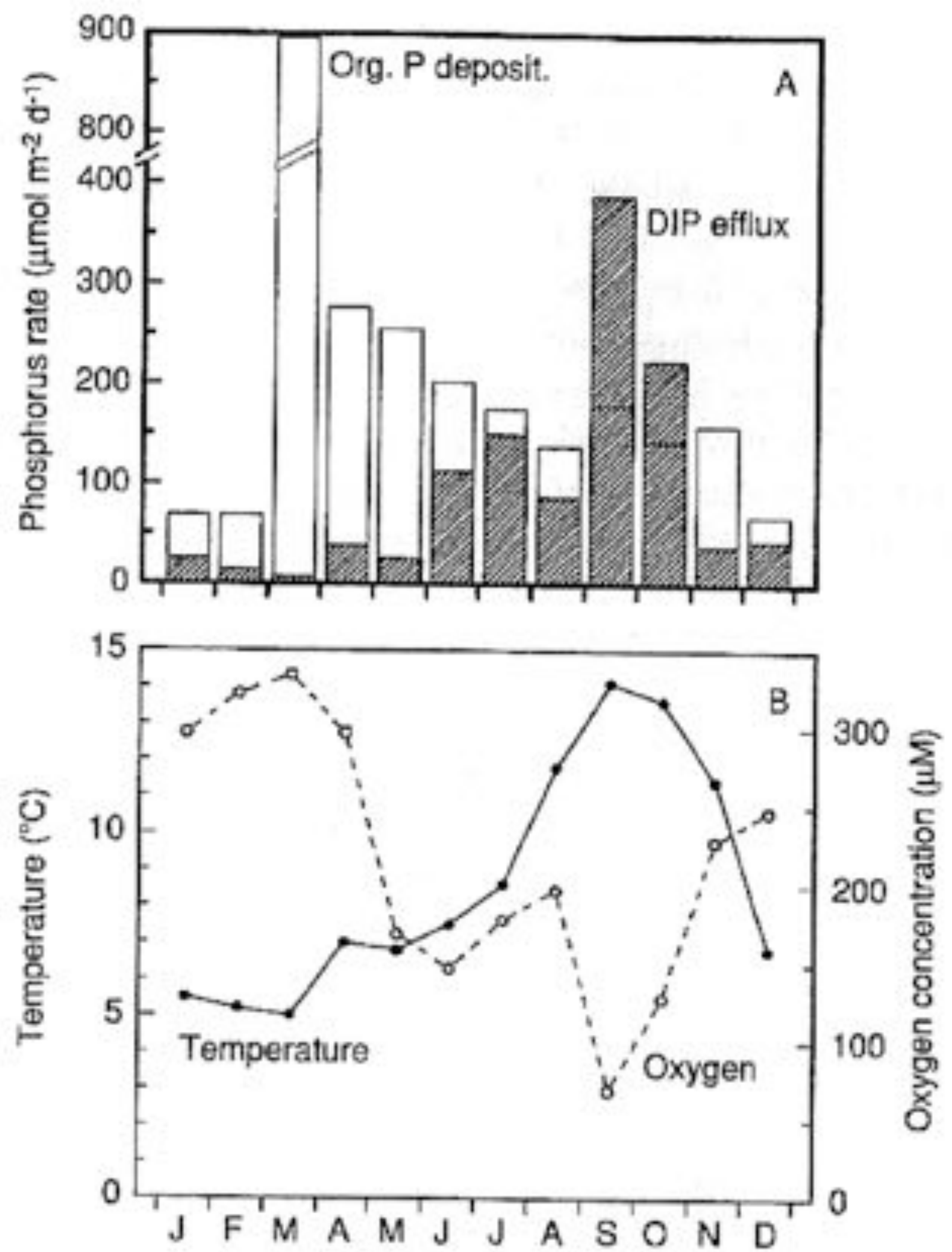
b. *Polyphosphate* – linked phosphate polymers



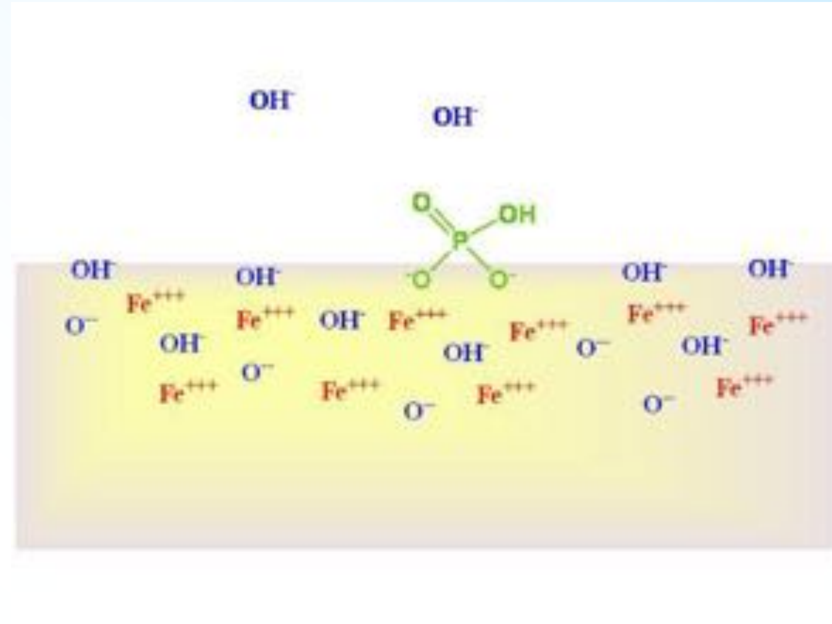
Dissolved Organic Phosphorus (DOP) – *e.g.*, Phospholipids, ATP, ADP



Ruttenberg, 2002



Seasonal P variations from Fe speciation

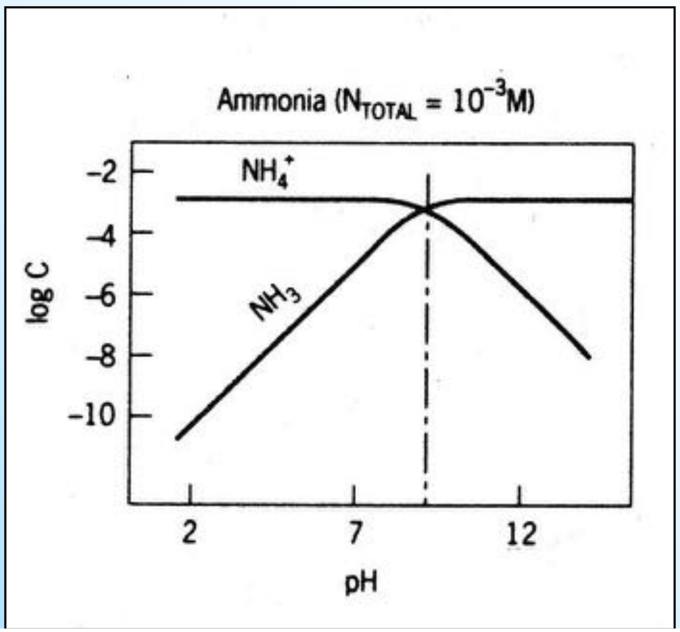


Canfield Fig. 11.10

B. Nitrogen

Redox-dependent speciation of dissolved forms:

	Species	Oxid State
Dissolved Inorganic Nitrogen (DIN)	NO_3^- (*nitrate*)	+V
	NO_2^- (*nitrite*)	+III
	N_2O (*nitrous oxide*)	+I
	N_2 (*dinitrogen*)	0
	NH_4^+	-III
Dissolved Organic Nitrogen (DON)	Organic-N	-III (*e.g.*, Urea $H_2N\text{-}CO\text{-}NH_2$)



NH_4^+ (*ammonium ion*)

NH_3 (*ammonia*)

Main Ocean Source of N

Nitrogen Fixation

Enzyme catalyzed reduction of N_2

$$N_2 + 8H^+ + 8e^- + 16\ ATP \rightarrow 2NH_3 + H_2 + 16\ ADP + 16P_i$$

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

Inactivated when exposed to O_2

How do photosynthesizers avoid inactivating nitrogenase?

Main Ocean Sink of N

Fixed Nitrogen (NO_3^-, NO_2^-, NH_4^+) is converted to N_2 in low oxygen zones of the ocean

Two Pathways

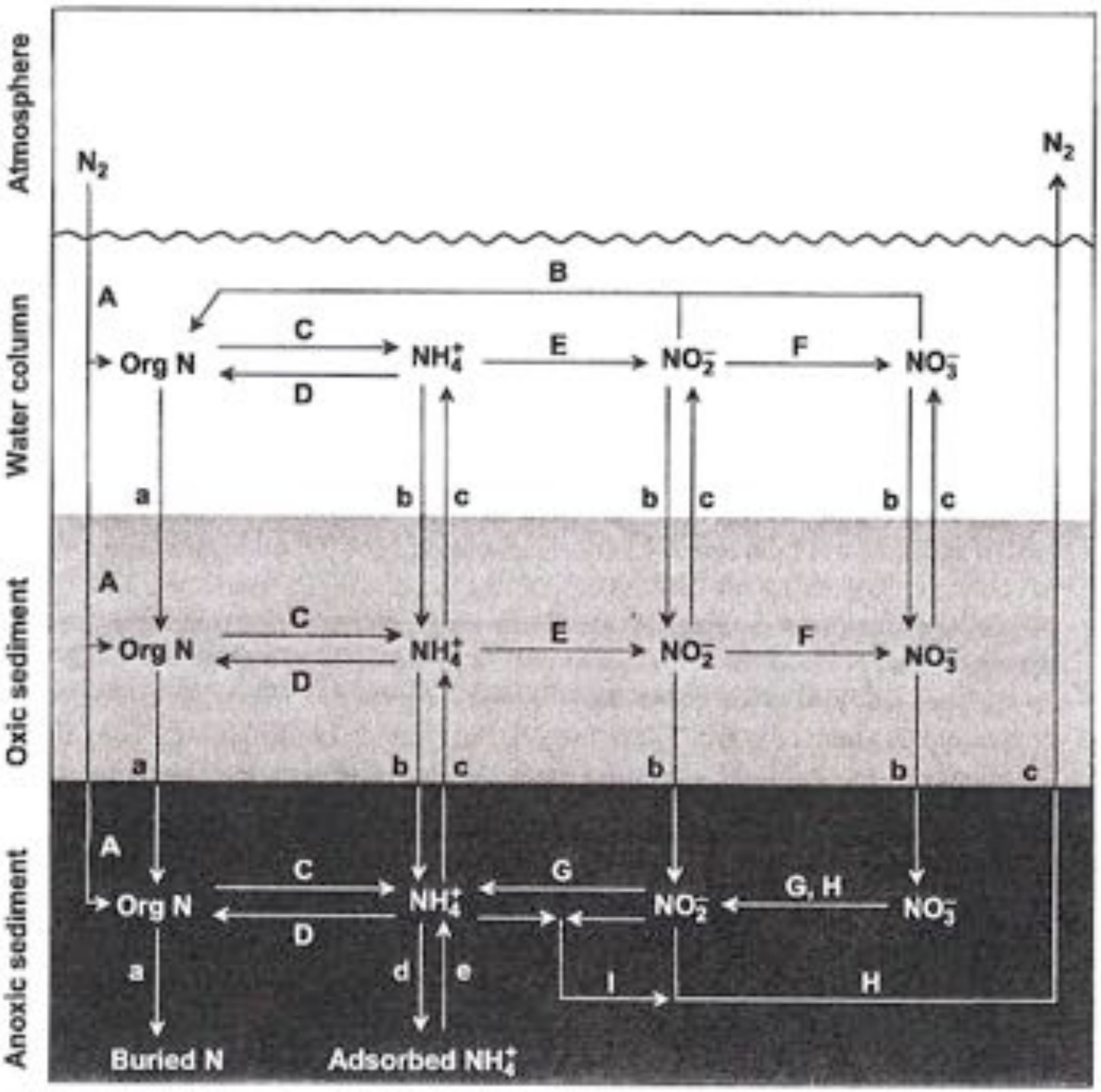
Denitrification (<2 to 10 mM O_2):

$$2\ NO_3^- + \text{organic matter} \rightarrow N_2$$

Anammox (<2 mM O_2)

$$NH_4^+ + NO_2^- \rightarrow N_2 + H_2O$$

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

Canfield Fig. 11.10

Nutrient Regeneration and AOU

The **Redfield-Richards** equation:

$$106\ CO_2 + 16\ HNO_3 + 1\ H_3PO_4 + 122\ H_2O \Longleftrightarrow [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 138\ O_2$$

The forward reaction is **Photosynthesis**
The reverse reaction is **Respiration**

The elemental changes during respiration:
(dissolved species)

ΔC	ΔN	ΔP	ΔO_2
+106	+16	+1	-138

ΔP = **Oxidative Phosphate** = P_{oxid} = P released during respiration

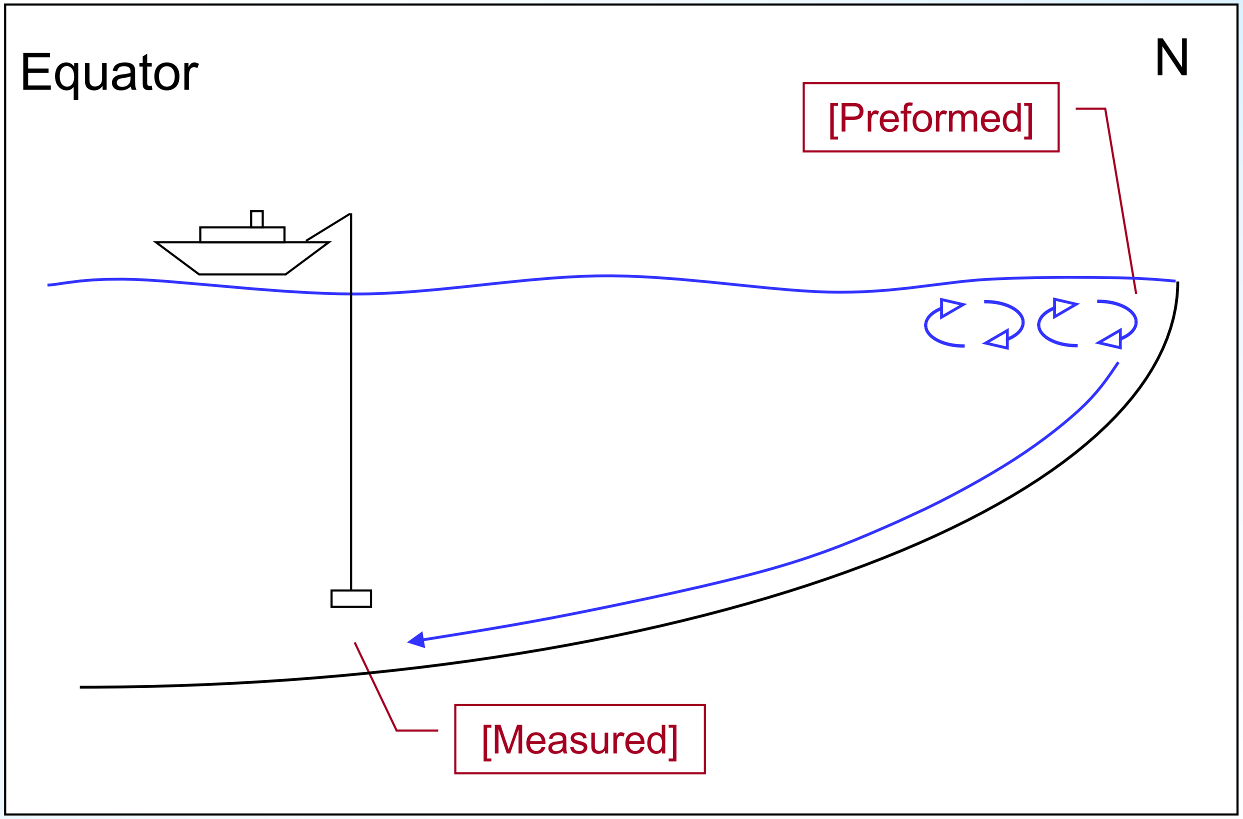
ΔO_2 = **Apparent Oxygen Utilization (AOU)**

Dissolved oxygen concentration is a tracer for respiration

Detrital POM + lateral water mass movement + aerobic respiration = O_2 consumption

AOU = Normal Atmospheric Equilibrium Conc – $[O_2]_{in\ situ}$

Measurement & Use of AOU



For biogeochemically regenerated elements in seawater, the Redfield-Richards Equation indicates:

[Measured] = [Preformed] + [Oxidative]

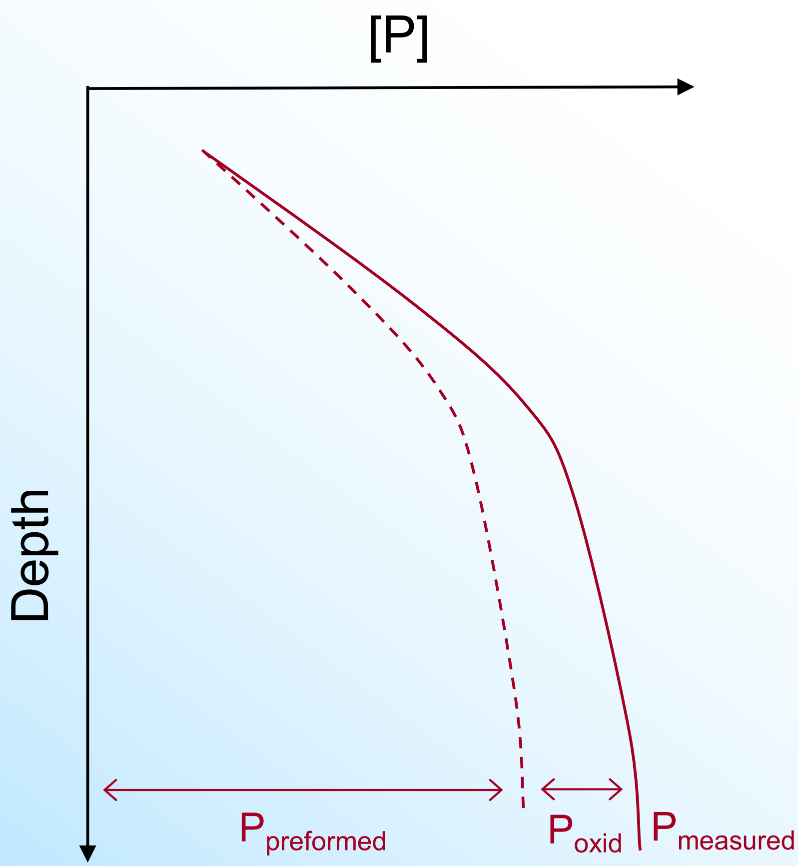
[Oxidative] ≡ Change in conc due to organic matter oxidation

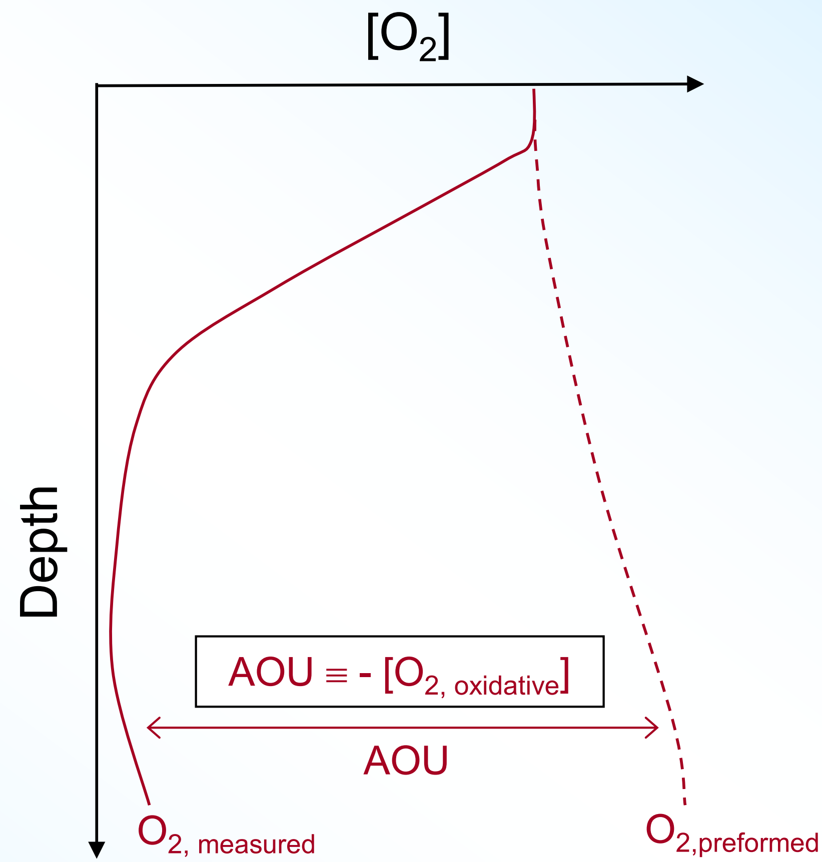
$$106\,CO_2 + 16\,HNO_3 + 1\,H_3PO_4 + 122\,H_2O \Longleftrightarrow [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 138\,O_2$$

The elemental changes during respiration:

ΔC	ΔN	ΔP	ΔO	ΔO_2
+106	+16	+1	-276	-138

[Measured] = [Preformed] + [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 (ΔC):

   ΔC / AOU = 106 / 138 = 0.77 (Solve for ΔC)

5. Calculate average rate of organic matter oxidation:

   Rate = ΔC / time since "formation" of the water mass

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

$$106\,CO_2 + 16\,HNO_3 + 1\,H_3PO_4 + 122\,H_2O \Longleftrightarrow [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 138\,O_2$$

The elemental changes during respiration: $\frac{\Delta C}{+106}$ $\frac{\Delta N}{+16}$ $\frac{\Delta P}{+1}$ $\frac{\Delta O}{-276}$ $\frac{\Delta O_2}{-138}$

Note:

If you know $[P_{preformed}]$ and $[P_{measured}]$, a similar method can be used, even if you don't know the AOU:

$$[P_{oxid}] = [P_{measured}] - [P_{preformed}]$$

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

This can also be done with N.

Use appropriate local Redfield (C:P) ratio

$$106\ CO_2 + 16\ HNO_3 + 1\ H_3PO_4 + 122\ H_2O \Longleftrightarrow [(CH_2O)_{106}(NH_3)_{16}(H_3PO_4)] + 138\ O_2$$

The elemental changes during respiration:

ΔC	ΔN	ΔP	ΔO	ΔO_2
+106	+16	+1	-276	-138

AOU and Denitrification

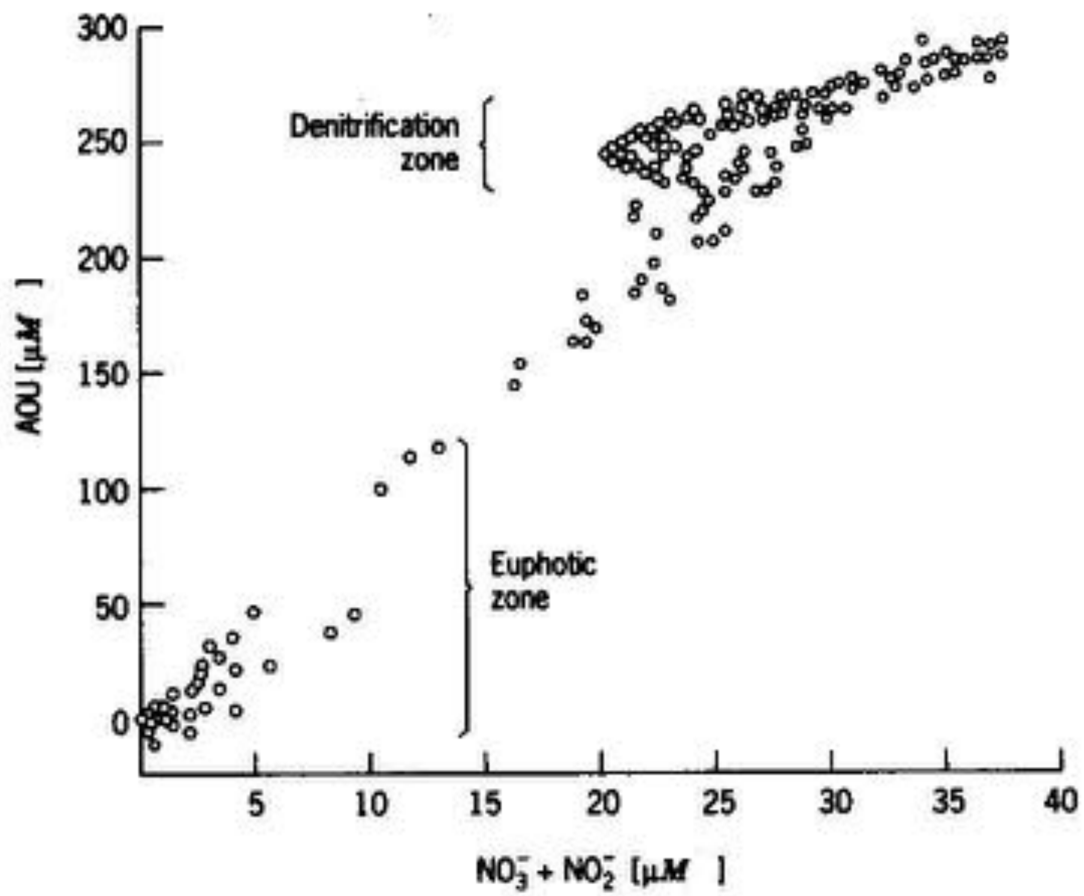
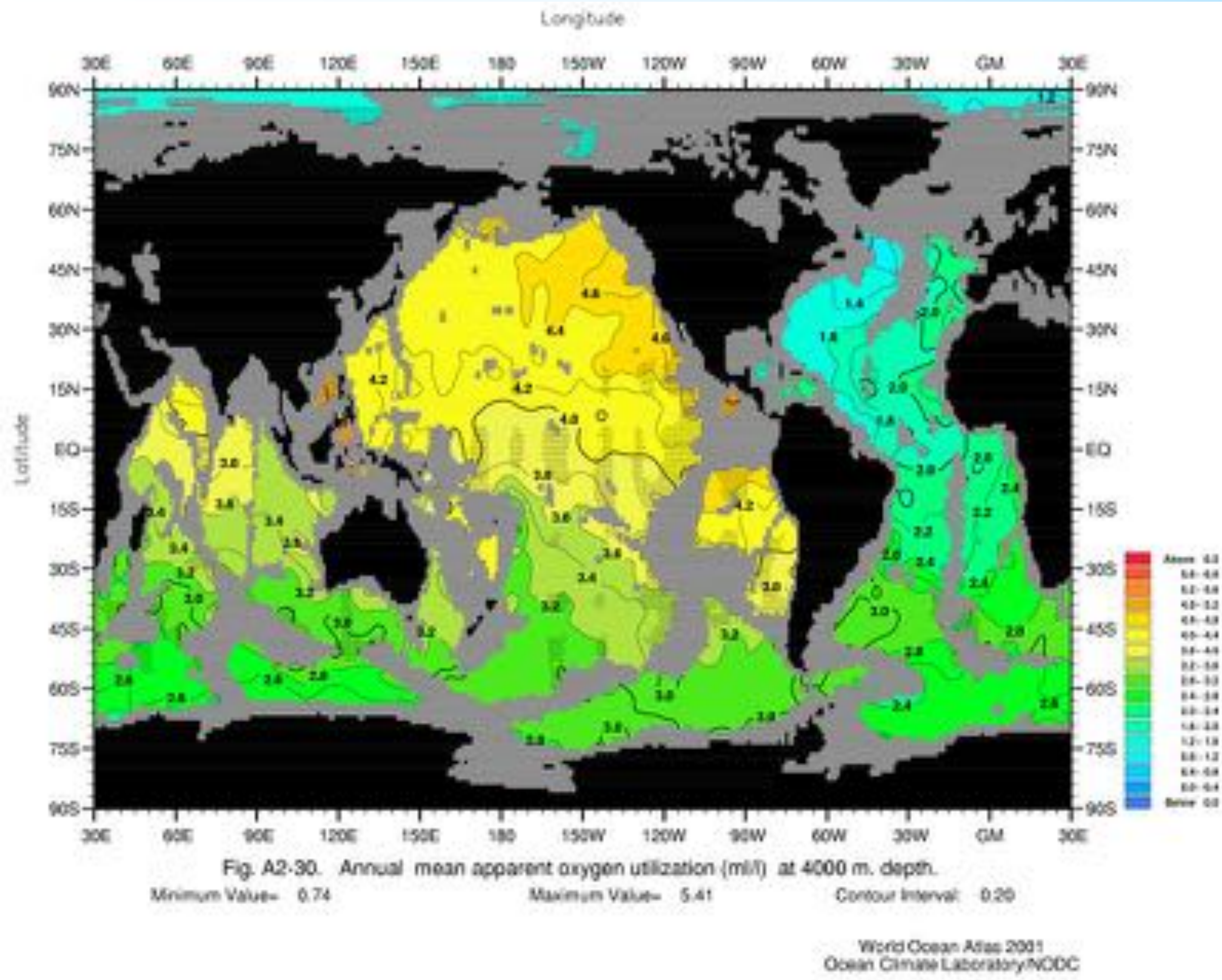


FIGURE 10.9. AOU versus $[NO_3^-] + [NO_2^-]$ in the waters of the Arabian Sea.

Denitrification (nitrate reduction):

$$2NO_3^- + CH_2O + 8H^+ + 6e^- \rightarrow N_2 + CO_2 + 5H_2O$$



Libes Figure 8.2

Food Web Structure

Different N Sources

New Production - NO_3 - as N source (from diffusion/upwelling from below and from the atmosphere via nitrogen fixation and nitrification)

Regenerated Production - NH_4^+ and urea as N source

New/Net/Export Flux

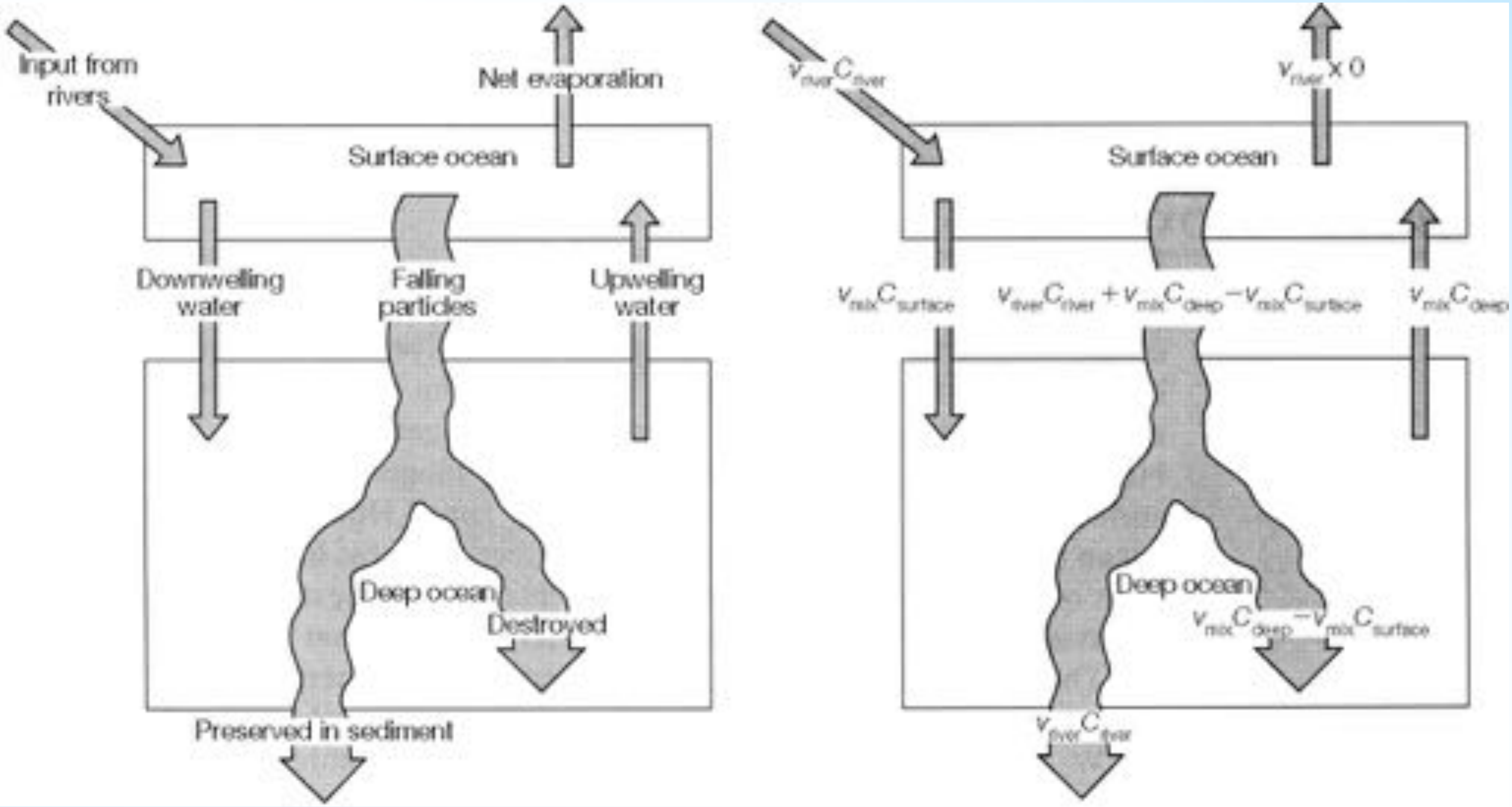
The **f-ratio**:

f = NO_3 uptake / NO_3 + NH_4 uptake (defined by Dugdale and Goering, 1969)

If we write P = gross production and R = respiration then we can also approximate f as:

$$f = \frac{P - R}{P}$$

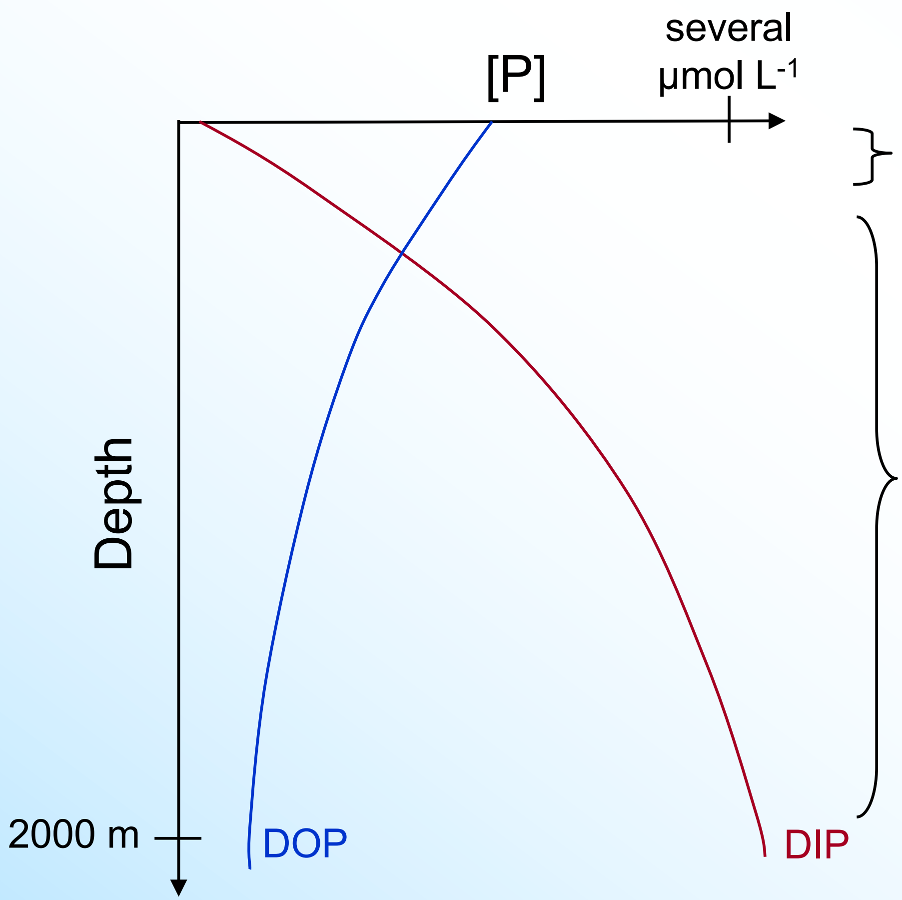
also called the ratio of **net to gross production**



Libes Figure 9.2

Mid-Ocean Nutrient Profiles - Phosphorus

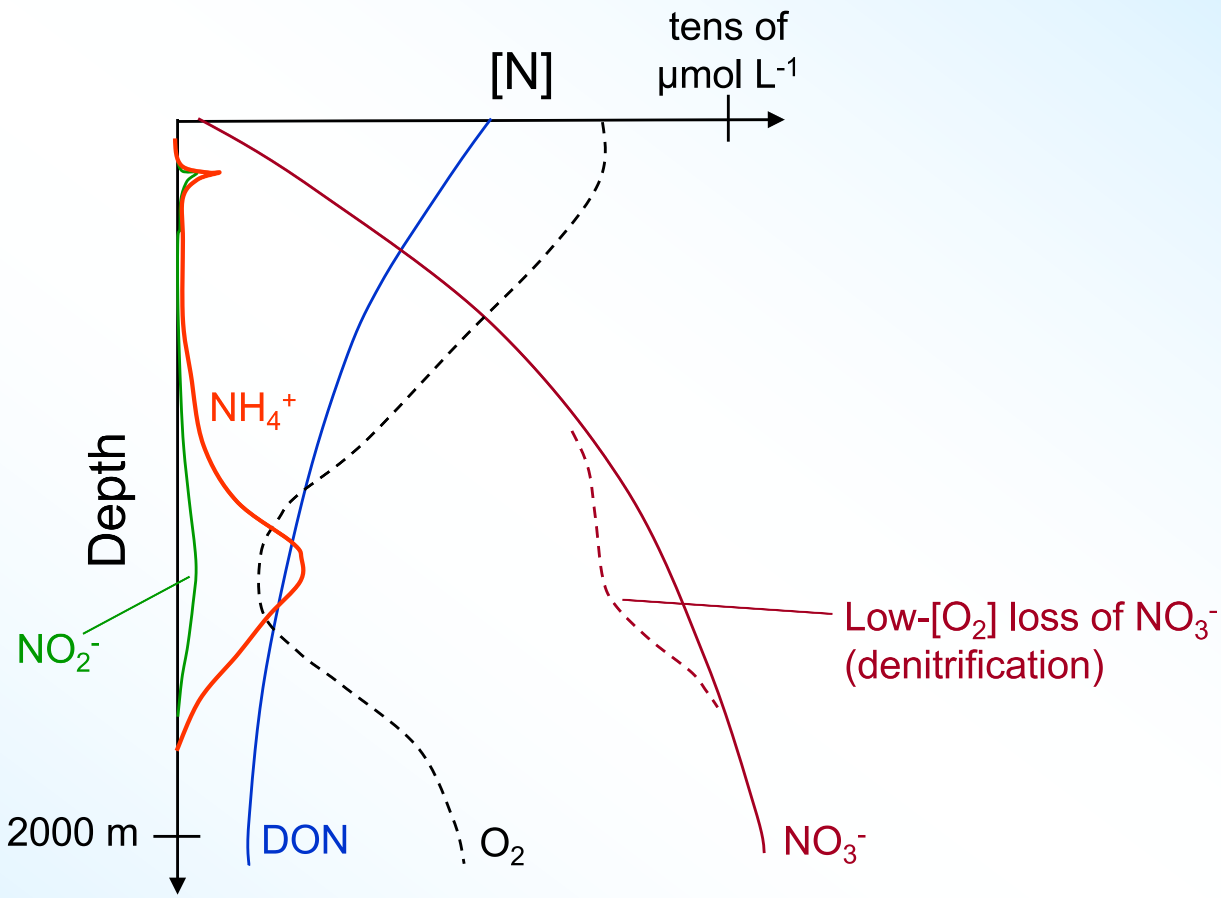
Main processes controlling vertical distribution of nutrients:



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):

$$2NO_3^- + CH_2O + 8H^+ + 6e^- \rightarrow N_2 + CO_2 + 5H_2O$$

Nutrient Vertical Profiles

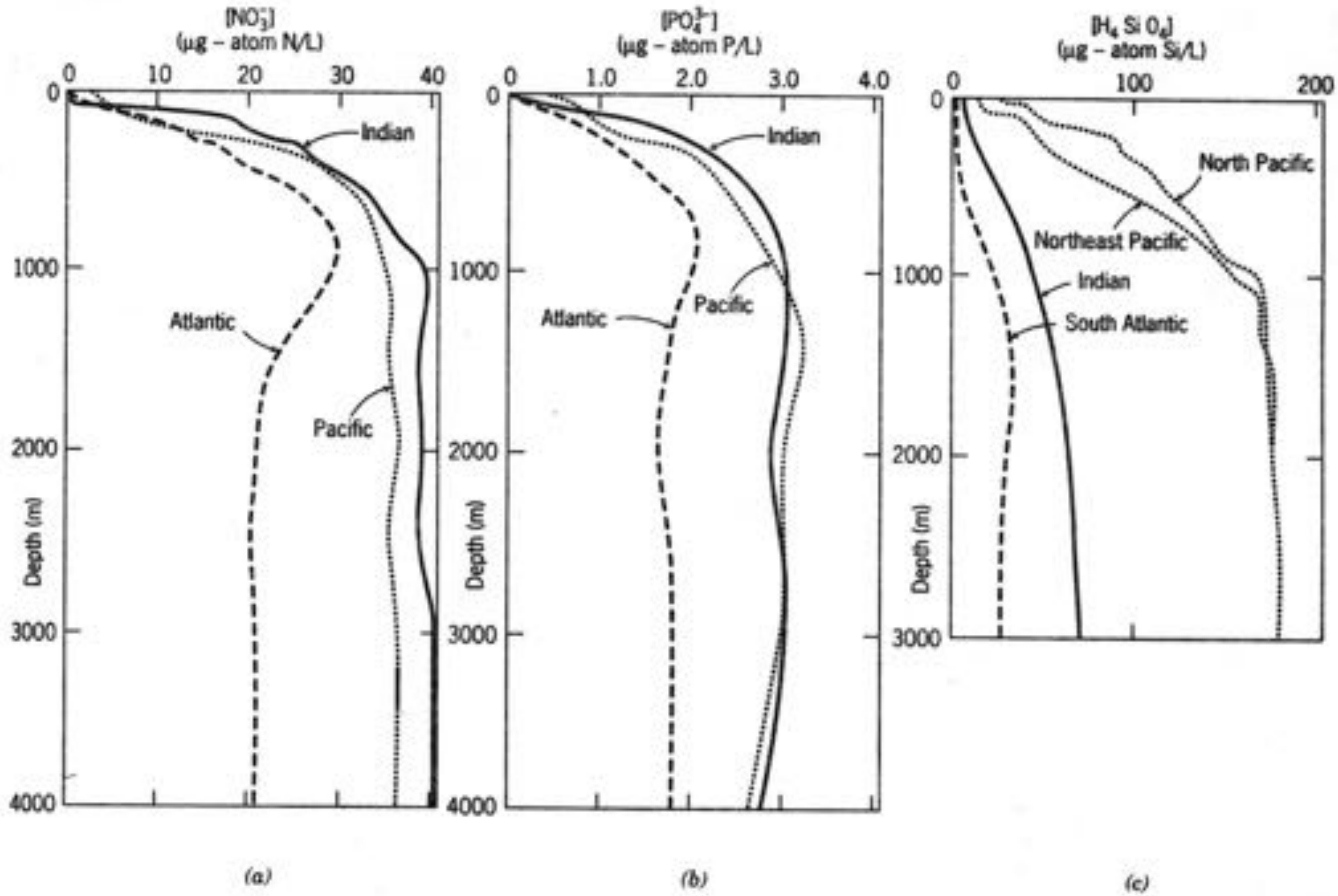


FIGURE 10.1. Vertical distribution of (*a*) nitrate, (*b*) phosphate, and (*c*) dissolved silicon in the Atlantic, Pacific, and Indian oceans. Note that 1 µg-atom/L is equivalent to 1 µ*M*. Thus 1 µg-atom NO_3-N/L is equivalent to 1µmol of dissolved nitrogen (in the form of NO_3^-) per liter of seawater.

Oxygen – Nutrient Diagrams

Redfield-Richards Equation in Action – NW Pacific

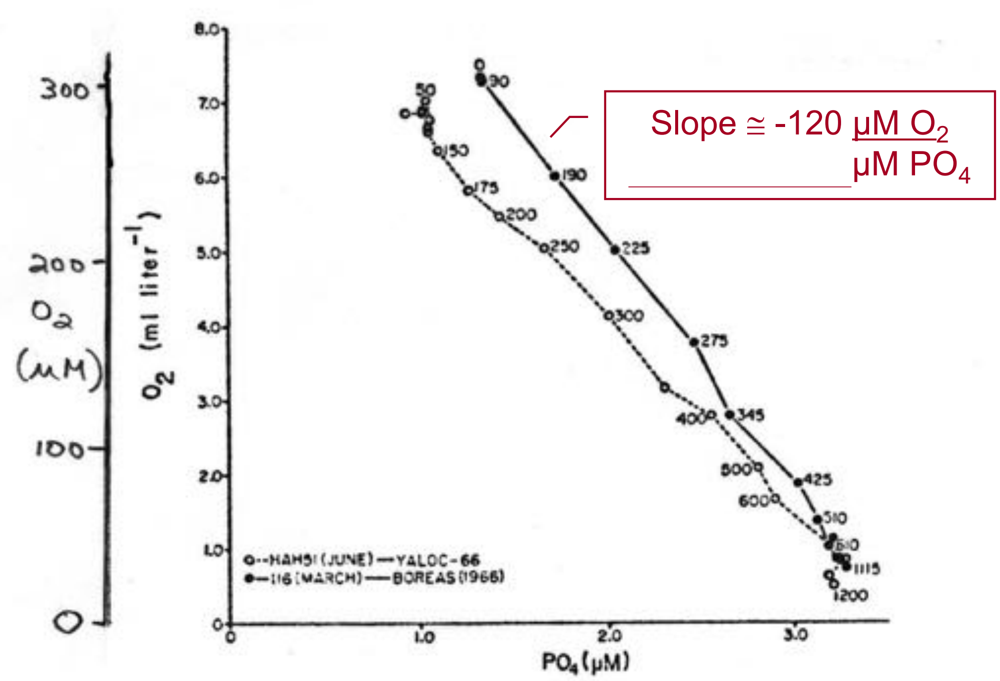


Fig. 4. Oxygen-phosphate diagram. Comparison between winter and summer data. The numbers by the data points represent depth in meters. The position of the station not given in the legend to Fig. 3 is: 116 (44°51.0′N, 174°57.0′E).

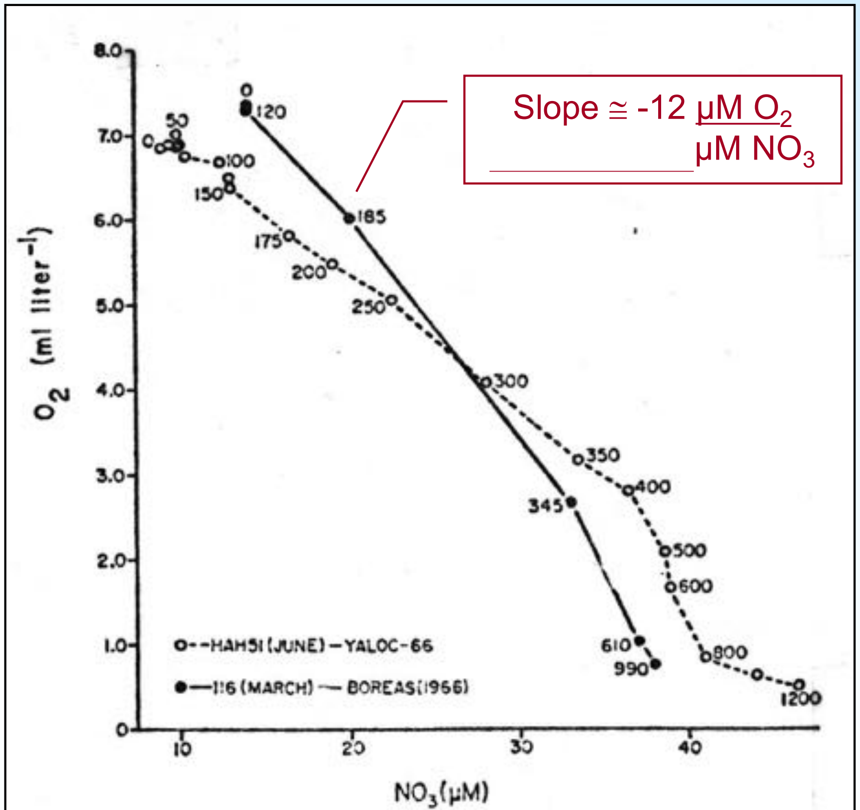


Fig. 5. Oxygen-nitrate diagram. Data presented as in Fig. 4.

Redfield: AOU/ΔP = 138/1 = 138

AOU/ΔN = 138/16 = 9

Actually, NO_3^- + NO_2^-. For simplicity, ignore NH_4^+

Dissolved Oxygen at 4000 m

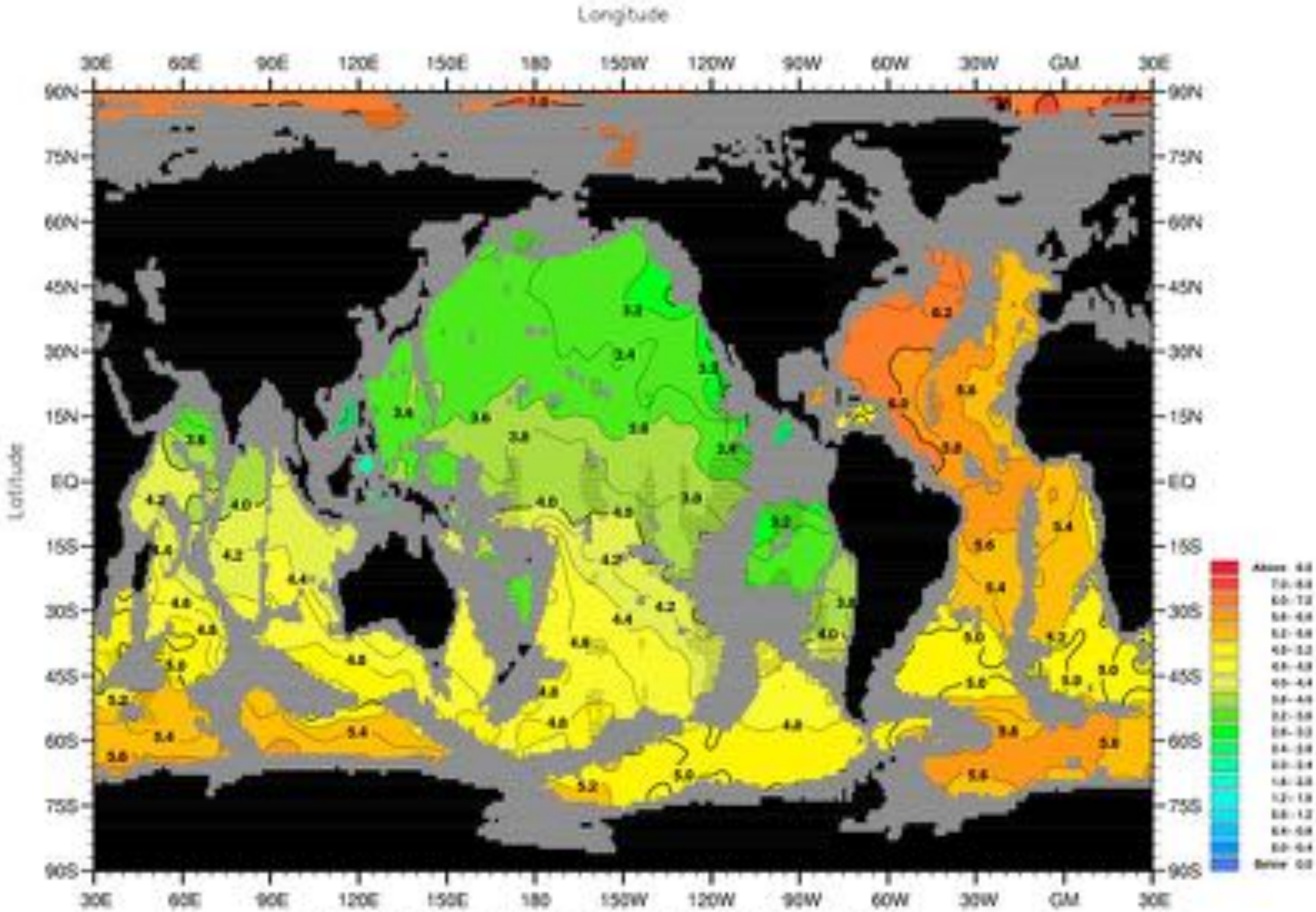


Fig. A2-30. Annual mean oxygen (ml/l) at 4000 m. depth.

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

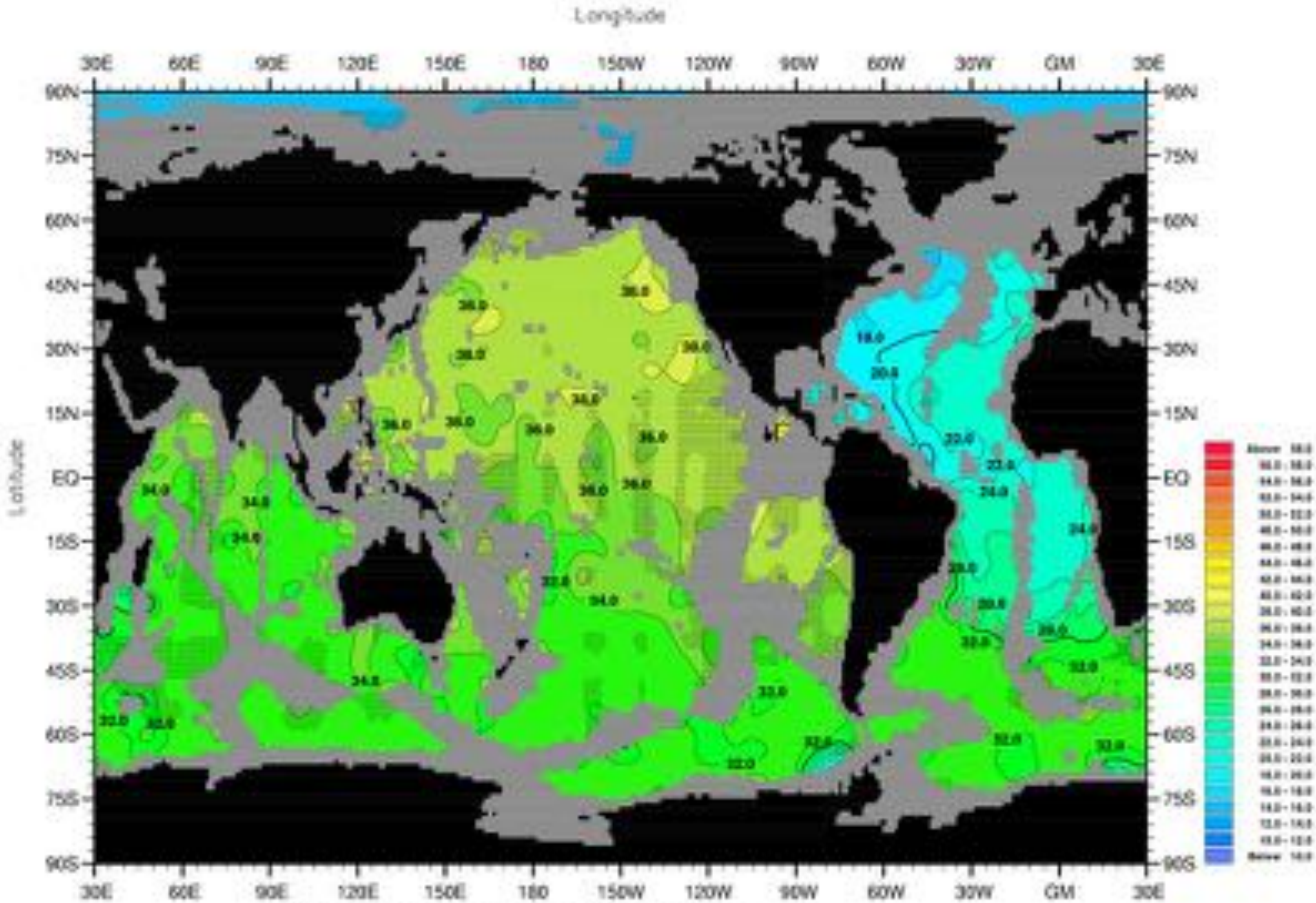


Fig. A2-30. Annual mean nitrate (µM) at 4000 m. depth.

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

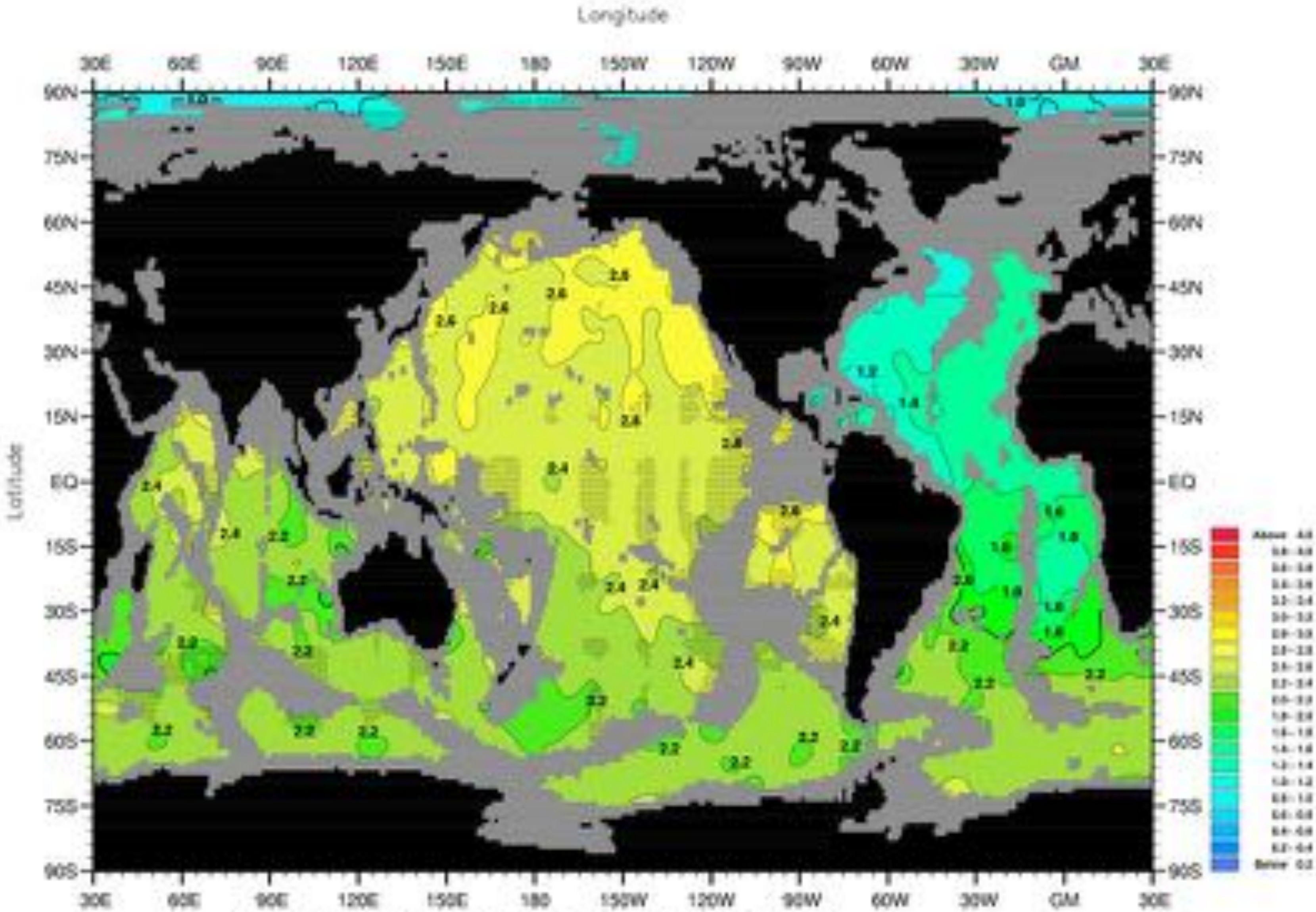


Fig. A2-30. Annual mean phosphate (μM) at 4000 m. depth.

Minimum Value= 0.14 Maximum Value= 3.05 Contour Interval: 0.20

World Ocean Atlas 2001
Ocean Climate Laboratory/NODC

"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.)

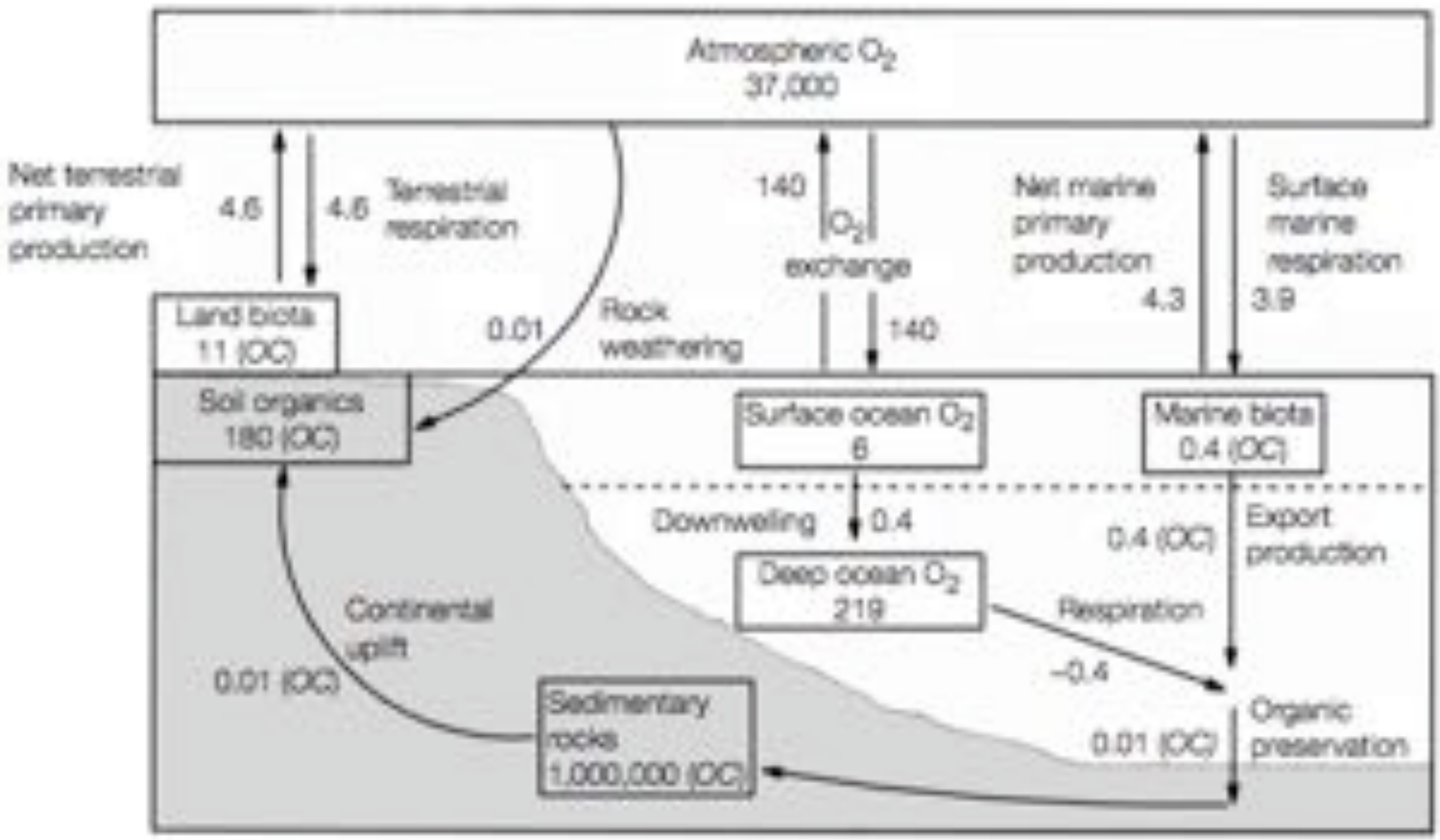
Particle composition in surface seawater:

		C : N : P		C : N
Spatial differences	North Pacific Gyre	152 : 18 : 1		8.4
	Central North Pacific	410 : 29 : 1	(highest C:N due to lack of nutrients)	14
	Equatorial Atlantic	163 : 21 : 1		7.8
Temporal differences	West. North Atlantic (Jan - winter)	59 : 5 : 1		11.8
	West. North Atlantic (April - spring bloom)	68 : 13 : 1	(lowest C:N due to nutrient availability)	5.2

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!!

The global cycle of molecular oxygen



J. Hedges (2002)

Revised Stoichiometric Ratios

Takahashi et al (1985) first argued that the correct approach for determining stoichiometric regeneration ratios was to utilize data along isopycnal surfaces. They found that the stoichiometric ratios (on σ_o = 27.0-27.20) varied for different locations in the Atlantic and Indian oceans (see table). They argued that the widely used RKR values of P:N:C:-O_2 of 1:16:106:138 should be replaced by 1:16:115:172 for the Atlantic and Indian Ocean (this include the C in hard shells).

The following table compares theoretical and actual mean stiochiometries for different oceans (at a σ_0 of 27.00-27.20):

Location	# Stations	P	N	CO_2	(O_2-2N)*	$-O_2$	$CaCO_3$
RKR	~	1	16	106	106	138	~
Atlantic	119	1	17.0± 0.4	96 ± 6	138 ± 9	171 ± 8	10 ± 4
Indian	43	1	14.9 ± 0.4	119 ± 5	142 ± 5	172 ± 5	17 ± 4
Atlantic+Indian	162	1	16.3 ± 1.1	103 ± 14	140 ± 8	172 ± 7	12 ± 5

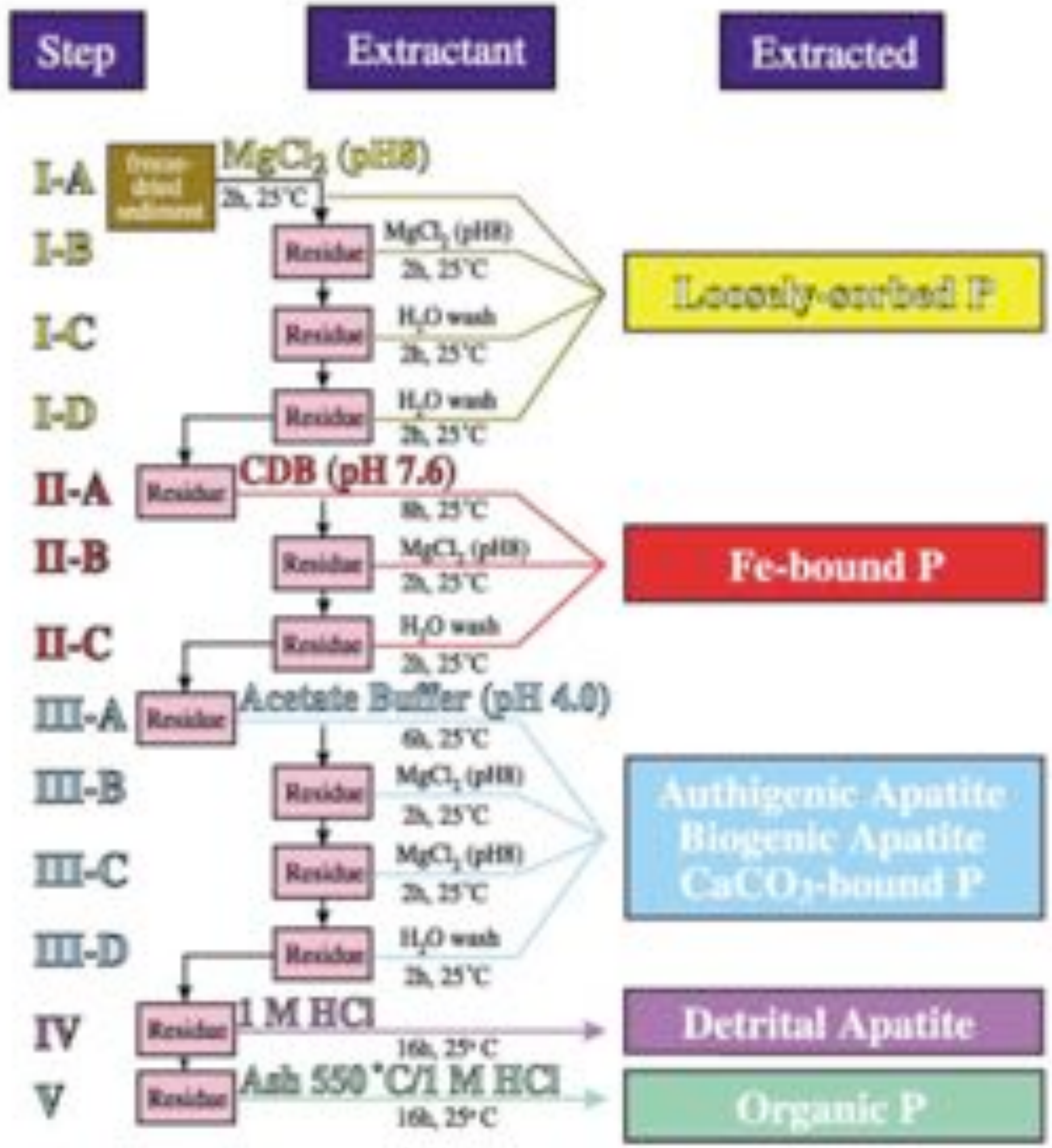
*oxidation of N is assumed to take 2 O_2

This approach was improved upon by Anderson and Sarmiento (1994) who calculated the stoichiometric ratios on 20 sites in the South Atlantic, Indian and Pacific Basins between 400 and 4000m. The P:N:C:-O_2 ratios of remineralization below 400m are estimated with uncertainties as 1:16±1:117±14:170±10. These values are very consistent with those of Takahashi et al (1985). In ocean regions where there is denitrification the coefficient for NO_3 is less (12±2). It is clear that more O_2 (~175 moles) is actually required to respire sinking organic matter than was originally calculated from the RKR equation (138 moles). The higher O_2 demand suggests that sinking organic matter has more of a lipid-like nature.

$CH_2O + O_2 \Rightarrow CO_2 + H_2O$ (a carbohydrate-like substrate)

Versus $CH_2 + 3/2\ O_2 \Rightarrow CO_2 + H_2O$ (a lipid-like substrate).

SEDEX Scheme for Different Forms of Phosphorus in Marine Sediments



Ruttenberg

Nitrite - An Indicator of "Suboxia"

Typically, nitrate and nitrite are measured together (reported as their sum). However, nitrite maxima can be observed:

Subsurface maximum (presumably due to suboxic zone in/on particles)

O_2-minimum zone maximum

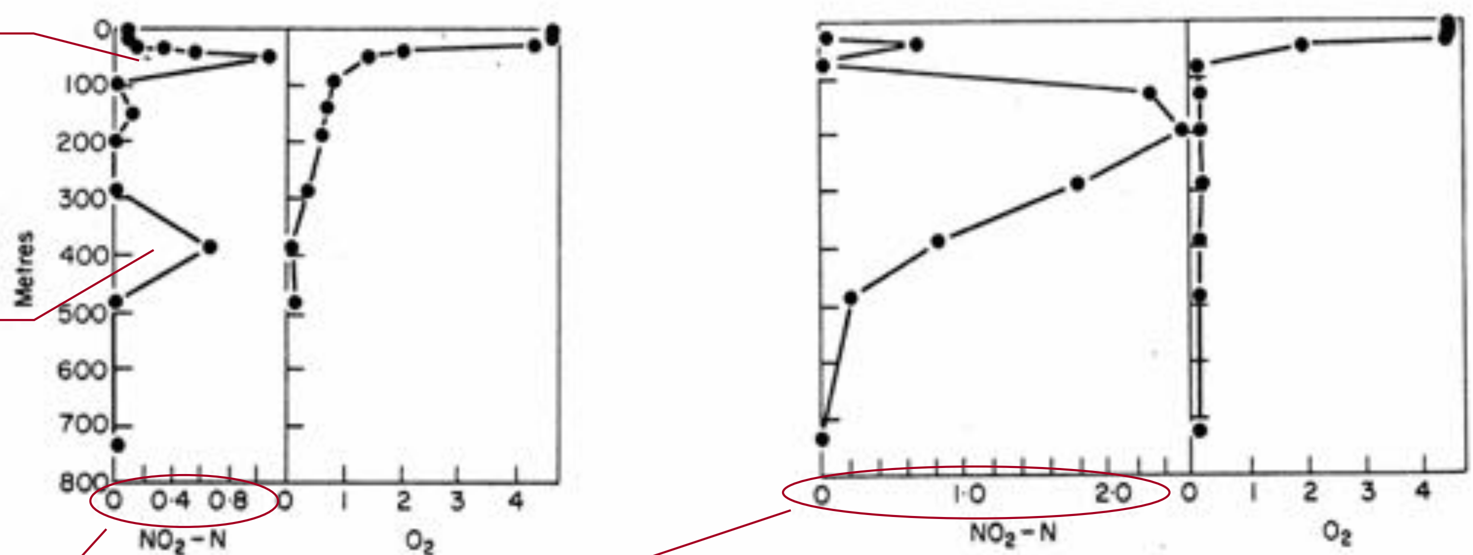
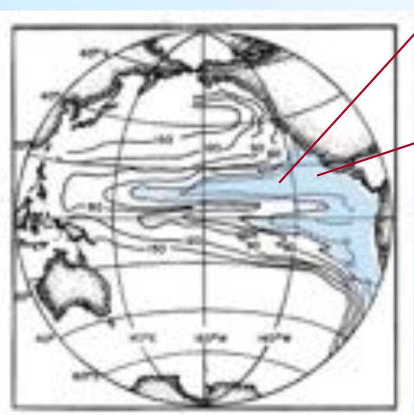


FIG. 11.16. Depth profiles of dissolved oxygen (cm³ l⁻¹) and nitrite-nitrogen (µg-at l⁻¹) in the eastern Pacific Ocean showing nitrite-nitrogen maxima in the presence of low concentrations of dissolved oxygen (From Brandhorst, 1959).



NH_4^+ profiles look similar (two maxima)